Chemistry and Technology of Explosives

Vol. I

by

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PREFACE

For quite a long time a reference book has been needed which would provide the reader with adequate information, both theoretical and practical, on the chemistry and technology of explosives. The objectives of the present book are to fill this gap in the chemical literature.

The first edition appeared in Warsaw in Polish in 1953-54. The second, in Czech, was printed in Prague in 1958-59. The third, in German, is being printed in Leipzig. The present fourth edition is a considerably revised and expanded version of the earlier ones.

The chemical, physical and physico-chemical properties of explosives are dealt with, and processes of manufacture are described whenever the substance in question is of practical importance.

The basis of all practical knowledge is in the underlying theory. The scientist working on technological problems in industry should never forget that science, however applied, remains a natural philosophy. This is why particular attention is paid here to the chemical and physico-chemical properties of the substances described in the book, and the author has endeavoured to bring this information up to date, hoping that the wide scope of this information will not obscure the main subject, but will help, instead, to avoid narrow specialization which creates the danger of not seeing the wood for the trees.

It is also hoped that in widening the scope of the book, it might become useful not only to students and experts on explosives, but also to all who are interested in the chemistry of such substances as nitro compounds, nitramines, nitric esters, nitric salts, azides etc. that may serve as intermediates for organic reactions.

As far as processes of manufacture of explosives are concerned, information is obviously restricted, as the exact details are seldom available. However, certain obsolete methods of manufacture are described in detail. They have been included in order to give some idea of the way such processes have developed on the basis of years of experience. This may be of some value, for the manufacture of explosives is bound to be dangerous and any method, even an obsolete one, may suggest how risks can be avoided or diminished and the kinds of precaution that can be applied.

However, it has been possible to include in the book details of a number of original processes used in the German and Japanese explosives industries during World War II which were revealed after the war mainly in CIOS, BIOS, FIAT and PB publications.

Although there was an enormous increase in the use of explosives for destructive purposes in the two World Wars it is still true to say that more explosives have been used in peace than in war. Modern civilization and modern progress would be impossible without explosives. Particular attention has therefore been paid to coal-mine explosives (Vol. III). Also a modest chapter on rocket fuels has been included in the English edition.

It is a pleasure to express my thanks to my friends for their interest in this work and their kind assistance. To all of them who helped me to bring my book up to date and to avoid mistakes so easy in so large a book, I express my warmest thanks.

My thanks are particularly due to: Professor K. K. Andreyev (Moscow), Professor J. H. Boyer (New Orleans), Dr. R. S. Cahn (London), Professor W. Cybulski (Mikolów, Poland), Dr. L. Deffet (Brussels), Monsieur A. Diels (Brussels), Professor Z. Eckstein (Warsaw), Professor H. Erdtman (Stockholm), Professor A. G. Gorst (Moscow), Professor J. Hackel (Warsaw), Dr. K. Hino (Sanyo-cho, Japan), Professor E. L. Hirst, F. R. S. (Edinburgh), Ingénieur Général Fleury (Paris), Professor R. N. Jones (Ottawa), Mr. H. Konopacki, M.Sc. (Warsaw), Mr. Kosciukiewicz, M.Sc. (Warsaw), Dr. Bernard Lewis (Pittsburgh, Pa.), Ingénieur en Chef Nicolas (Paris), Professor R. G. W. Norrish, F.R.S. (Cambridge), Professor (Mrs) E. Yu. Orlova (Moscow), Dr. J. Plucinski, (Wroclaw), Professor E. Plazek (Wroclaw), Professor A. Quilico (Milan), Dr. S. Raczynski (Warsaw), Professor D. Smolenski (Wroclaw), Dr. S. Ropuszyriski (Wroclaw), Ingénieur General Tavernier (Paris), A. T. Thomas, M. SC. (Orpington), Professor A. J. Titov (Moscow), Academician A. V. Topchiyev (Moscow), Dr. J. Trommel (Ouderkerk aan de Amstel, Netherlands), Dr. R. W. Van Dolah (Pittsburgh, Pa.), Professor T. H. Westheimer (Cambridge, Mass.), Professor C. A. Winkler (Montreal), Dr. E. Wozniak (Warsaw), Professor G. F. Wright (Toronto), Dr. Mutsuo Yokogawa (Sanyocho, Japan), Professor Sukonori Yamamoto (Tokyo).

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Finally I would like to express my thanks to all editors and authors who have granted their permission to reproduce the figures and diagrams reprinted from their work.

With the large field dealt with in the book, many important papers must have been overlooked and I should be grateful if readers would call my attention to any omissions so that corrections and additions could be made in the future.

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1961

CLASSIFICATION OF EXPLOSIVES

EXPLOSIVES may be classified both from the chemical point of view and according to their uses. From the chemical viewpoint we distinguish between chemical individual substances and mixtures.

The former are divided into:

(1) nitro compounds
(2) nitric esters
(3) nitramines
(4) derivatives of chloric and perchloric acids
(5) azides
(6) various compounds capable of producing an explosion, for example fulminates, acetylides, nitrogen rich compounds such as tetrazene, peroxides and ozonides, etc.

Individual substances are explosive if their molecules contain groups which confer upon them explosive properties. The first attempt at a systematic approach to the relation between the explosive properties of a molecule and its structure was made by van't Hoff [l]. He pointed out, that in the molecules of explosive compounds the following groups were present:

O-O in peroxides and ozone and ozonides
O-Cl in chlorates and perchlorates
N-Cl in nitrogen chloride
N=O in nitro compounds, nitric acid esters and salts
N=N in diazo compounds, hydrazoic acid, its salts and esters
N=C in fulminates and cyanogen
CEC in acetylene and acetylides.

A further effort to establish a relationship between explosive properties and structure has been made more recently by Plets [2]. He proposed a theory of "explosophores" and "auxoploses" in a way analogous to Witt's suggested chromophores and auxochromes in the dyes, and Ehrlich's suggested toxophores and autotoxes in chemotherapeutics.

According to Plets the explosive properties of any substance depend upon the presence of definite structural groupings, called ***explosophores.*** The auxoploses fortify or modify the explosive properties conferred by the explosophore. Plets divided all explosives into eight classes containing the following groups as explosophores:

(1) $-NO_2$ and $-ONO_2$, in both inorganic and organic substances
(2) $-N=N-$ and $-N=N=N-$ in inorganic and organic azides
(3) $--NX_2$, for example in NCl_3 (X- a halogen)
(4) $-N=C$ in fulminates
(5) $-OC1O_2$ and $-OC1O_3$ in inorganic and organic chlorates and perchlorates respectively
(6) -O-O- and -O-O-O- in inorganic and organic peroxides and ozonides respectively
(7) -CEC- in acetylene and metal acetylides
(8) M-C metal bonded with carbon in some organometallic compounds.

Although this classification is in principle correct, the distinction between the terms “explosophore” and “auxoplose” is very vague and of little practical value.

A further step in the classification of explosives was made by Lothrop and Handrick [3]. They collected and classified all the available information on the performance of explosives and related it to four factors: oxygen balance, “plosophoric” groups, “auxoplosive” groups, heat of explosion.

A *plosophore* has been defined as a group of atoms which is capable of forming an explosive compound on introduction into a hydrocarbon. According to these authors there are two classes of plosophores differing sharply in effectiveness and consistency in producing power. Hence it is suggested that these be called “primary” and “secondary” plosophores.

Primary plosophores include nitrate esters, aromatic and aliphatic nitro groups and the nitramine group.

The secondary plosophores that comprise the remainder include such groups as azo, azide, nitroso, peroxide, ozonide, perchlorate, etc.

If more than one type of these groups is present such a molecule may be named a *hybrid* according to Lothrop and Handrick.

Groups which do not themselves produce explosive properties, but may influence them in the same way that auxochromic groups vary the colour intensity and shade of a dye, are called *auxoplosives* by these authors. We may quote hydroXY~, carboxyl, chlorine, sulphur, ether, oxygen, amine, etc. as examples of such groups.

* Although the classification of groups existing in explosive molecules suggested by Lothrop and Handrick may be accepted, their far-reaching postulations concerning a close relation between the oxygen balance and performance of explosives aroused strong criticism [4]. It is known that the oxygen present, for example, in carbonyl or hydroxyl groups, has little effect on the performance of an explosive. This is due to the high heat of formation of C-O and C-O-H bonds. On the contrary, the low (negative) heats of formation of N--O and CEC bonds are of great significance in relation to the performance of explosives.

That is the reason why the performance of picric acid (trinitrophenol) is only vary slightly higher than that of trinitrobenzene and why the performance of trinitroanisole is much the same as that of trinitrotoluene.

The low value of the explosive power of oxygen atoms bonded with carbon and hydrogen atoms in such a group as COOH had already been stressed by Stettbather [5], who also pointed out that an exception is provided by peroxides and ozonides which form exothermic bonds that considerably enhance explosive performance-

However, the slightly better performance of picric acid compared with trinitrobenzene is probably the result of the former's greater ability to detonate. The ease of detonation of picric and styphnic acids as compared with trinitrobenzene is well known. D. Smolenski and Czuba [6] recently pointed out that dinitrophenol detonates more readily than dinitrobenzene.

It is also well known from the classic work of L. Wöhler and Wenzelberg [7] that the sensitivity to impact of aromatic nitro compounds increases with increase in the number of substituents for a given member of the nitro groups.

Explosive mixtures can be divided into:

(1) those with at least one explosive component
(2) others where there is no explosive component.

The classification of mixtures will be dealt with in detail in Vol. III.

According to their uses explosives are divided into high explosives, propellants (‘low explosives”) and primary explosives or initiators.

High explosives may be class&d according to their physical properties as powdery, meltable, semi-meltable and plastic. Propellants may be grouped on the basis of chemical composition into gun powder and similar mixtures, nitrocellulose (single base) and nitroglycerine (double base) powders. With respect to their uses and some properties they are divided into black powder, smokeless and flashless powders, and rocket propellants.

Primary explosives and their mixtures are divided into those used for filling ignition caps and those used in detonators.

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CHAPTER I

NITRATION AND NITRATING AGENTS

GENERAL INFORMATION

NITRATION is one of the earliest known organic chemical reactions. It is mentioned in the writings of the alchemists. As early as in the first half of the XVIIIth century Glauber obtained picric acid by acting on wool and horn with nitric acid. Soon reactions between nitric acid and a variety of organic substances became one of the alchemical reactions most frequently used. They were usually carried out by heating a substance with nitric acid, often to boiling point. Thus picric acid was obtained from certain organic substances such as indigo, silk, resins, etc.

In 1833 Braconnot obtained nitric esters of cellulose and starch by acting with nitric acid on plant fibres and starch, at low temperature. In 1834 Mitscherlich nitrated benzene to nitrobenzene. But it is only since 1842, when Zinin reduced nitrobenzene to aniline, that rapid development of the chemistry of nitro compounds and their application to organic industry has occurred.

At present nitration is one of the most widely applied direct substitution reactions. This is due to several factors. For example nitration usually proceeds easily, its products can readily be separated from the spent acid, and there is a wide range of possibilities in the practical use of nitro compounds, both as intermediates and end products. The presence of a nitro group in the starting product made it possible to obtain a number of basic organic intermediates such as aniline and benzidine. Dyes with more than one nitro group, such as picric acid were obtained. It has been found that higher nitrated nitro compounds and nitric acid esters have explosive properties and are of practical importance. Some nitro compounds are used in perfumes. Medicinal properties have lately been discovered in certain nitro compounds, e.g. chloramphenicol.

Nitration is a reaction which has contributed greatly to the development of the substitution rule [I]. Although nitration had been well known and widely used for many years both in the laboratory and in industry, little was known about the nature and mechanism of this reaction until recently. However, in the last two decades much progress has been made in this field.

With the aid of the new techniques offered by modem physics and physical chemistry and by the application of the modem electronic theory of chemical bonds, certain difficult problems have been elucidated in the course of extensive research so that now what might be defined as a modern theory of nitration can be outlined, although it is still far from being perfect.

Nitration can be carried out either directly by introduction of the nitro group in place of hydrogen atom or by adding it to a double bond, or else indirectly, by introducing into a compound a group which can readily be substituted by the nitro group.

The following nitrating agents are most frequently used for the direct introduction of the nitro group:

(1) concentrated nitric acid

(2) mixtures of concentrated nitric acid and concentrated sulphuric acid (or oleum) in different proportions-these are usually known as nitrating mixtures

(3) alkali nitrates in the presence of sulphuric acid

(4) dilute nitric acid

(5) nitrogen dioxide

(6) a solution of nitrogen dioxide in sulphuric acid

(7) nitrogen dioxide in the presence of catalysts.

For laboratory experiments and sometimes in industry more expensive nitrating agents may be used, as for example solutions of nitric acid in inert organic solvents (chloroform, carbon tetrachloride, ether, nitromethane, etc.), or a solution of nitric acid in phosphoric or acetic acids or in acetic anhydride. The use of these nitrating agents may be of some practical value and will be discussed later on in detail.

For nitrating on the laboratory scale, mixtures of nitric acid esters or acyl nitrates, e.g. acetyl nitrate CH_3CONO_3, and sulphuric acid may also be used.

Several lesser known nitrating agents, which can find practical use on a laboratory scale are metal nitrates in the presence of acetic acid or acetic anhydride, described by Menke [2], tetranitromethane and hexanitroethane in an alkaline medium, used by Schmidt [3], and nitroguanidine in solution in sulphuric acid, used for the nitration of aromatic amines and phenols.

Besides these direct methods of introducing nitro groups, several indirect methods are known that consist in the introduction of a group which can readily be substituted by a nitro group. In one of these which is widely used in the nitration of phenols, a compound is sulphonated and subsequently, by reaction with nitric acid, the sulpho group is replaced by the nitro group.

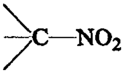
Other indirect nitration methods applied on an industrial scale, for nitrating phenols, comprise: introducing a nitroso groups into the phenol and then oxidizing it to the nitro group, and a method involving oxidation of a primary amino group to the nitro group.

In experimental work indirect methods of introducing nitro groups find wide application as, for example, the substitution of a halogen (iodine or bromine in an alkyl iodide or bromide) by the Nitro group, by means of silver nitrite (the Victor Meyer reaction), and the new modification of this method described recently by Kornblum et al. [4, 4a], in which alkyl halides are reacted with sodium nitrite.

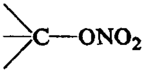
In aromatic compounds, an amino group may be substituted by the nitro group by diazotization and reacting with nitric acid in the presence of cuprous salts (the Sandmeyer reaction). This method is used for laboratory work only and is described in textbooks on preparative organic chemistry.

With respect to the chemical structure of compounds resulting from nitration processes, three types of nitration reactions are distinguished which may be referred to as:

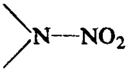
(1) C-nitration, leading to the formation of "true" nitro compounds, having the nitro group attached to a carbon atom:



(2) O-nitration, leading to the formation of nitric acid esters, with the nitro group attached to an oxygen atom:



(3) N-nitration, leading to the formation of nitramines with the nitro group attached to a nitrogen atom of an amine or amide group:



NITRIC ACID

The physical constants of chemically pure nitric acid are

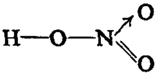
specific gravity	1.51
specific heat	0.5 k&/kg
melting point	-41.6°C
boiling point	+86°C
heat of formation	-41.66 kcal/mole

At the boiling point nitric acid undergoes partial decomposition which proceeds chiefly according to the equation:

$$2HNO_3 \rightarrow 2NO_2 + H_2O + \tfrac{1}{2}O_2 \qquad (1)$$

At higher temperatures the degree of decomposition is greater and at 256°C it is complete.

In conformity with the accepted notation for simplified electronic formulae, the structural formula of nitric acid according to Sugden is



As this formula indicates in the nitro group one atom of oxygen is linked to the nitrogen atom by a double bond, the other-by a semipolar linkage (see Chapter V on the structure of the nitro group, p. 168). Bond distances and bond angles have been calculated by Maxwell and Mosley [5] (Fig. 1a), using their own experiments on the electron diffraction of nitric acid vapour and measurements of the Raman spectrum of anhydrous nitric acid by Chedin [6].

Nitric acid molecules are linked by hydrogen bonds. This assumption was based originally on the results of studies of the nitric acid absorption spectrum in the very near infra-red (ca. 1μ) by Badger and Bauer [7], Dalmon [8], Dalmon and Freymann [9] and also on the X-ray investigation by Luzzati [10] (Fig. 16).

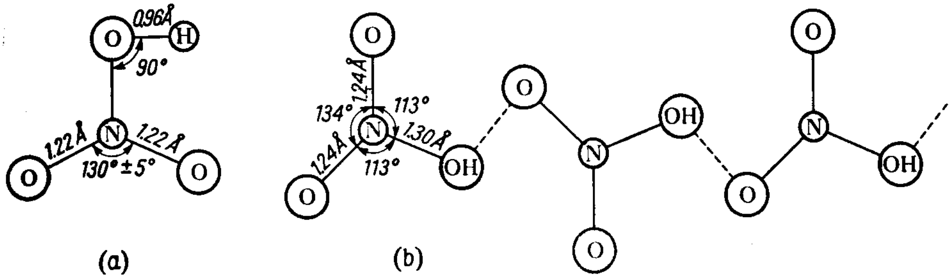
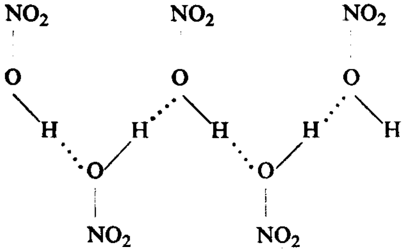


FIG. 1. (a) Bond distances and bond angles of the molecule of nitric acid (Maxwell and Mosley [5]); (b) Crystalline nitric acid: molecules of nitric acid associated through hydrogen bonds (Luzzati [10]).

More recent infra-red investigations have confirmed the existence of hydrogen bonds. According to Ingold, Cohn and Poole [40] they exist even in the vapour phase.

The association of the molecules is presented by a chain (I) or a ring (II) formula. In both cases hydrogen bonds are present between the OH and NO_2 groups.



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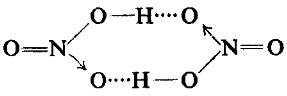

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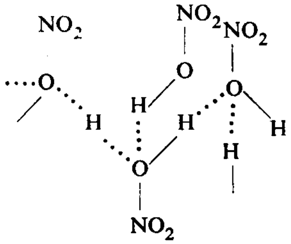
Gillespie and Millen [11] suggested another form of presentation of the association of nitric acid molecules by means of hydrogen bonds. They assumed that oxygen atoms linked by hydrogen bonds are tetrahedrally coordinated as in water molecules (III) :



III

They believe that this formula is better than the others in explaining the ability of nitric acid to dissociate. Moreover it is consistent with the low basicity of the nitro groups (which is discussed later, see p. 218).

A more detailed review of research work on the absorption spectra of nitric acid is given later (see p. 19-27).

Nitric acid forms hydrates with water: $HNO_3 \cdot H_2O$ (m. p. -38°C) and $HNO_3 \cdot 3H_2O$ (m. p. -18.5°C). The chief evidence for these hydrates is obtained from the thermal analysis of the system nitric acid-water (Fig. 2). Other experimental facts also confirm the existence of addition compounds of nitric acid and water. Thus the *refractive* ***index*** shows, according to Veley and Manley [12], a linear relation over the range from 78 to 91% concentration. At 91% a sharp inflection occurs, and above 98.5% the slope of the curve is reversed. The ***electrical conductivity*** also shows anomalies over this concentration range, passing through a minimum.

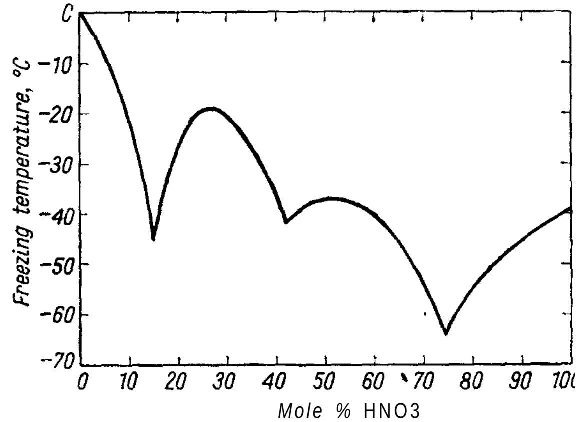
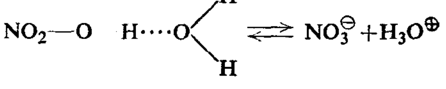


FIG. 2. Thermal analysis of nitric acid-water system.

The considerable heat evolved on dilution of nitric acid with water proves that the nitric acid hydrates are stable. With an excess of nitric acid the heat amounts to 3.5 kcal per mole of water. It has been suggested that the nitric acid hydrate, $HNO_3 \cdot H_2O$, present in concentrated nitric acid is undissociated and that the water molecules are attached to the nitric acid molecules by hydrogen bonds. Thus there would be the equilibrium :



$$NO_2{-}O\ H\cdots O\begin{matrix}\diagup H\\ \diagdown H\end{matrix} \rightleftarrows NO_3^{\ominus} + H_3O^{\oplus} \qquad (2)$$

Nitric acid acts on organic compounds both as a nitrating and as an oxidizing agent. The reaction depends on the compound being nitrated and on the concentration of the nitric acid. In accordance with a general rule, a concentrated nitric acid acts mostly as a nitrating agent. When diluted its nitrating action diminishes accordingly and finally gives way to an oxidizing action. The more dilute the nitric acid the more vigorous (up to a limit) is the oxidizing action. Extensive research into the physical properties of nitric acid, especially that which has been carried out recently, has been aimed at finding an explanation of this double function of nitric acid.

The limiting concentration of the nitric acid in a nitration process depends largely on the nitrated compound itself. Some phenols, for example, can be nitrated with nitric acid in concentrations of below 5%, while benzene does not nitrate at those concentrations. Aliphatic hydrocarbons can be nitrated even with 13 % nitric acid.

Knowing how a nitration process is likely to proceed is possible only when the structure of the nitrating agent itself is known. This is why a great deal of research work has been devoted lately to the elucidation of the structure of nitric acid when pure and in mixtures with other mineral acids.

The most frequently used nitrating mixture is the one comprising nitric plus sulphuric acids. The role of the sulphuric acid has been the subject of many investigations. These are described in the following section.

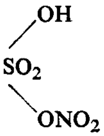
The most recent review of the physicochemical properties of nitric acid is that of Stern, Mullhaupt and Kay published in 1960 [12a].

NITRIC ACID IN ADMIXTURE WITH OTHER MINERAL ACIDS

EARLIER WORKS

Muspratt and A. W. Hofmann [13] were the first to use a mixture of nitric and sulphuric acids for nitrating nitrobenzene to dinitrobenzene.

Initially sulphuric acid was considered to act as a “dehydrating agent” in a nitrating mixture with nitric acid. This view was expressed in the literature for the first time by Spindler [14]. The first attempt to elucidate the form of nitric acid in admixture with sulphuric acid was a hypothesis formulated by Markovnikov [15]. It assumed that the two acids form a mixed anhydride, i.e. nitrosulphuric acid :



Later Sapozhnikov [16] developed a theory, based on density, electrical conductivity and partial vapour pressure measurements. He assumed a state of equilibrium between the hydrates of the two acids in their mixtures:

$$HNO_3 \cdot nH_2O + xH_2SO_4 \longleftrightarrow HNO_3 \cdot (n-x)H_2O + xH_2SO_4 \cdot H_2O \qquad (3)$$

Since the affinity of water for sulphuric acid is higher than that for nitric acid, nitric acid gradually becomes dehydrated with increase in concentration of sulphuric acid. Finally, at x = n, nitric acid becomes anhydrous.

$$HNO_3 \,.\, nH_2O + nH_2SO_4 + HNO_3 + nH_2SO_4 \,.\, H_2O \qquad (4)$$

At high concentrations (mixtures with a low water content) Sapozhnikov found certain anomalies in the vapour pressure of HNO_3 and in its electric conductivity. He ascribed them to the formation of nitric anhydride N_2O_5. Thus the equation will be:

$$2HNO_3 + H_2SO_4 \rightarrow N_2O_5 + H_2SO_4 \,.\, H_2O \qquad (5)$$

Later, to confirm his theory, Sapozhnikov gave some data on the O-nitration of cellulose with nitric acid (see Vol. II) and on the nitration of naphthalene (p. 427).

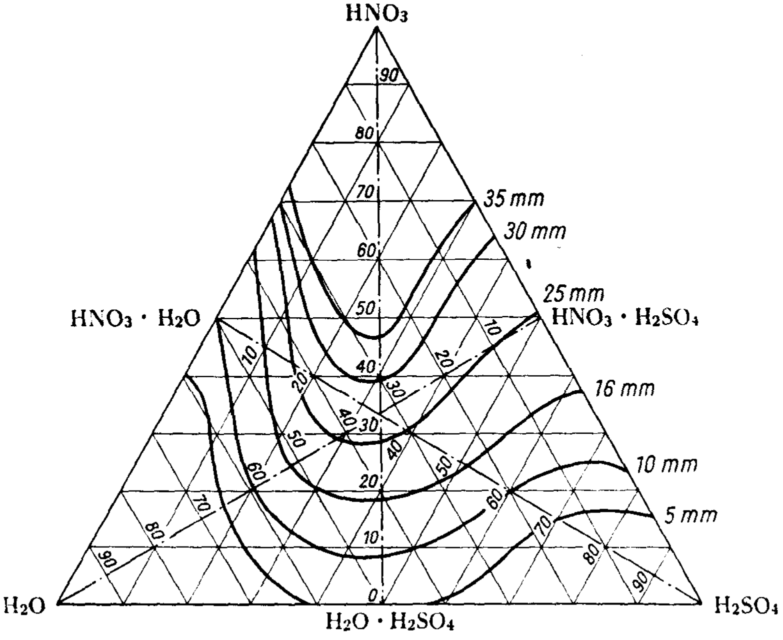


FIG.. 3. Isobars of partial vapour pressure of nitric acid in nitric acid-sulphuric acid-water mixtures (Sapozhnikov [16]).

The nitration curves for these compounds when nitrated with nitrating mixtures are similar to the vapour pressure curves of nitric acid in mixtures, presented after Sapozhnikov in Fig. 3.

Sapozhnikov's view was partly confirmed by Walden [17]. Halban and Eisenbrand found [18] that the absorption spectrum of pure nitric acid in the ultraviolet differed completely from its spectrum when in solution in anhydrous sulphuric acid. The authors explained this observation by assuming the existence of the nitric anhydride or the mixed nitric-sulphuric anhydride. This assumption seemed to be all the more probable as in some earlier papers the idea had already been expressed that N_2O_5 might exist in concentrated nitric acid. Thus in 1898 veley and Manley [12] suggested it on the basis of the existence of an electric conductivity minimum at a nitric acid concentration of 96-97% HNO_3 and later, in 1903, the same authors found evidence in refraction coefficient measurements, then Küster and Münch [19] in 1905, published further evidence based on measurements of the properties of the anhydrous nitric acid.

In his later studies Hantzsch assumed, according to the Brönsted theory of acids and bases, that nitric acid acts as a base towards sulphuric acid. According to Brõnsted, an acid is a compound able to give off a proton while a base is a compound able to take up a proton.

The acidic character of a compound At appears in the presence of another compound B_1, which itself behaves like a base:

$$A_1 \rightarrow B_1 + H^+$$

As a free proton cannot exist it must be attached to a base B_2. As a result, an acid A_2 is formed:

$$H^+ + B_2 \rightarrow A_2$$

The two reactions sum up to give a new one:

$$A_1 + B_2 \longleftrightarrow A_2 + B_1$$

in which the proton is transferred from an acid A_1 or A_2 to a base B_2 or B_1.

One of the components of the system may be a solvent. This is the case, for example, with a solution of nitric acid in sulphuric acid. The sulphuric acid, with a very small affinity for the proton, plays the role of an acid and nitric acid behaves like a base.

Usanovich [20] and Lewis [20a] have generalized the Brõnsted theory. The latter considered adds to be compounds which are able to employ a lone pair of electrons from another molecule; bases are compounds having a lone pair of electrons which may be used by another molecule.

Hantzsch opposed the theory of N_2O_5 existing in the nitrating mixture HNO_3 + + H_2SO_4 Due to the importance of the Hantzsch theory in the development of our views on the nature of the nitration process, we shall discuss it in detail. In a number of works Hantzsch [21-23] developed a theory based on Schäfer’s experiments [24] on the absorption spectrum in ultra-violet light. Schäfer’s chief observation was, that the spectrum of anhydrous nitric acid in a non-aqueous solvent (hexane, sulphuric acid, etc.) is analogous with the spectra of nitric acid esters.

On the basis of these data Hantzsch assumed that, generally speaking, acids have two forms:

(1) true acids with a spectrum similar to that of metal salts

(2) pseudo-acids with a spectrum similar to that of esters.

According to Hantzsch, the structure of a true nitric acid is $NO_3^-H^+$ or $N(O_3)^-H^+$. The hydrogen atom is attached by electrostatic force only and that is why it dissociates readily, while the structure of concentrated nitric acid is that of the undissociated pseudo-acid $NO_2.OH$ or $N(O_2)OH$.

Both forms are in equilibrium. The pseudo-acid form acts as a nitrating and esterifying agent. The addition of water shifts the equilibrium towards the formation of the dissociated form of the true acid, which has no nitrating properties:

$$NO_2.OH \overset{H_2O}{<\!\!->} NO_3^-H^+ \tag{6}$$

Thus, the addition of sulphuric acid to nitric acid increases the concentration of the pseudo-acid. The sulphuric acid, being the stronger, gives off a proton to pseudo-nitric acid and causes the formation of the following mono- and bivalent ions :

$$NO_2.OH + H_2SO_4 -> NO(OH)_2^+ + HSO_4^- \tag{7}$$

$$NO_2.OH + 2H_2SO_4 -> N(OH)_3^{2+} + 2HSO_4^- \tag{8}$$

Hantzsch named the ion $H_2NO_3^+$ *nitracidium,* and the ion $H_2NO_3^{2+}$ *hydro-nitrucidium.* In particular, the eqn. (8), according to which the $H_3NO_3^{2+}$ ion is formed, appeared to be correct in the light of Hantzsch’s cryometric studies [21] published in 1909. He found that the freezing point of sulphuric acid fell very considerably when nitric acid was added, indicating that the value of the van’t Hoff i-factor (in the equation PV = ***inRT)*** ranges from 3.4 to 4.0. Among other cryometric investigations, measurements by Oddo and Scandola [25], Hammett, et al. [26-28], Robles and Moles [29] should be mentioned. On the whole they are in agreement with Hantzsch’s data.

To obtain further arguments for the confirmation of his theory in 1925 Hantzsch [21] examined the ultra-violet absorption spectra of nitric acid. On dilution with water a band appears which may be ascribed to the NO_3^- ion. The band is not present in solutions of nitric acid in sulphuric acid, since, as the author says, the ions $H_2NO_3^+$ and $H_3NO_3^{2+}$ must appear in such circumstances.

Halban [18] reported, in the paper already referred to, that the difference between the absorption spectrum of pure nitric acid and that of its mixture with sulphuric acid is due to the presence of N_2O_5 in the mixture, while Walden [17] believed instead that it was the ***nitronium ion,*** NO_2^+, which will be discussed later, that was present in the mixture.

Hantzsch tried to obtain further evidence for the existence of the above mentioned ions, using the electric conductivity method but without success. Finally he tried to isolate the sulphates of the two hypothetical ions nitracidium and hydronitracidium:

$$(H_2NO_3)^+(HSO_4)^- \text{ and } (H_3NO_3)^{2+} (HSO_4)^{2-}$$

Although he did not succeed in isolating these salts he postulated, for confirmation of his theory, that the compound with the empirical formula $N_2O_5.4SO_4.3H_2O$ isolated by Weber as early as in 1871 is a salt of pyrosulphuric acid :

$$(H_2NO_3)^+ (HS_2O_7)^- \text{ or } (H_3NO_3)^{2+}(S_2O_7)^{2-}$$

An observation by Holmes [30] seemed to confirm Hantzsch’s hypothesis; Holmes demonstrated by thermal analysis the existence of the molecular compound

$(H_2SO_4)_5.HNO_3$ or N_2O_5. 10 SO_3. 11 H_2O with a melting point of +23°C. In 1949 Dade [31] demonstrated in the same way the existence of the compound $2N_2O_5$. $.11SO_3.9H_2O$ (m. p. +18.8°C) and Heertjes and Revallier [31a] the existence of the compound $HNO_3.2SO_3$, which according to Spasokukotskii [59] is nitronium pyrosulphate $NO_2^+.HS_2O_7^-$.

At last in papers published between 1925 and 1928, Hantzsch referred to the analogy between above-mentioned compounds and those of nitric and perchloric acids [21-23]. He reported that he had succeeded in isolating crystalline nitracidium and hydronitracidium perchlorates :

$$(H_2NO_3)^+(C1O_4)^- \quad \text{and} \quad (H_3NO_3)^{2+}(C1O_4)^{2-}$$

According to Hantzsch nitracidium and hydronitracidium nitrates are present in concentrated nitric acid:

$$(H_2NO_3)^+(NO_3)^- \quad \text{and} \quad (H_3NO_3)^2+(NO_3)_2^-$$

The Hantzsch theory was supported by Lauer and Oda [32], who examined the nitration of anthraquinone and nitrobenzene with mixtures of nitric and sulphuric acid, the sulphuric acid containing from 20% water to 5% sulphur trioxide.

They found that the activation energy of the nitration reaction was 21.65 kcal/mole when the water content of the sulphuric acid was in the range 4.4-13%, while it was only 13.30 kcal/mole when anhydrous sulphuric acid was present. The reaction rate was higher in the presence of these concentrations of water than in the non-aqueous medium. Hence Lauer and Oda came to the following conclusions:

1. In a mixture with 89% sulphuric acid, nitric acid exists in two forms -true nitric acid and pseudo-nitric acid, according to Hantzsch's theory. Only the pseudo-acid form acts as a nitrating agent. On dilution with water the concentration of pseudo-acid falls.

2. In mixtures with 89-98% sulphuric acid, nitric acid exists principally as pseudo-nitric acid with a certain quantity of sulphate of nitric acid also present.

3. When 98-100% sulphuric acid is used, the nitric sulphate content increases.

4. In a non-aqueous mixture containing free SO_3 it is only the nitric sulphate which acts as a nitrating agent.

A quite different hypothesis was suggested by Euler [33] in 1903. He assumed that a solution of nitric acid in sulphuric acid contains the nitronium or nitryl ion, NO_2^+. Subsequently in 1922 he confirmed this hypothesis.

This view was supported later by Walden [17]. Considering the high electrical conductivity of nitric acid he believed that HNO_3 should be regarded as an amphoteric electrolyte, an idea expressed by the equilibrium equation:

$$HNO_3 <-> H^+ + NO_3^- <-> OH^- + NO_2^+ \qquad (9)$$

On the basis of conductometric studies and taking into account the catalytic action of nitrogen dioxide in the nitration Klemenc and Schöller [34] suggested that a hypothetical “E-acid” is formed in the reaction of nitric acid with nitrogen dioxide and is the entity responsible for nitration:

$$\underset{}{2HNO_3 + NO_2 \leftrightarrow \underset{\text{E-acid}}{H_2N_3O_8}} \tag{10}$$

According to those authors the nitration reaction occurs as follows:

$$2RH + H_2N_3O_8 \rightarrow 2RNO_2 + NO_2 + H_2O \tag{11}$$

There was no doubt at that stage of the investigation that nitric acid reacts with sulphuric acid. Yet the research work described had put forward a problem without giving a clear answer. It was only in recent investigations that, due to more accurate physico-chemical methods, especially to the application of Raman spectrum analysis, inferences about the interaction of the nitrating mixture components have been confirmed.

MORE RECENT STUDIES

Cryometric investigations

Hantzsch’s work and his conclusions have lately been revised and criticized. In his extensive work published in 1941, Titov [35] drew attention to the fact that none of the existing view about the action of sulphuric acid on nitric acid explained Hantzsch’s observation that the value of the van’t Hoff i-factor for nitric acid dissolved in sulphuric acid may be close to 4.

Titov quotes the following equations, based on different existing views:

$$HNO_3 + 2H_2SO_4 + (HO_3S)ONO_2 + H_2SO_4.H_2O \tag{12}$$

(equation based on Markovnikov’s view)

$$2HNO_3 + H_2SO_4 + N_2O_5 + HSO_4^- + H_3O^+ \tag{13}$$

(equation based on Sapozhnikov’s view) and Hantzsch’s eqns. (7) and (8) quoted earlier.

According to Titov, the simplest way of explaining Hantzsch’s observations is in the form of an equilibrium equation, in which the nitronium cation* occurs:

$$HNO_3 + 2H_2SO_4 \leftrightarrow NO_2^+ + 2HSO_4^- + H_3O^+ \tag{14}$$

Titov believed that Hantzsch’s nitracidium and hydronitracidium ions should be considered as the hydrated nitronium ions:

$$H_2NO_3^+ + H^+ \rightarrow NO_2^+ + H_3O^+ \tag{15}$$

$$H_3NO_3^{2+} \rightarrow NO_2^+ + H_3O^+ \tag{16}$$

This view was confirmed experimentally when in 1950 Ingold [36] and his co-workers isolated crystalline nitronium salts (p. 19).

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* Nitronium ion is sometimes called nitryl or (more correctly) nitroxyl ion (see p. 13).

Using more precise methods of cryometric measurements Ingold [37] and co-workers had already found in 1946 that the value of van't Hoff i-factor for HNO_3 in sulphuric acid is 4.4. Ingold explained this by eqn. (18).

It should be pointed out that a similar equation for a solution of nitrous acid in sulphuric acid was suggested by Hantzsch as early as in 1909, and confirmed in his further publications of 1930-37:

$$HONO + 2H_2SO_4 \leftrightarrow NO^+ \; 2HSO_4^- + H_3O^+ \qquad (17)$$

(with the nitrosonium cation, NO^+).

The value of ***i*** can be explained by an equation assuming the formation of the nitronium ion, NO_2^+:

$$HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + 2HSO_4^- + H_3O^+ \qquad (18)$$

Similarly for solutions of N_2O_5 or N_2O_4 in sulphuric acid, Ingold [38-40] and his co-workers found ***i*** = 6, which would correspond to the equations:

$$N_2O_5 + 3H_2SO_4 \rightarrow 2NO_2^+ + H_3O^+ + 3HSO_4^- \qquad (19)$$

$$N_2O_4 + 3H_2SO_4 \rightarrow NO_2^+ + H_3O^+ + 3HSO_4^- \qquad (20)$$

These equations have been confirmed by an examination of the nitrating properties of such mixtures.

Titov [35] also expressed the opinion that nitric acid esters in sulphuric acid yield nitronium ions, for example in the reaction with ethyl nitrate:

$$C_2H_5ONO_2 + 2H_2SO_4 \rightarrow NO_2^+ + C_2H_5OH_2^+ + 2HSO_4^- \qquad (21)$$

The basic argument of Titov concerning the existence of the nitronium ion in such solutions seems to be right, especially in view of the cryometric investigations of L. P. Kuhn [41], who found that for a solution of ethyl nitrate in sulphuric acid, i = 6. This would correspond to the equation:

$$C_2H_5ONO_2 + 3H_2SO_4 \rightarrow NO_2^+ + 2HSO_4^- + H_3O^+ + C_2H_5O.SO_3H \qquad (22)$$

The similarity between the ultra-violet absorption spectrum of nitric acid and that of ethyl nitrate in sulphuric acid confirms this conception.

Gillespie and Graham [42] have carried out a cryometric examination of solutions of nitric acid in oleum. The results obtained are in agreement with the following equation, postulating formation of the nitronium ion:

$$HNO_3 + 2H_2S_2O_7 \rightarrow NO_2^+ + HS_2O_7^- + 2H_2SO_4 \qquad (23)$$

According to Titov's paper of 1941 nitric anhydride dissociates into the nitronium and nitrate ions:

$$N_2O_5 \rightarrow NO_2^+ + NO_3^- \qquad (24)$$

Cryometric investigations carried out by Gillespie, Hughes and Ingold [42a] confirm this equation. The authors examined the system $nN_2O_5 + H_2O$, where $n > 1$. According to their studies, anhydrous nitric acid, present in this system, undergoes a self-dissociation in the following way:

$$3HNO_3 \rightarrow NO_3^- + NO_2^+ + HNO_3.H_2O \quad (25)$$

Calculations have shown, that the NO_2^+ and NO_3^- ions content in anhydrous nitric acid at -40°C is 1.2 and 1.7% by weight respectively. The content of water is 0.5% (in form of the nitric acid hydrate).

Bennett and his co-workers [43] confirmed this interpretation of the cryometric investigations. To prove definitely the existence of the NO_2^+ ion, they attempted to show that when electrolysed, the ion is transported towards the cathode. They did not succeed in obtaining full evidence for this, although they found that nitric acid moves away from the anode. It was only when the electrolysis was carried out in the presence of oleum and barium salts, that the transport of nitric acid towards the cathode was confirmed. Studying the cathodic polarization of nitric acid Mint [44] observed the evolution of nitrogen dioxide at the cathode. This may be an additional piece of evidence for the transport of an ion containing nitrogen (probably NO_2^+) towards the cathode.

Brand [45] gave a very simple method for the analysis of nitrating mixtures confirming the theory of the formation of the nitronium ion in solutions of nitric acid in oleum. It is well known that free SO_3 present in a solution may be titrated with water until fuming disappears. This method gives fairly accurate results. The volume of water added for the titration of a mixture HNO_3 + oleum is smaller than the quantity used for the titration of pure oleum without HNO_3. This would be evidence of the reactions:

$$HONO_2 + NO_2^+ + OH^- \quad (26)$$

$$OH^- + H^+ \rightarrow H_2O \quad (27)$$

The volume of water added in the titration of SO_3 is smaller by this amount.

Brand has shown that in a solution of nitric acid in sulphuric acid, the formation of water and the HSO_4^- ion occurs, which combine with free SO_3. The amount of the SO_3 bound corresponds to the equation:

$$HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + 2HSO_4^- + H_3O^+ \quad (18)$$

However, it is not only sulphuric acid added to nitric acid that increases the latter's nitrating properties, Such substances as boron fluoride (R. J. Thomas et al. [46]) or hydrogen fluoride (Simons ***et al.*** [47]) when added to nitric acid have a similar effect.

These phenomena can be accounted for by assuming formation of the nitronium ion according to the equations:

$$BF_3 + HNO_3 \rightarrow NO_2^+ + BF_3OH^- \quad (28)$$

$$2HF + HNO_3 \rightarrow NO_2^+ + H_3O^+ + 2F^- \quad (29)$$

Conductometric studies

Further conductometric studies of nitric acid by Médard [48] and later Dalmon [49] have shown that on adding water to the anhydrous acid, conductivity falls to a minimum at concentrations of 96-97% HNO_3, and then on further dilution it rises again.

This is explained by the fact that anhydrous nitric acid is dissociated, but in the presence of small quantities of water is converted into an undissociated hydrate $HNO_3.H_2O$. It is only on further dilution that the hydrate dissociates.

In conductometric measurements of two-component system where HNO_3 was one of the components, Usanovich and his co-workers [50-50c] confirmed the view that nitric acid has an amphoteric character-it can be an acid or a base depending on the other component. Thus, it acts as a base towards sulphuric acid and as a strong acid towards water. It also acts as an acid towards CH_3OOH and CCl_3COOH and combines with these compounds, but behaves as a base with $CH_2ClCOOH$ and $CHCl_2COOH$.

Addition of compounds such as H_2SO_4, H_3PO_4, towards which nitric acid acts as a base, increases the nitrating properties of HNO_3. On the contrary, the addition of compounds such as water or nitrobenzene, towards which nitric acid behaves as an acid, decreases the nitrating action of HNO_3.

Hantzsch's argument, that with strong acids like sulphuric or phosphoric, the ions $H_2NO_3^+$ and $H_3NO_3^{2+}$ are formed, led Usanovich to the inference that it was just these cations that were the nitrating agents for aromatic compounds. On the other hand, the addition of water results in the formation of NO_3^- ions, which therefore seem to be the nitrating agents for aliphatic hydrocarbons. Swinarski and Dembiriski [51] and Swinarski and Piotrowski [52] have examined the electrical conductivity of nitric and sulphuric acid mixtures with and without water. The results of these measurements are shown in the diagram, presenting the relationship between conductivity and HNO_3 concentrations.

The principal conclusions drawn by the authors are:

1. The high conductivity of anhydrous H_2SO_4 is probably due to dissociation

$$2H_2SO_4 \leftrightarrow H_3SO_4^+ + HSO_4^- \qquad (30)$$

2. A sharp increase in the conductivity of the mixture, on adding water in quantities below 9% H_2O, indicates the complete ionization of nitric acid. Probably the dissociation may be expressed by eqn. (18) which has already been referred to

$$HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + 2HSO_4^- + H_3O^+ \qquad (18)$$

3. The conductivity diminishes with further increase in concentration of HNO_3. The reason for this may be the formation of less mobile ions, for example Hantzsch's hydrated nitronium ion:

$$HNO_3 + 2H_2SO_4 \rightarrow H_3NO_3^{2+} + 2HSO_4^- \qquad (31)$$

The authors pointed out the similarity of the conductivity curves (Fig. 4) and viscosity curves (Fig. 14) which they observed. The shapes of both curves may be explained in the same way, namely by the formation and disappearance of $(H_3NO_3)^{2+}$ and NO_2^+ ions.

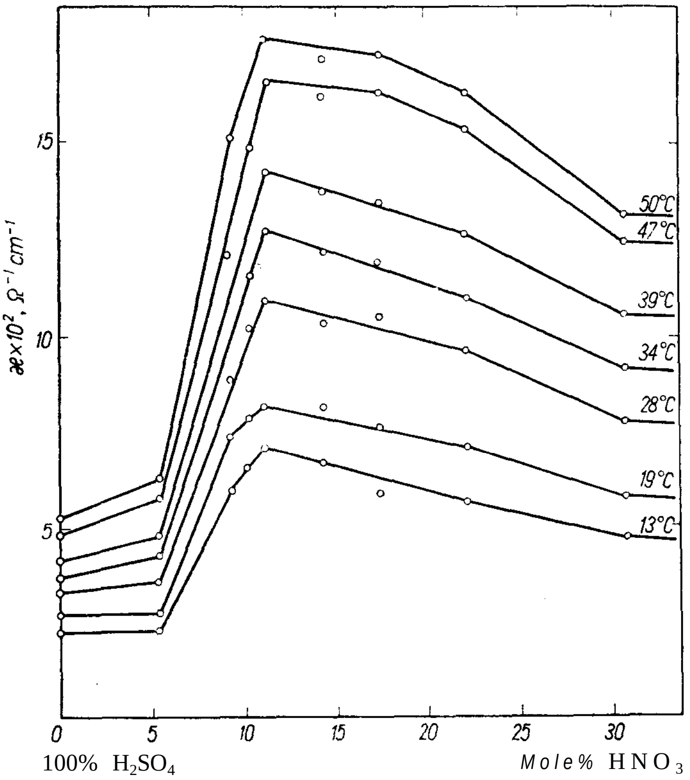


FIG. 4. Conductivity of nitrating mixtures at various temperatures (Swinarski and Piotrowski [52]).

Swinarski and Piotrowski also examined the conductivity of pure nitric and sulphuric acids as a function of temperature (Fig. 5). The curve for nitric acid has a maximum at 20°C. At 40°C the conductivity falls.

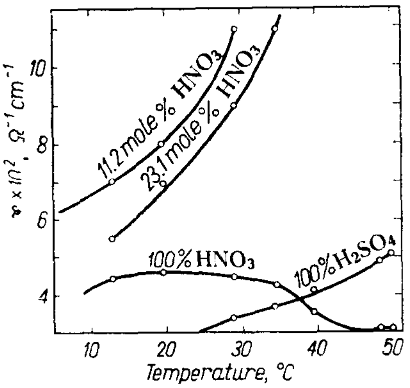


FIG. 5; Conductivity of nitric and sulphuric acid at various temperatures (Swinarski and Piotrowski [52]).

Two phenomena seem to be superposed. One is the normal increase of conductivity with temperature, the other is the equilibrium (32) which is shifted to the right at higher temperatures:

$$NO_2^+.H_2O + NO_3^- \leftrightarrow 2HNO_3 \leftrightarrow N_2O_5 + H_2O \qquad (32)$$

On the basis of their experiments on electrolysis of 80-100% nitric acid Swinarski and Bialozynski [53] came to the conclusion that the nitronium ion exists mainly in hydrated form $NO_2^+.nH_2O$.

Isolation of salts in which nitric acid is a cation. Hantzsch's experiments on the preparation of nitracid and hydronitracid perchlorates have also been verified. Ingold and his co-workers [36,34,39] have indeed prepared salts of empirical formula corresponding to $(H_3NO_3)^{2+}(C1O_4)_2^-$. They also stated that the substance was a mixture of nitronium perchlorate $(NO_2)^+(ClO_4)^-$ and the well known perchloric acid hydrate $(H_3O)^+ (ClO_4)^-$. They separated the two components by fractional crystallization from nitromethane. But they did not succeed in the preparation of the compound $(H_2NO_3)^+(ClO_4)^-$.

To Weber's compound (p. 12) the formula of nitronium pyrosulphate is at present assigned $(NO_2)^+(HS_2O_7)^-$.

Examination of Raman and infra-red absorption spectra (which will be discussed later) confirmed the nitronium salt structure of all these compounds.

Ingold and his co-workers regarded nitric anhydride as nitronium nitrate $(NO_2)^+(NO_3)^-$ (see also eqn. 24). They obtained nitronium di- and trisulphates by treating nitric anhydride with SO_3:

$$(NO_2)_2^+ \ (S_2O_7)^{2-} \text{ and } (NO_2)_2^+ \ (S_3O_{10})_2^{2-}$$

Woolf and Emeléus [54] have prepared a number of other crystalline nitronium salts, for example:

$$NO_2^+ \ HS_2O_7^-$$
$$(NO_2^+)_2S_2O_7^{2-}$$
$$(NO_2^+)_2S_3O_{10}^{2-}$$
$$NO_2^+BF_4^-$$
$$NO_2^+SbF_6^- \text{ etc.}$$

Examination of the nitric acid spectrum (alone and in mixture with sulphuric acid)

Ultra-violet absorption spectrum. The first investigations into the ultra-violet absorption spectra of nitric acid, containing certain quantities of water, were carried out by Hartley [55]. He observed that the band at about 302 mμ characteristic for the nitrate ion disappears gradually with increase in concentration of nitric acid.

Among other investigations special attention should be paid to Schafer's investigations [24] between 1910 and 1916 referred to above, and also to the work of Halban and Eisenbrand [18].

Halban and Eisenbrand investigated the absorption spectrum of nitric acid at concentrations up to 68% (15.3 N) and noted the decrease in the intensity of the NO_3^- ion band with increasing concentration. They also observed a maximum at 265 mμ in the spectrum of solutions of anhydrous acid in anhydrous ether and attributed this to the presence of the unionized NO_2-OH molecule (Fig. 6). However, Hantzsch did not confirm this part of their work He found no maximum in the absorption curve of 100% nitric acid, nor in the curve of a solution of nitric acid in anhydrous ether. He did note, however, that a band appeared on addition of a trace of water to such an ethereal solution.

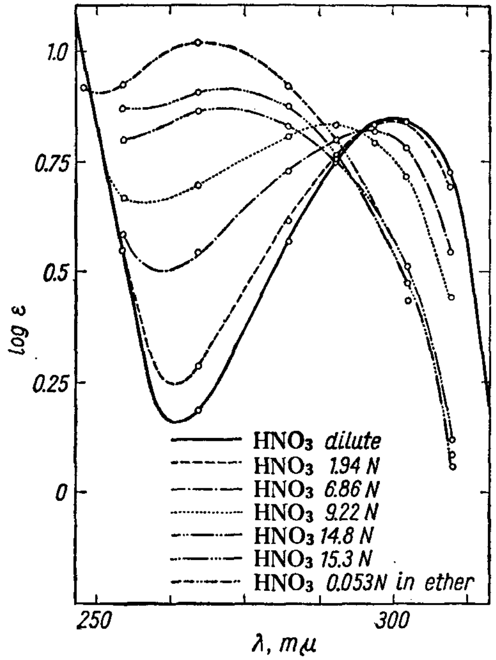


FIG. 6. Ultra-violet absorption spectra of nitric acid (Halban and Eisenbrand [18]).

Further experiments on ultra-violet absorption spectra of nitric acid in organic solvents have been carried out by a number of authors (Dalmon and Bellin [56], Kortiim [57]. Eventually R. N. Jones, Thorn et al. [58] expressed the view that nitrogen pentoxide is present in nitric acid of 95-96% and higher concentrations.

This was based on the following observations. At concentrations between 80 and 95%, an undissociated NO_2OH predominates which would be responsible for the absorption maximum near 260 mμ. This molecule or ion ("260 mμ chromogen") is present in maximal concentration at 91 to 92%. At 95 to 96%, changes occur in the spectrum which can be attributed to the presence of free

N_2O_5 in the solution. The failure of Hantzsch to find an absorption maximum in the solution of nitric acid in ether was, according to Jones and his co-workers, due to the presence of N_2O_5 in his acid. Indeed, these authors reported that solutions of N_2O_5 in nitric acid do not show a maximum (Fig. 7).

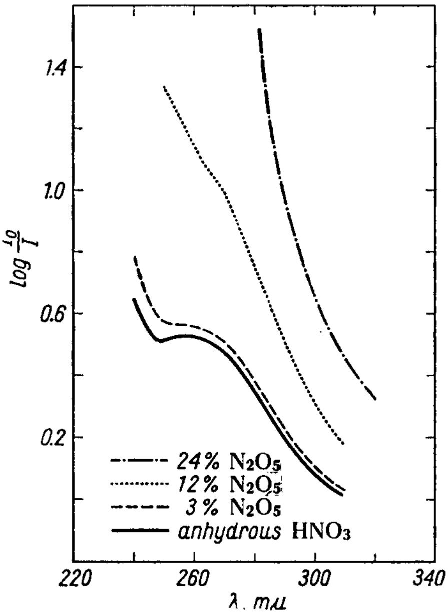
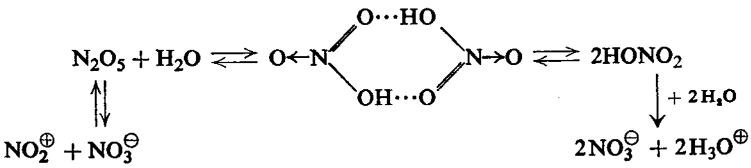


FIG. 7. Ultra-violet absorption spectra of solutions of N_2O_5 in anhydrous nitric acid. (R. N. Jones, Thorn, Lyne and E. G. Taylor [58]).

Jones expressed the view that the identification of "260 mμ chromogen" with undissociated nitric acid molecule (Hantzsch's pseudo-acid) is largely a speculative hypothesis for which there is insufficient evidence. He suggested that the 260 mμ band is produced by the NO_2^+ ion or by the undissociated N_2O_5 molecule. The high intensity of this absorption may obliterate the weak absorption of the nitrate ion at 302 mμ.

He summarized his views in the following system of equilibria:



(33)

Spasokukotskii [59] explained the results of these investigations in a similar way. He believed that the absorption maximum at 265 mμ corresponds to the nitronium ion NO_2^+, which is formed by a process of "self-ionization":

$$3HNO_3 \leftrightarrow NO_2^+ + H_3O^+ + 2NO_3^- \qquad (34)$$

which takes place together with the ordinary ionization:

$$HNO_3 + H_2O \leftrightarrow H_3O^+ + NO_3^- \qquad (35)$$

Increase in concentration involves the formation of N_2O_5, consequently the concentration of NO_2^+ ions decreases the equilibrium of the reaction

$$NO_3^- + NO_2^+ \leftrightarrow N_2O_5 \qquad (24)$$

being shifted to the right (compare the reaction on p. 19).

The maximum absorption band at 5% water corresponds to the shifting of the equilibrium to the left, when more NO_2^+ is formed.

In view of the practical application of solutions of ammonium nitrate in nitric acid in the Koffler-Bachman process for the manufacture of Cyclonite (Vol. III.) the investigations of these solutions by R. N. Jones and Thorn [58a] are important. They examined solutions containing up to 54 g of ammonium nitrate in 100 g of solution. The results are recorded in Fig . 8. Small additions of ammonium nitrate cause a decrease in the intensity of the absorption maximum near 262.5 mμ. Further addition of ammonium nitrate then causes the intensity of absorption to increase, and it falls again at a higher concentration. The considerable bathochromic shift of the absorption maximum in a mixture containing 54% of NH_4NO_3 is probably caused partly by the additive effect of the nitrate ion absorption maximum at 301.5 mμ contributed by the ion NO_3^- of the added salt.

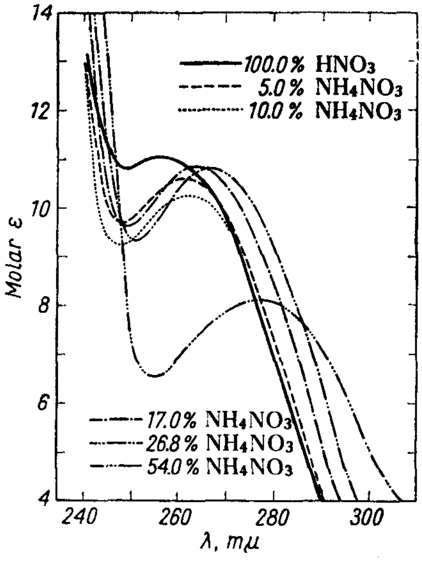


FIG. 8. Ultra-violet absorption spectra of nitric acid-ammonium nitrate solutions (R. N. Jones and Thorn [58a]).

Raman spectrum. Extensive Raman spectrum studies have played a special role in the elucidation of the structure of nitric acid. They have thrown a good deal of light on the changes which nitric acid undergoes on dilution with water, sulphuric acid, oleum, etc.

Chedin [6,60,61] gave the following results of the examination of the nitric acid Raman spectrum at concentration of the acid from 6.3 to 99.8% (Table 1).

TABLE 1

THE RAMAN LINES OF NITRIC ACID AT DIFFERENT CONCENTRATIONS

99.8%	95%	89.%	64%	52.1%	30.2%	24.5%	6.3%
611 cm-1	613 cm^{-1}	620 cm^{-1}	642 cm^{-1}	657 cm^{-1}	—	—	—
674	678	681	693	702	718 cm^{-1}	717 cm^{-1}	—
922	923	932	957	969	990	—	—
1048	1048	1052	1053	1053	1053	1053	1053 cm^{-1}
1103	—	—	1124	1128	—	—	—
1295	1300	1306	1308	1315	—	—	—
1537	1537	—	—	—	—	—	—
1679	1679	1679	1686	—	—	—	—

According to Chédin, the Raman line at 1050 cm^{-1} can be assigned to the NO_3^- ion.

Chédin and Fénéant [62] found the following bands and lines in their further investigations of high frequency Raman spectra:

$$\text{weak lines at } \begin{cases} \sim 2550 \text{ cm}^{-1} \\ \sim 2700 \\ \sim 3150 \end{cases}$$
$$\text{and a strong line at } \quad 3400$$

On adding water the intensity of the band 3400 cm^{-1} decreases while that of the other bands increases. It seems very likely that the bands at ~3400 cm^{-1} belong to nitric acid molecules linked by hydrogen bond (pp. 7-8), while the lines at 2550, 2700 and 3150 cm^{-1} probably belong to nitric acid hydrate molecules.

Médard [48] and in 1935 Chédin [60] stated, that solutions of nitric acid in sulphuric acid produced a Raman spectrum with two characteristic lines: at 1050 and 1400 cm^{-1}. As we have seen the 1050 cm^{-1} line is present in nitric acid of various concentrations, while the line 1400 cm^{-1} has not been observed.

Further investigations of Chédin [60a-62] and of Susz, Briner and Favarger [63] have shown that a solution of nitric anhydride (N_2O_5) in nitric acid produces both 1050 and 1400 cm^{-1} lines. From this the assumption has been advanced that the two lines indicate the presence of N_2O_5 in mixtures of nitric and sulphuric acids. Thus it seemed that Sapozhnikov’s theory (p, 10) had been confirmed. However, further investigations have shown that this interpretation of the results is not quite right. For Chédin stated that solutions of N_2O_5 in carbon tetrachloride, chloroform, nitromethane and phosphorus oxychloride produced the 707, 860, 1033, 1240 and 1335 cm^{-1} lines (in addition to the solvent line), while there were no 1050 and 1400 cm^{-1} lines, whereas solid N_2O_5 showed the presence of both the 1050 and 1400 cm^{-1} lines.

On the grounds of Walden's observations (in his cryometric studies), that nitric anhydride exists in $POCl_3$ solution in a non-associated form, and that according to Russ and Pokorny [64] it is associated when in solid form, Chédin has come to a conclusion that the Raman 1050 and 1400 cm^{-1} lines correspond to associated N_2O_5, while the 707, 860, 1033, 1240, and 1335 cm^{-1} lines correspond to the non-associated, monomolecular form of N_2O_5. Consequently N_2O_5 in nitric acid or in nitric and sulphuric acids solution would appear to exist in an associated form.

As the presence of the nitronium ion NO_2^+ in nitric acid and in its mixtures with sulphuric acid had again been suggested, the view has been expressed that the 1400 cm^{-1} line should be assigned to that ion, and the 1050 cm^{-1} line to the nitrate ion NO_3^- (Chedin drew attention at an earlier date to that). It was also revealed that the hydrosulphate ion (HSO_4^-) present in sulphuric acid and in mixtures of sulphuric and nitric acids also produces the 1050 cm^{-1} line.

Nitric anhydride produces a spectrum composed of the two lines, since it undergoes dissociation according to the eqn. (24) given on p. 15.

According to the eqn. (18) on p. 15, nitric acid also yields the nitronium ion with sulphuric acid.

This interpretation of the Raman spectrum was verified in 1946 by Ingold and his co-workers [36] for mixtures of nitric acid with other concentrated acids. Thus, for example, mixtures of nitric and perchloric or selenic acids produce a high intensity 1400 cm^{-1} line, but not a trace of the 1050 cm^{-1} line. Instead of the latter, lines corresponding to the perchlorate and selenate ions appear.

On the basis of these experiments it has been established that the 1400 and 1500 cm^{-1} lines correspond to completely different molecules. It has also been established decisively that the 1400 cm^{-1} line appears on the addition of another strong acid to nitric acid and that most likely it corresponds to the NO_2^+ ion, which is formed in such a solution.

In 1936 Chédin [60a] also examined the Raman spectrum of the solution of nitric acid in oleum. He observed, of course, the 1400 cm^{-1} line, and also another one, between 1075 and 1095 cm^{-1}. At first the two lines had been assigned to the $N_2O_5(SO_3)_n$ complex. Yet the work of Millen and Ingold [36,37] has shown that $KHSO_4$ also produces a line ranging from 1075 to 1095 cm^{-1}; the frequency varied with concentration. At present the line is assigned to the hydropyrosulphate ion $HS_2O_7^-$ which is probably formed according to the equation:

$$HSO_4^- + H_2S_2O_7 \leftrightarrow H_2SO_4 + HS_2O_7^- \tag{36}$$

Since in this system the HSO_4^- ion is also present, giving the 1050 cm^{-1} line, the two frequencies 1095 and 1050 cm^{-1} are superimposed and the resultant frequency is 1095-1075 cm^{-1}, depending on the intensity of the 1050 cm^{-1} frequency.

The Raman spectra of solutions $N_2O_5 + nH_2O$, with $n>1$, confirm the view that nitric anhydride dissociates according to the equation presented on p. 19.

The anhydrous nitric acid which is formed in this system is dissociated into the same ions (eqn. (1) p. 6).

The diagram (Fig. 9) shows the concentration of NO_2^+ ions in various nitrating mixtures determined by measurements of the intensity of Raman lines. The limits of the ability to nitrate nitrobenzene by various mixtures almost coincide with the limit of detectability of NO_2^+ by the Raman spectrum analysis.

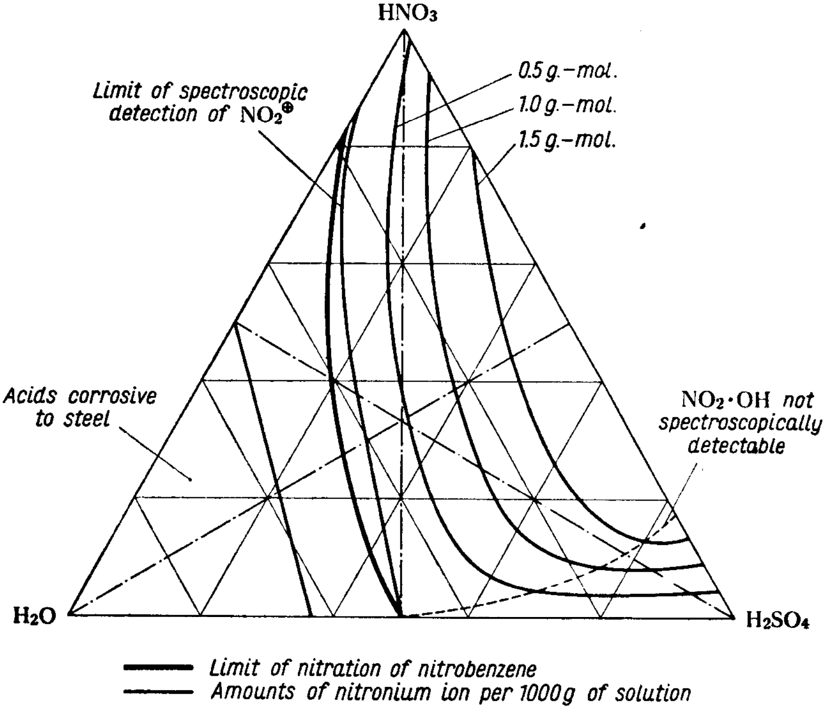
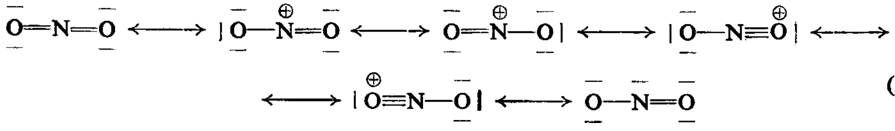


FIG. 9. Concentration NO_2^+ ions in mixtures HNO_3-H_2SO_4-H_2O (Gillespie and Millen [11]).

According to Chédin and Fénéant [62a] the maximum concentration of NO_2^+ (ca. 4.5 g-ion/l.) exists in the solution of 20-40% HNO_3 in sulphuric acid.

Structure of the nitronium (nitryl) ion NO_2^+

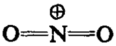
In 1941 Titov [35] considered the structure of the nitronium ion as a number of resonating structures :



$$\overline{\underline{O}}=N=\overline{\underline{O}} \longleftrightarrow |\overline{\underline{O}}-\overset{\oplus}{N}=\overline{\underline{O}} \longleftrightarrow \overline{\underline{O}}=\overset{\oplus}{N}-\overline{\underline{O}}| \longleftrightarrow |\overline{\underline{O}}-N\equiv\overset{\oplus}{O}| \longleftrightarrow$$
$$\longleftrightarrow |\overset{\oplus}{O}\equiv N-\overline{\underline{O}}| \longleftrightarrow \overline{\underline{O}}-\overline{\underline{N}}=\overline{\underline{O}} \qquad (37)$$

Titov postulated that the NO_2^+ ion may be regarded as isosteric with carbon dioxide O=C=O, thus suggesting a linear structure for the ion.

Indeed, according to Bennett, Brand and Williams [43] the fully symmetrical structure of NO_2^+



$$O{=}\overset{\oplus}{N}{=}O$$

should be accepted on the basis of the Raman spectrum. They also pointed out the similarity between CO_2 and NO_2^+, the only difference being that NO_2^+ ion has one extra unit charge on the central nucleus as compared with the CO_2 molecule. Therefore it is to be expected that the frequency of fundamental vibration of NO_2^+ should be somewhat higher than for that of CO_2 (ca. 1320 cm^{-1}). These considerations are consistent with the observed value 1400 cm^{-1} for NO_2^+. Moreover the degree of depolarization (ca. 0.20 according to Chédin) confirms that the line must arise from a totally symmetrical vibration.

This structure was confirmed in 1948 by Cox, Jeffrey and Truter [65] by X-ray examination of nitronium perchlorate. The distance N-O was found to be 1.1 Å (Fig. 10). Grison, Eriks and Vries [65a] gave the figure 1.154±0.01 Å.

FIG. 10. Structure and bond distances in NO_2^+ cation.

Infra-red absorption spectra. For a long time the experimental difficulty of working with nitric acid in the infra-red region due to corrosion of the cells by nitric acid hindered examination of the infra-red absorption spectrum of nitric acid. Originally therefore, only the near infra-red region was studied.

Thus Badger and Bauer [7] examined the spectrum of 100% nitric acid vapour alone and in dioxane solution in the region near 1 µ. Dalmon [8,49], Dalmon and Freymann [9], and Freymann [66] have studied the spectra of nitric acid and its solutions in dioxane, carbon tetrachloride and water.

By using glass and polyethylene cells with silver chloride windows Ingold and his co-workers [40] succeeded in examining the infra-red spectra of nitric and deuteronitric acid vapour, Fréjacques [67] examined the spectra of liquid and gaseous nitric acid, and Bethel1 and Sheppard [68] investigated the infra-red spectra of fuming nitric acid.

Fréjacques failed to detect the NO_2^+ bands in the spectra and this cast some doubt on the existence of the NO_2^+ ion in concentrated nitric acid. However, Marcus and Fresco [69] in their extensive investigation of the infra-red spectra of nitric acid discovered that the absorptivity of the NO_2^+ ion is very low. The NO_2^+ bands can be observed only when a thick layer (18.4 µ) of nitric acid is used. The NO_2^+ frequencies are: 2360 and 3745 cm^{-1}. (The Raman frequency 1400 cm^{-1} cannot be present in the infra-red spectrum as it is produced by fully symmetrical vibrations of NO_2^+).

The intensity of the band 2360 cm^{-1} is enhanced by the addition of nitronium fluoroborates, sulphuric acid, phosphorous pentoxide, or small amounts of acetic anhydride. It is produced by addition of sodium nitrate, potassium dihydrogen phosphate, water or larger amounts of acetic anhydride.

Recently Hofman, Stefaniak and T. Urbanski [70] examined the spectra of nitric acid alone and in solutions in sulphuric acid. The following are the frequencies they obtained for nitric acid of 98.2-99.5% concentration:

1665 cm^{-1}	a medium band, assymmetric stretching vibrations of the NO_2 group
1368 cm^{-1}	a very strong band of the nitrate ion (NO_3^-)
1297 cm^{-1}	a strong band, symmetric stretching vibrations of the NO_2 group
948 cm^{-1}	a weak band, bending vibrations of NO_2 group
774 cm^{-1}	a weak band, deformation by out-of-plane vibrations.

Dilute nitric acid (6%) gives bands at 3400 and 1642 cm^{-1} which should be assigned to the stretching and deformation vibrations, respectively of the OH group in water. Two more bands at 1385 and 770 cm^{-1} have the same origin as in concentrated acid.

Vapour pressure measurements

The exceptionally low vapour pressure of HNO_3 in admixture with sulphuric acid is a proof that nitric acid is present, in such a mixture, not in the free state, but as a compound. Gelfman [69] measured the vapour pressures of mixtures of $HNO_3 + H_2SO_4 + SO_3$ and drew some conclusions from the values obtained. He stated that the vapour pressure minimum corresponds to the weight ratio SO_3: HNO_3 =2.5. The vapour pressure rises as this ratio increases-at first slowly, then more rapidly, especially when the ratio SO_3: HNO_3 = 6.5. Near the minimum, the vapour consists chiefly of HNO_3 and near the maximum mainly of SO_3. Gelfman suggested on the basis of Sapozhnikov's work (p. 10) and that of Chédin on the Raman spectra of nitric and sulphuric acid mixtures, that the vapour pressure minimum is due to the formation of a stable compound $N_2O_5.4SO_3$, and the less stable compounds $N_2O_5.3SO_3$ and $N_2O_5.5½SO_3$.

This view has been criticized by Spasokukotskii [59] who explains Gelfman's observations in the light of Brand's equilibrium equations.

Spasokukotskii points out that undissociated compounds of the $N_2O_5.nSO_3$ type cannot exist in solution in sulphuric acid since both nitric acid and nitric anhydride undergo dissociation, yielding the NO_2^+ ion. At the weight ratio SO_3:HNO_3 = 2.5, the molar ratio is 2 which would be consistent with the equation:

$$HNO_3 + 2SO_3 \leftrightarrow NO_2^+ + HS_2O_7^- \quad (38)$$

Besides, it would just correspond to Gelfman's compound $N_2O_5.4SO_3$. In the case of smaller amounts of SO_3 the equation would be:

$$2HNO_3 + 3SO_3 \leftrightarrow 2NO_2^+ + S_2O_7^{2-} + H_2SO_4 \quad (39)$$

which again would correspond to another compound suggested by Gelfman, viz. $N_2O_5.3SO_3$.

Vandoni [72] repeated the experiments of Sapozhnikov on the vapour pressure of HNO_3 over mixtures of HNO_3-H_2SO_4-H_2O using an improved technique. In the main, he confirmed the earlier results, but he introduced some corrections to the figures obtained by Sapozhnikov. Thus he used nitric acid free from nitrogen oxides which were present in the acid used by Sapozhnikov. Vandoni has shown that the absorption of vapours of nitric acid by potassium (the method applied by Sapozhnikov) is not complete. Instead of HNO_3 vapour pressure values, Vandoni utilized the activity of HNO_3, i.e. the ratio H/H, between the vapour pressure of HNO_3 over the surface of the solution (H) and the vapour pressure of pure HNO_3 (H_0 = 14.1 mm Hg at 0°C).

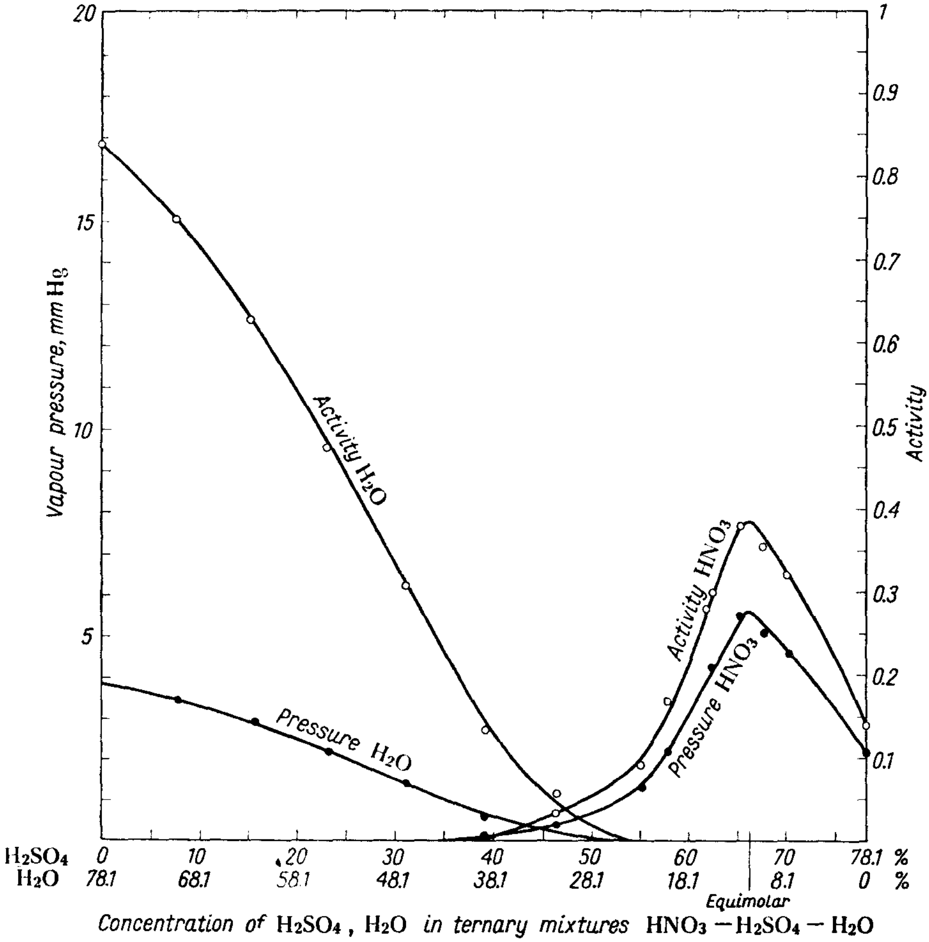


FIG. 11. Vapour pressure and activity H/H_0 of HNO_3 in the solution HNO_3-H_2SO_4-H_2O containing 21.9% HNO_3 (Vandoni [72]).

Vandoni's diagrams of the activity of HNO_3 and H_3O, when the content of HNO_3 is 21.9 and 50% (i.e. in the most common nitrating mixtures) are given in Figs. 11 and 12 respectively.

The triangular diagram of Sapozhnikov was modified by Vandoni, on the basis of his own experimental data, to the diagram of HNO_3 activities (Fig. 13). Thus instead of isobars of HNO_3 vapour pressures he constructed curves of equal activities. The advantage of such a diagram is, among other things, that unlike vapour pressure, activity is independent of temperature.

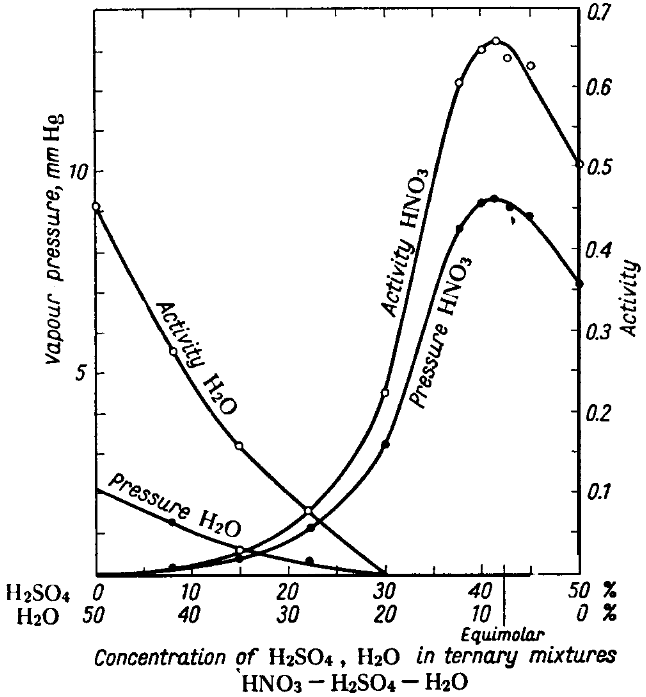


FIG. 12. Vapour pressure and activity H/H_0 of HNO_3 in the solution HNO_3-H_2SO_4-H_2O containing 50% HNO_3 (Vandoni [72]).

Activity as a function was introduced by Lewis in 1908, and a full description was given by Lewis and Randall [74] in 1923. The activity a_i of a substance "i" can be defined [75.76] as a value corresponding to the mole fraction of the substance "i" in the given phase. This value is in agreement with the thermodynamic potential of the ideal mixture and gives the real value of this potential.

Lewis and Randall give an example of calculating the activity of a solute from its vapour pressure. When a solution is in equilibrium with the vapour of the solute x_2, we may measure the vapour pressure of x_2 over a range of concentrations, and by knowing the fugacity of the vapour at each pressure we may obtain the activity of the solute in the solution. When we may assume that the vapour is a perfect gas, the activity a_2 in the solution may be taken as proportional to p_2, the vapour pressure of the solute. Hence. as we pass from the mole fraction N_2 to an infinitely dilute solution of mole fraction N^x_2

$$\frac{a_2}{p_2} = \frac{a_2^x}{p_2^x}$$

Now by Henry's law, 2 approaches a constant value, at infinite dilution which may be denoted by $\frac{N_2^x}{p_2^x}$ But by definition of our standard state, $a_2^x = N_2^x$, and therefore at any concentration

$$a_2 = p_2 \frac{N_2^x}{p_2^x}$$

$$\frac{a_2}{N_2} = \frac{p_2}{N_2} \cdot \frac{p_2^x}{N_2^x}$$

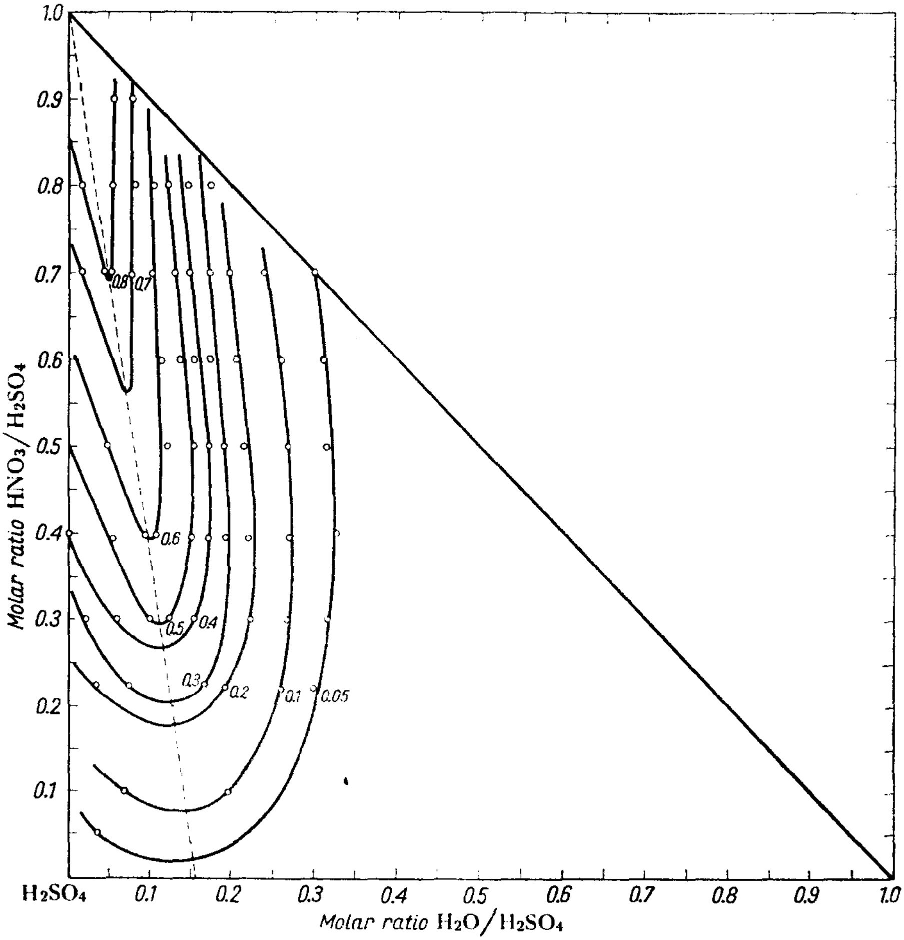


FIG. 13. Activity H/H_0 of HNO_3, in solutions HNO_3-H_2SO_4-H_2O at 0°C (Vandoni [72]).

Thermochemical measurements

On the basis of measurements of the heat generated on mixing nitric and sulphuric acid Gelfman [71] drew the conclusion that the two acids do not yield any stable molecular compounds.

On the basis of similar measurements of the heat of solution of SO_3 in nitric acid it was found that the compounds of HNO_3 and SO_3 are more stable. According to Gelfman the compound $HNO_3.2SO_3$ can be obtained in a crystalline form, Moreover, Gelfman believed that the compounds $HNO_3.18SO_3$ and $3HNO_3.SO_3$ do in fact exist.

Density measurements

Klimova, Zaslavskii and their co-workers [77,77a] have measured the densities of anhydrous nitric and sulphuric acid mixtures. They obtained characteristic slopes in the density curve of the mixtures at molar ratios HNO_3:H_2SO_4 = 1:2 and 1: 1. Hence they inferred that in the solution containing 24 by wt.% of HNO_3, the cation $H_3NO_3^{2+}$ is present; with a decrease in H_2SO_4 concentration this is converted into the $H_2NO_3^+$ cation (39 by wt.% HNO_3).

Moreover, interpretation of the density curves of the acids and water mixtures led them to the conclusion that on gradually adding water, hydrolysis of Hantzsch's ions occurs:

$$H_3NO_3^{2+} + H_2O \leftrightarrow H_2NO_3^+ + H_3O^+ \qquad (40)$$

$$H_2NO_3^+ + H_2O \leftrightarrow HNO_3 + H_3O^+ \qquad (41)$$

Since according to Hantzsch the $H_2NO_3^+$ ion is the principal nitrating agent, these reactions could account for the fact that organic compounds are best nitrated with a nitric and sulphuric acid mixture with a water content of 10%.

Viscosity measurements

Measurements of the viscosities of nitric acid-sulphuric acid-water mixtures have been the subject of research work by several authors. Zaslavskii, Klimova and Guskova [78] have observed a maximum, corresponding to the combination of ions:

$$(H_3NO_3)^{2+} \quad (HSO_4)_2^-$$

With increase in water content the maximum in the curve shifts towards lower concentrations of HNO_3 and disappears when the dilution has attained a degree corresponding to 1 mole of water for 1 mole of the above compound.

Recently Swinarski and Dembinski [51] and Swinarski and Piotrowski [52], have examined the viscosities of the three component solutions HNO_3-H_2SO_4-H_2O. The diagram in Fig. 14 shows the results of these investigations, in terms of changes in viscosity with increase in HNO_3 content. The authors pointed out a similarity between the viscosity curve they obtained and the electric conductivity curve (see Fig. 4, p. 18).

The curve shows a distinct maximum at 20 mole % HNO_3. The authors explained this by postulating the formation of a hydrated NO_2^+ ion:

$$HNO_3 + 2H_2SO_4 + H_3NO_3^{2+} + 2HSO_4^- \qquad (31)$$

An increase in concentration of HNO_3 causes a decrease in viscosity, presumably because of dissociation:

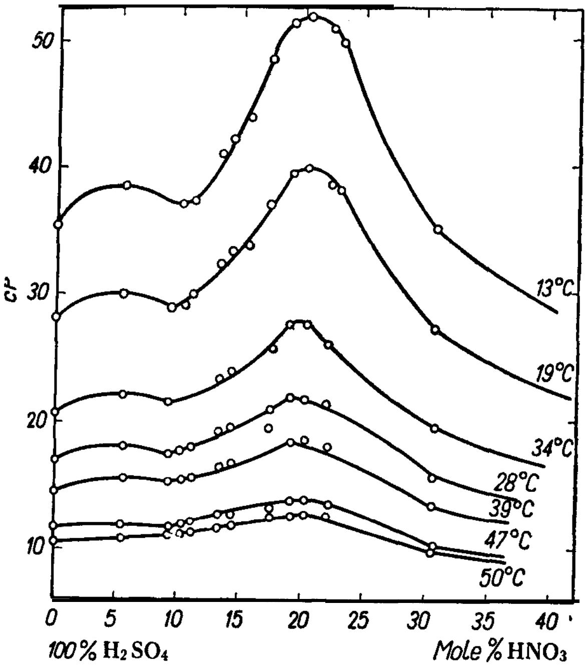


FIG. 14. Viscosity of solutions HNO_3-H_2SO_4-H_2O. Change in viscosity with increase of HNO_3 content at various temperatures (Swinarski and Piotrowski [52]).

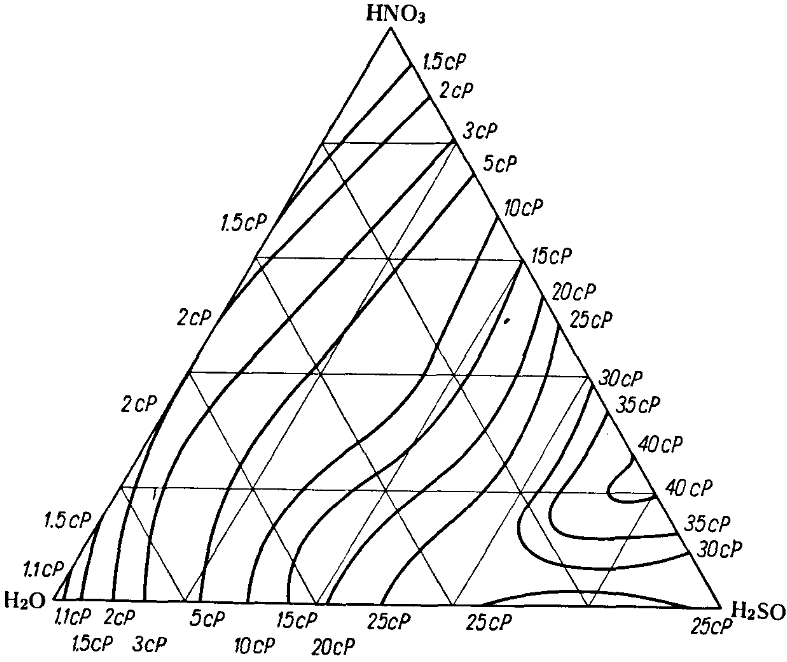


FIG. 1% Curves Of equal viscosities of the solutions HNO_3-H_2SO_4-H_2O (Hackel, T. Urbanski, Kutkiewicz and Sternidski [80]). (Composition in mole %)

$$H_3NO_3^{2+} \rightarrow NO_2^+ + H_3O^+ \tag{16}$$

Krejci, Novotny and Ruzicka [79] have also recently examined the viscosities of mixtures of nitric and sulphuric acids with water from the point of view of their practical importance.

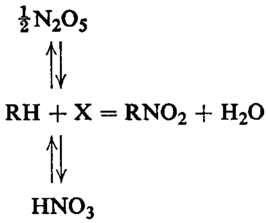
In 1961 Hackel, T. Urbanski, Kutkiewicz and Sterninski [80] have examined the viscosities of these mixtures and presented the results as the curves of a triangular diagram (Fig. 15). It can be seen that a maximum viscosity exists for the solution containing 20-25 mole % of sulphuric acid, i.e. for the compound $(HNO_3)_3.H_2SO_4$.

APPLICATION OF KINETIC STUDIES TO ELUCIDATE THE STRUCTURE OF NITRATING MIXTURES

The first attempts to study nitration kinetics were made by L. Meyer and co-workers [81,82]. It was in their publication that for the first time a statement appeared that the nitration reaction is irreversible and that its rate decreases with time.

Martinsen [83] observed already in 1905 that the rate of nitration of nitrobenzene with a mixture of nitric and sulphuric acids depends on the concentration of sulphuric acid, viz. it increases with the concentration up to 88.7% H_2SO_4, after which further increase in sulphuric acid concentration results in a decreasing rate of nitration.

In 1924, Klemenc and Schöller [34] stated that *m*- xylene-2,6-disulphonic acid is nitrated with nitric anhydride in sulphuric acid twice as rapidly as when it is nitrated with nitric acid in sulphuric acid, the molar concentration being the same. This was illustrated in the following scheme, where the nitrating agent was denoted by X:



$$\begin{tikzcd} & \frac{1}{2}N_2O_5 \arrow[d, shift left] & \\ RH + & X \arrow[u, shift left] \arrow[d, shift left] & = RNO_2 + H_2O \\ & HNO_3 \arrow[u, shift left] & \end{tikzcd} \tag{42}$$

It is clear, that the scheme corresponds to the eqn. (5). It follows that the concentration of NO_2^+ ions from N_2O_5 is twice as high as that of NO_2^+ ions from HNO_3 (see eqn. 19).

J. A. Hetherington and Masson [84], basing their views on the studies of benzene nitration kinetics, stated that the reaction of nitrobenzene nitrated with a mixture of HNO_3, H_2SO_4 and H_2O would stop before all the nitric acid was used if the amount of sulphuric acid in the mixture was insufficient to form the $H_2SO_4.H_2O$

hydrate with water, originally present in the mixture and formed in the reaction. Hence they proposed the following equilibrium equation for the nitrating mixture:

$$H_2SO_4, + H_3O+ + NO_3^- <-> H_3O^+ + HSO_4^- + HNO_3 \quad \textbf{(43)}$$

The more the equilibrium is shifted to the right the higher the reaction rate.

According to Hetherington and Masson undissociated nitric acid is a nitrating agent and in its interaction with nitrobenzene a complex with the $C_6H_5NO_2H^+$ cation is formed, which subsequently reacts with HNO_3 to yield dinitrobenzene.

In his experiments on the nitration of naphthalenesulphonic acid Lantz [85] found that the rate of nitration with a nitric acid and sulphuric acid mixture was highest when the concentration of sulphuric acid used was about 90% H_2SO_4

From these experiments, and on the basis of the Brönsted acids and bases theory, as well as Hantzsch's theory, Lantz has concluded that in a nitrating mixture the hydrated sulphuric acid $H_2SO_4.H_2O$ acts as a base towards anhydrous sulphuric acid. Thus an equilibrium acid-base system is established:

$$H_2SO_4 + nH_2SO_4{*}H_2O <-> HSO_4^- + H_2SO_4.H_3O^+ \quad (44)$$

The HSO_4^- ions formed participate in the reaction

$$2H_2SO_4 + HNO_3 <-> 2HSO4- + H_3NO_3 \quad (31)$$

shifting the equilibrium of reaction (31) to the left, which results in a decrease in concentration of $H_3NO_3^{2+}$ cations and in an increase in concentration of HNO_3.

These substances-the cation and the undissociated acid-both have nitrating properties.

In the case of higher concentrations of water, the following reaction might take place :

$$HNO_3 + H_2O <-> NO_3^- + H_3O^+ \quad (35)$$

Then the nitrating action of nitric acid would stop.

Lantz also draws attention to the fact that the equilibrium of reactions (44) and (31) are greatly affected by the nature of the substance, being nitrated. The rate of the nitration reaction also depends on the structure of the nitrated substance. The more basic groups it contains the more distinct the acidic character of the nitrating agent and the more vigorous the nitration reaction.

Westheimer and Kharasch [86] also chose reaction kinetics as a method of studying the actual composition of nitrating mixtures. They found, that the rate of a nitration reaction depends chiefly on the acidity of the medium and not on its dehydrating properties. Therefore, the reaction rate is highest when 90% sulphuric acid is used as a solvent for nitric acid, while the reaction remains unaffected when a substance of strong dehydrating properties such as phosphoric anhydride is added to the mixture.

When 90% sulphuric acid is used as a solvent, increase in concentration of HNO_3 in a nitrating mixture results in reducing the rate of nitration, since the acidity of the mixture is reduced. In the case of more concentrated sulphuric acid temperatures, according to the data given by several authors. The shapes of the curves are the same for all measurements.

Bennett's explanation of the existence of a maximum in the nitration rate at the sulphuric acid concentration mentioned above is as follows. Since in nitration with the nitronium ion a proton is split off from the nitrated substance (reaction 22, p. 60) the presence of proton acceptors in the nitrating mixture should favour the nitration reaction. Such a role is played for example by HSO_4^- ions, sulphuric acid, which is able to form the $H_3SO_4^+$ cation with the proton, and HSO_7^- ions, that exist in mixtures containing oleum.

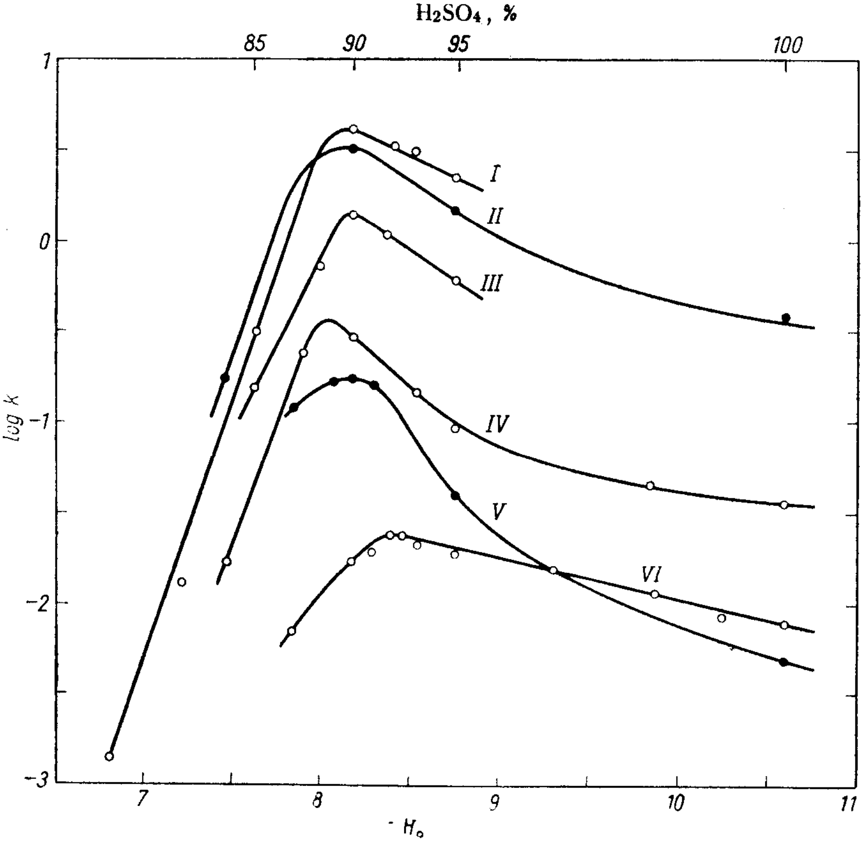


FIG. 16. Variation of the rate of the nitration constant against the concentrations of sulphuric acid in the nitrating mixture: I - Nitration of nitrobenzene at 25°C (Westheimer and Kharasch [89]). II - Nitration of nitrobenzene at 25°C (Martinsen [83]); III - Nitration of dinitromesitylene at 25°C (Westheimer and Kharasch [86]); IV - Nitration of nitrobenzene at 0°C (Martinsen [83]); V - Nitration of anthraquinone at 25°C (Latter and Oda [32]); VI - Nitration of dinitrotoluene at 90°C (Bennett [S]). He is Hammett acidity function defined by the equation

$$H_0 = -\log\left(\frac{a_{\mathrm{H}}+f_{\mathrm{B}}}{f_{\mathrm{BH^+}}}\right).$$

Reproduced from Gillespie and Millen [11].

Thus, the nitration rate would depend on two factors: on attaching the nitronium ion and on removing, i. e. binding, the proton. An increase in water concentration in a nitrating mixture gives rise to an increase in the HSO_4^- ion concentration and thus enhances the process of removing the proton from the nitrated compound. Yet, at the same time, it reduces the nitronium ion concentration. Changes in the nitration rate with the water content of a nitrating mixture would be the resultant of the sum total of the two effects.

However, investigations on the nitration of deuterobenzene raised doubts about the influence of the velocity of splitting off the proton on the nitration reaction rate.

By using deuteronitric acid Ingold, Raisin and Wilson [38] established that no substitution of hydrogen atoms by deuterium atoms occurred (in this respect the action of deuteronitric acid differs from that of deuterosulphuric acid, leading to the formation of deuterated benzenes up to the fully substituted hexadeuterobenzene).

From these results and later experiments (Ingold and co-workers [36,37, 39]) on the influence of solvents on the nitration rate Ingold came to the conclusion that splitting off the proton in the nitration of aromatics does not effect the reaction kinetics. This conclusion differed from that of Bennett and his co-workers [87].

Recently Melander [88] attempted to clarify the influence of the proton loss on the nitration reaction rate by investigating this process using a number of aromatic compounds: benzene, toluene, bromobenzene and naphthalene, in which one hydrogen atom had been replaced by tritium.

It is well known that there is no general rule applicable to the difference in the rates of the reactions involving compounds having hydrogen or its heavier isotopes ^2H (deuterium) and ^3H (tritium) in their molecules. In some cases the heavier isotopes react more slowly, in others more quickly.

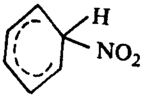
Melander points out that unless hydrogen is firmly attached by a covalent bond and can change its position (as in tautomerism), heavy isotopes react more slowly. The influence of heavy water on the rate of neutralization of a pseudo-acid such as nitroethane, as observed by Wynne-Jones [89], may be cited as an example. According to him the rate of the reaction involving deuterium loss was about ten times lower than when the proton was lost.

Melander in his experiments on sulphonation of the monotritero aromatics, triterobenzene and 4-triterobromobenzene, found the replacement of tritium by the sulpho group proceeded much more slowly than the replacement of protium (Hydrogen H).

However, on nitrating the following aromatic compounds, having one atom of hydrogen H replaced by tritium: triterobenzene, 2-triterotoluene, 4-triterotoluene, 2-triterobromobenzene and α– triteronaphthalene, Melander found that the rate of nitration of these compounds did not differ from the rate of nitration of hydrocarbons which did not contain heavier hydrogen isotopes.

Melander nitrated naphthalene to α– dinitronaphthalene and other compounds to dinitro derivatives. When nitrating ordinary aromatic compounds (not containing heavier hydrogen isotopes) with a nitrating mixture containing water plus a quantity of tritium oxide, he also investigated whether the hydrogen-tritium exchange was taking place and found that in these conditions the exchange either did not occur at all or was very insignificant. These observations confirmed those of Ingold on benzene nitration with deuteronitric acid.

According to Melander, the experimental facts show that the nitration reaction is a two-stage mechanism. In the first stage the intermediate compound



would be formed and it is only in the second stage that the proton was split off.

Similar tests on nitration of monodeuterobenzene were carried out by W. M. Lauer and Noland [90]. They found that the deuterium content in the nitration products (nitro- and dinitrobenzene) was proportional to its content in the initial compound, thus confirming Melander's observations on tritium.

Bonner, Bowyer and G. Williams [91] stated that the rate of nitration of nitrobenzene with nitric acid in 97.4 and 86.7% sulphuric acid was much the same as the rate of nitration of pentadeuteronitrobenzene with the same mixture. Thus, the results obtained by W. M. Lauer and Noland and by Banner and his co-workers supported Melander's earlier observation, that the rupture of the C-H bond was not a determining factor for the rate of nitration of aromatic compounds.

All these investigations confirm that the nitration process is a two-stage substitution reaction, where the first slope consists in attaching the nitronium ion, according to eqns. (22) and (23), p. 60, or according to Melander (as above).

Bunton, Halevi and Llewellyn [92] studied the oxygen atom exchange between nitric acid and water, using heavy oxygen ^{18}O as the labelled element. They found that the higher the exchange rate, the higher the concentration of nitric acid. At low HNO_3 concentrations the reaction proceeded in the presence of nitrous acid. At high HNO_3 concentrations the presence of nitrous acid was not indispensable for the exchange.

When comparing the rate of this reaction with the rate of nitration of aromatic compounds with nitric acid of various concentrations, Bunton and Halevi [93] came to the conclusion that the oxygen exchange between nitric acid and water proceeded faster than the nitration reaction. It was only for high concentrations of HNO_3 and for readily nitrated compounds that the values of the rates of both the reactions were of the same order.

Bunton and Halevi have examined the following reactions (O* denotes heavy oxygen) :

$$HNO_3 + HNO_3 \leftrightarrow H_2NO_3^+ + NO_3^- \qquad (a)$$

$$H_2NO_3^+ \leftrightarrow NO_2^+ + H_2O \qquad (b)$$

$$\text{nitration}: \quad NO_2^+ + RH \leftrightarrow RNO_2 + H^+ \qquad (c)$$

$$\text{oxygen exchange}: \quad NO_2^+ + H_2O^* \leftrightarrow H_2NO_3^{*+} \qquad (d)$$

$$H_2NO_3^{*+} \leftrightarrow H^+ + HNO_3^* \qquad (e)$$

and have inferred that both nitration and oxygen exchange involve formation (b) and destruction (c, d) of the nitronium ion. Reactions (c) and (d) are competitive with preference for reaction (d). The nitracidium ion is formed in reaction (d).

In 1948, Titov [35] also studied the problem of the existence of a maximum in the nitration rate at certain concentration of sulphuric acid. He assumed, like Hetherington and Masson, (see p. 33), that cations might be formed in nitration by the attachment of protons to nitro compounds, for example:

$$C_6H_5NO_2 + H^+ \rightarrow C_6H_5NO_2H^+$$

The $C_6H_5NO_2H^+$ cation undergoes a substitution reaction with much more difficulty than the nitro compound $C_6H_5NO_2$ itself, since the addition of a proton gives rise to a sharp drop of prototropic behaviour of the compound.

The rate of nitration of nitrobenzene to dinitrobenzene may be expressed, according to Titov, by the equation:

$$\frac{d[C_6H_4(NO_2)_2]}{dt} = k_m\,[NO_2^+]\,[C_6H_5NO_2^+]\;k_k\,[NO_2^+]\,[C_6H_5NO_2H^+]$$

It is only the first factor in the right side of the equation which affects the nitration rate, since the second factor is very small because of the low rate of nitration of the $C_6H_5NO_2H^+$ ion.

An increase in sulphuric acid concentration results in increase in the concentration of the $C_6H_5NO_2H^+$ cation, hence in a decrease in the $C_6H_5NO_2$ concentration which in turn brings about a decrease in the nitration rate. On the other hand the concentration of the NO_2^+ ion increases with increase in sulphuric acid concentration.

Titov believes, as in Bennett's interpretation, that summing up the two effects results in a maximum in the reaction rate at a certain concentration of H_2SO_4.

Ingold, Hughes and Reed [39] studied the kinetics of nitration of aromatic compounds with nitric acid only and found that it was a first order reaction. Its rate, V_N, may be expressed by an approximate equation:

$$V_N = k_1[ArH]$$

at $[HNO_3]$ = const.

Ingold and his co-workers [36,37,39] inferred from the results of their studies that the nitration rate, V_S, in the presence of sulphuric acid might be expressed roughly by the equation:

$$V_S = k_1[ArH][HNO_3]$$

In the nitration of numerous compounds, and particularly those containing many nitro groups, e.g. nitration of dinitro- to trinitro compounds, or nitro derivatives of naphthalene, which are sparingly soluble in a nitrating mixture, nitration takes place in a two-phase system: acid-organic compound, the acid phase being a saturated solution of the organic compound. If the compound is liquid at nitration temperature, then the organic liquid phase is a saturated solution of acid in the nitrated substance. In this case the reaction rate depends among other things on the concentration of the organic compound in the acid, on the concentration of the acid in the organic compound, on the interfacial area and on the diffusion rate at the phase boundary. If a nitrated compound is solid at reaction temperature, the nitration rate depends in the first place on the concentration of the compound in acid, on the interfacial area and on the rate of diffusion of the acid into the solid phase. Of course, the interfacial area depends above all on the mixing of the two phases. Moreover, attention must be paid to the statement, first expressed by Hetherington and Masson [84], that the nitration reaction proceeds solely in the acid phase, especially when solid substances are nitrated.

In the light of the present state of knowledge on the problem it is more exact to say that the nitration reaction proceeds principally in the acid phase.

Consequently, mixing during nitration strongly affects the nitration result: vigorous stirring increases the nitration rate. This will be dealt with on pp. 266 and 314.

The favourable effect of strong dispersion on the nitration process can also be observed in nitration of easily emulsifiable substances. For example, Kobe and Doumani [94] found that commercial *p-* cymene can be nitrated more readily, than pure cymene, and this can be explained by the fact that the former of the two compounds is more readily emulsified.

The extension of the interfacial area by emulsification explains Miyagawa's [95] observation that the nitration rate can be considerably increased by the action of ultrasonics on a reacting system. For example, nitration of *m-* xylene to trinitro-*m-* xylene, which generally takes 2 hr, takes only 30 min when ultrasonics are used. There is no evidence as yet whether and how ultrasonic waves effect group orientations.

Attempts have been made by Bennett and his co-workers [43,87] to analyse in more detail the kinetics of a two-phase reaction system. However, so far it has proved impossible in the absence of more detailed data on the concentrations in the two phases. Bennett only found that in the nitration of dinitrotoluene to trinitrotoluene the H_2O:H_2SO_4 ratio in the organic phase is much higher than that in the acid phase. The proportion of acid in the organic phase is only 5-10% (in relation to this phase).

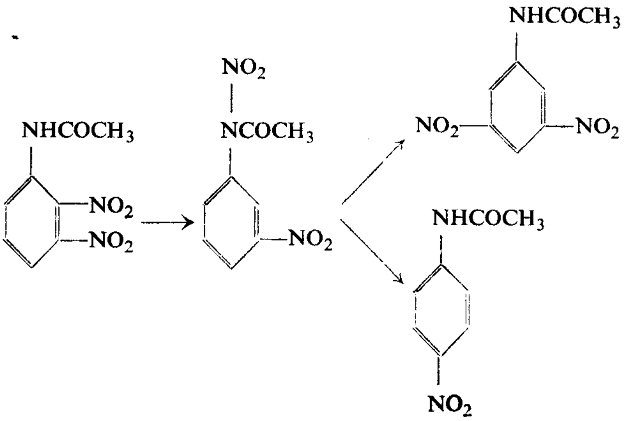
It has also been found that for any nitric acid concentration, the nitration rate is nearly proportional to the molar excess of sulphuric acid as related to the water content of the nitrating mixture. The nitrating acid excess is a factor of special importance in esterification of alcohols ("O-nitration"),

O-nitration of cellulose with mixtures of acids is a widely applied type of esterification reaction in a heterogeneous system. One of the factors influencing the reaction rate here is the rate of diffusion of the acid into the fibre.

The process of starch O-nitration by the Hackel and Urbanski's method (see Vol. II, Fig. 164) shows how homogeneity of the system affects the O-nitration grade.

Recently Pausacker and Scroggie [96] have suggested that the nitration reaction may be reversible. Their assumption has been based on the observation that the heating of 2,3-dinitroacetanilide with sulphuric acid yields mainly 2,5-di nitroaniline (46% yield), 3,4-dinitroaniline (23% yield) and a small quantity of 2,3-dinitroaniline (5%).

However, more recent studies by these workers [97] show that the mechanism of these reactions consists in the reverse of the Bamberger rearrangement. It is known that the Bamberger rearrangement in aromatic nitramines consists in the nitro group wandering from nitrogen to carbon. The compounds studied by the authors would undergo reverse rearrangement, followed by the Bamberger rearrangement:



It has been found by the same authors that heating 2,3-dinitrophenol with sulphuric acid leads to partial isomerization to 2,5-dinitrophenol.

Other dinitro compounds, viz. those substituted in the 2,5- and 3,4-positions, do not undergo such rearrangement. This fact is evidence that only that group can migrate which meets with steric hindrance (i.e. the nitro group in the ortho position to the adjacent group or groups).

No evidence of reversibility of aromatic C-nitration has so far been found.

Thus T. Urbanski and Ostrowski [98] have kept solutions of various nitro derivatives of toluene in cont. sulphuric acid at 90-95°C for ca. 60 hr. *o*- Nitrotoluene (I), *m*- nitrotoluene (II), *p*- nitrotoluene (III), 2,4,6-trinitrotoluene (IV) and 2,4,5-trinitrotoluene (V) were examined. No appreciable change was found of the boiling points of (I) and (II), and of the melting points of (III)-(V). Only in the case of *m*- nitrotoluene and 2,4,5-trinitrotoluene the solution gave a very slight blue colour with diphenylamine. This might have been produced by trace splitting of the mobile *m*- nitro group and could not be considered as any evidence of an equilibrium in the systems examined.

Nitric acid and sulphur dioxide

Varma and Kulkarni [99] studied the nitrating action of nitric acid saturated with SO_2. This solution acts much more vigorously than the usual nitrating mixture of nitric and sulphuric acids. Thus, phenol undergoes violent reaction and carbonization with HNO_3+SO_2. According to these workers aniline, methyl- and dimethylaniline also react with the mixture with an almost explosive violence to yield carbonized products. Because of the vigour of the reaction there are hardly any prospects of the practical use of the mixture. On the contrary, it seems that in many cases (nitration of phenols and aromatic amines) the presence of SO_2 in nitrating mixtures may be undesirable and even dangerous.

Nitric acid and fluorine compounds

It has been shown that the addition of sulphuric acid to nitric acid is not the sole method of producing an intensification of the nitrating properties of nitric acid. The addition of such substances as boron fluoride (R. T. Thomas *et al. [46])* or hydrofluoride (Simons *at al.* [47]) to nitric acid produces a similar effect.

These phenomena can also be explained by the formation of the nitronium ion, according to eqns. (28) and (29) (p. 16).

Nitric acid and perchloric acid

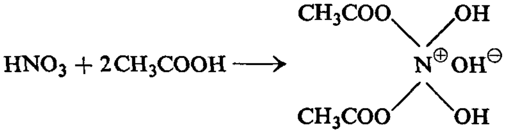
Nitration can also be carried out by solutions of nitric acid with perchloric acid [99a].

Bonner and Frizel [99b] describe O-nitration of isoamyl alcohol with a solution composed of fuming nitric acid (or N_2O_4) and perchloric acid of 55-62% $HClO_4$.

Nitric acid and acetic acid or anhydride

Acetic anhydride creates dehydrating conditions, therefore a mixture of nitric acid with acetic anhydride has strong nitrating properties. Moreover in esterification with nitric acid, the acetic acid present in the mixture or formed in the reaction does not hydrolyse the nitric acid ester formed.

Nitric and acetic acids. According to A. Pictet and Genequand [100], acetic acid combines with nitric acid (d = 1.52) to give a kind of mixed orthonitric and acetic anhydride, the so-called diacetylorthonitric acid (b. p. 127.7°C):



(47)

The same compound is formed when acetic anhydride and nitric acid (***d*** = 1.4) are mixed.

However, no research work on the structure of the compound has been carried out yet. In particular there is no evidence to decide whether diacetylorthonitric acid is a true chemical compound or only an azeotrope.

Only recently Miskidzhian and Trifonov and their co-workers [101] examined the physico-chemical properties of solutions of nitric acid in acetic acid, such as the freezing point, viscosity, density, refraction, surface tension, electrical conductivity and heat of mixing. These authors came to the conclusion that nitric and acetic acids combine, yielding an addition compound $HNO_3.CH_3COOH$. The existence of Pictet's compound has not been verified.

Confirmation of these conclusions was provided in 1954 by Titov [35] who has studied the corrosion of steel in solutions of nitric acid in acetic acid. He found that the solution having the composition $HNO_3.CH_3COOH$ was the least corrosive.

Shatenshtein [102] drew attention to the fact that nitric acid in anhydrous acetic acid was much less dissociated than when in water, and that this could be explained by the protolytic properties of the solution components and by the low dielectric constant of acetic acid.

Recently Mint and Kecki [103] examined the Raman spectra of solutions of nitric acid in anhydrous and hydrated acetic acid. They have shown that at a concentration of 2 moles HNO_3 per litre of CH_3COOH, i.e. for the solution containing 12.6% HNO_3 in acetic acid, the 1304 cm^{-1} line, probably corresponding to the nitronium ion, NO_2^+, can be seen. The intensity of the line increases with concentration of nitric acid. Thus we can say that the acetic acid facilitates the formation of the nitronium ion.

The objective of Usanovich's work, mentioned above [50] was to elucidate the structure of mixtures of nitric acid with acetic or chloroacetic acid by means of conductometric measurements.

When studying the kinetics of the nitration reaction of phenol with nitric acid in the presence of acetic acid Briner and Bolle [104] found that the rate of nitration with this solution was higher than that with nitric acid of the same concentration.

A comparative study has also been made of the Raman spectra of the systems:

$$HNO_3\text{-}H_2SO_4\text{-}H_2O$$

$$HNO_3\text{-}HClO_4\text{-}H_2O$$

$$HNO_3\text{-}CH_3COOH\text{-}H_2O$$

by Mint, Kecki and Osiecki [105]. This led them to a conclusion that an increase of the acidity of the medium not only caused the dissociation of nitric acid to diminish, but also the Raman quantum efficiency of the 1300 cm^{-1} line to rise. This line corresponds to vibrations of the undissociated HNO_3 molecule. This in turn would indicate that the level of polarity of the bonds between the nitrogen and oxygen atoms of the NO_2 group was decreased as a result of the influence the medium exerts on the $HONO_2$ molecule. This would lead to an increase in the polarity of the bond between the NO_2 and OH groups and hence a weakening of this bond.

The authors express the view that the undissociated HNO_3 molecule is the nitrating agent in the solution HNO_3 - $CH_3COOH\text{-}H_2O$. The reactivity of the molecule is increased as a result of the polarized and weakened $HO\text{-}NO_2$ bond.

In 1950 Ingold, Hughes and Reed [39], when studying the kinetics of nitration with nitric acid in the presence of acetic acid, found the reaction to be of zero order in the case of aromatic compounds which are readily nitrated (benzene and its homologues), and its rate V_a could be expressed by the approximate equation:

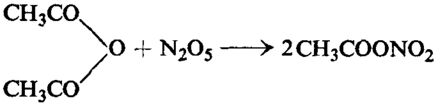
$$V_a = k_0 \text{ at } [HNO_3] = \text{const.}$$

While in case of compounds more difficult to nitrate (di- and tri-chlorobenzenesj. the reaction is of the first order and its rate V'_a may be expressed by the equation :

$$V'_a = k_1 [ArH] \text{ at } [HNO_3] = \text{const.}$$

According to the authors, the nitronium ion is the main nitrating agent in the presence of acetic acid.

Nitric acid and acetic anhydride. In their further work in 1907 Pictet and Khotinsky [106] found that acetic anhydride formed acetyl nitrate with N_2O_5:



$$(CH_3CO)_2O + N_2O_5 \longrightarrow 2CH_3COONO_2 \qquad (48)$$

Cohen and Wibaut [107] found when studying the kinetics of interaction of nitric acid and acetic anhydride, that after mixing the two substances, free nitric acid was present in the mixture during the first 75-100 min, then the HNO_3 concentration decreased in consequence of the reaction:

$$HNO_3 + (CH_3CO)_2O \leftrightarrow CH_3CONO_3 + CH_3COOH \qquad (49)$$

The reaction did not stop at this stage but proceeded further since the nitrating action of acetyl nitrate on acetic anhydride yielded acetic nitroanhydride and consequently the concentration of acetyl nitrate decreased.

According to Cohen and Wibaut, it was nitric acid which was the nitrating agent at the beginning and later acetyl nitrate took its place.

Konovalov [108] observed an important fact as long ago as 1895. He reported that aromatic hydrocarbons with side chains were nitrated with this mixture chiefly in the side chain. Shorygin and Sokolova [109] confirmed this observation in 1930.

The kinetics of nitration of aromatic hydrocarbons with nitric acid in the presence of acetic anhydride was first studied by Tronov, Kamay and Kovalenko [110]. Their studies will be discussed later.

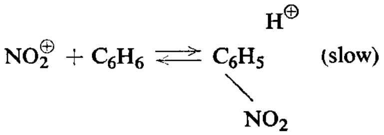
Menke [2] inferred from the results of his studies on nitration of aromatic hydrocarbons with mixtures of nitric acid and acetic anhydride that the latter acted not only as a dehydrating substance but also as a catalyst.

Recently Paul [111] examined kinetics of the nitration of benzene using solutions of nitric acid in acetic anhydride and acetic acid at 25°C. In a number of his experiments he also added sulphuric acid in a small quantity (ca. 0.01 M).

The results favour nitronium ion attack on benzene as the rate-determining step:

$$HNO_3 + H^+ \leftrightarrow H_2NO_3^+ \qquad (a)$$

$$H_2NO_3^+ + (CH_3CO)_2O \leftrightarrow NO_2^+ + 2CH_3COOH \qquad (b)$$



$$NO_2^{\oplus} + C_6H_6 \rightleftharpoons \overset{H^{\oplus}}{\underset{NO_2}{C_6H_5}} \quad \text{(slow)} \qquad (c)$$

Such a mechanism accounts for the first-order dependence of the rate on reaction the nitric acid concentration in presence of sulphuric acid.

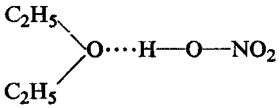
A higher-order dependence on nitric acid concentration in the absence of added strong acid (H_2SO_4) was also observed. This, according to Paul, is a consequence of the dual role assumed by nitric acid itself providing the proton acquired in step (a). The nitric acid-acetic anhydride reaction is not a simple one, and requires more study.

Nitration with mixtures of metal nitrates and acetic anhydride (or acid) was studied by Menke, and later by Spiegel and Haymann [112] and Bacharach [113]. It has been shown that only the nitrates which readily hydrolyse, such as ferric, nickel, cobalt, aluminium nitrates, have nitrating properties.

Solutions of nitric acid in organic solvents

Nitric acid in organic solvents does not produce the 1050 and 1400 cm^{-1} lines. On examination of absorption spectra in the infra-red, the conclusion has been drawn that nitric acid in chloroform or carbon tetrachloride solutions is less associated than when in a sulphuric acid solution (Dalmon [8,9,49]).

It follows from these investigations by Dalmon, that in an ether solution the nitric acid molecule probably combines with the ether molecule by means of a hydrogen bond:



Calorimetric measurements by Hantzsch and Karve [22] have shown that the heat of dilution of nitric acid with ethyl ether is higher than that with water. Hantzsch therefore suggested that nitric acid forms a compound with ether (probably through the hydrogen bond) as above. Dioxane also forms a similar compound with nitric acid.

Measurements of the vapour pressures of solutions of nitric acid in ether carried out by Dalmon and his co-workers confirmed the existence of the compound. It was shown that the vapour pressure of ether, which at 0°C was 185 mm Hg, decreased on addition of nitric acid and attained 1 mm Hg when equimolar proportions of the two components were present in the solution.

Ingold, Hughes and Reed [39] have studied the kinetics of nitration with nitric acid in the presence of nitromethane and found the reaction to be of zero order in the case of readily nitrated aromatic compound, and of first order with compounds more difficult to nitrate as in the presence of acetic acid. Here also it was probably the nitronium ion that was responsible for nitration.

Nitric acid salts in mixtures with other acids

In the days when anhydrous nitric acid was not easily available, nitric acid salts ($NaNO_3$, KNO_3) mixed with sulphuric acid were widely used for nitration. Such mixtures acted similarly to the mixture of nitric and sulphuric acids. Later, as synthetic nitric acid became one of the most readily available chemical products, and the production of nitric acid salts from nitric acid had started, nitrating mixtures with sodium or potassium nitrates were abandoned. This is the principal explanation for the scarcity of investigations on the structure and action of such mixtures. It is believed that in such mixtures the nitronium ions are present, according to the equation :

$$NaNO_3 + 2H_2SO_4, \rightarrow NO_2^+ + 2HSO_4 + Na^+ + H_2O \qquad (50)$$

Ingold and his co-workers proved in 1950 [39] that on introducing the NO_3^- anion into nitric acid in the presence of acetic acid or nitromethane the reaction rate decreased, since the formation of the NO_2^+ ion was hindered by the NO_3^- ion:

$$2HNO_3 \leftrightarrow H_2NO_3^+ + NO_3^- \text{ (fast reaction)} \qquad (51)$$

$$H_2NO_3^+ \leftrightarrow NO_2^+ + H_2O \text{ (slow reaction)} \qquad (52)$$

The nitration reaction rate depends on the kind nature of the cation. Mixtures of nitric and sulphuric acids nitrate the most slowly, and lithium nitrate acts the most rapidly. With regard to activity cations may be ranged in the following way:

$$H < NH_4 < K < Na < Ag < Li$$

This order also corresponds to the ease of conversion of bisulphates into pyrosulphates, which for the order presented is the highest for lithium salts (Klemenc and Schöller [34], K. Lauer and Oda [32], Lantz [83]).

Ceorgievskii [114] found that the yield of a nitration reaction also depends on the nature of the cation. For example, when benzene was nitrated to nitrobenzene, the best results were obtained with copper nitrate and sulphuric acid.

Fredenhagen [121] developed a method sometimes referred to as “Fredenhagen nitration” [122]. The nitrating agent consists of a nitrate, e.g. potassium nitrate in anhydrous or highly concentrated hydrogen fluoride.

Metal nitrates in the presence of Friedel-Crafts catalysts

Apart from the investigations on nitration with the nitrates of some metals in the presence of sulphuric or nitric acid Topchiyev [115] has carried out extensive studies on nitration with metal nitrates in the presence of $AlCl_3$, $FeCl_3$, $SiCl_4$, and BF_3. He showed that all the nitrates had nitrating properties, and he ordered the nitrates he studied according to their increasing nitration activity in the presence of $AlCl_3$:

$$Ba < Pb < NH_4 < Na < K < Ag$$

With KNO_3 and $NaNO_3$ the yield of nitrobenzene was 70 and 73% respectively, calculated on benzene.

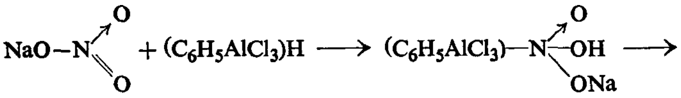
$AlCl_3$ and BF_3 were shown to be the most efficient catalysts, $FeCl_3$ was less efficient and the efficiency of $SiCl_4$ was the lowest.

The best yield of this nitration reaction is obtained at room temperature and in the presence of an excess of the aromatic hydrocarbon. An interesting feature of this nitration is that it is not accompanied by any oxidation processes. The method may find practical applications.

Topchiev has suggested the following hypothesis concerning the mechanism of nitration with nitrates in the presence of $AlCl_3$ or BF_3. Benzene is activated by aluminium chloride to give an addition product, according to the equation:

$$C_6H_6 + AlCl_3 \rightarrow (C_6H_5AlCl_3)H \tag{53a}$$

The product reacts with sodium nitrate, yielding another addition product which decomposes to give nitro compound:



$$NaO{-}\overset{\nearrow O}{\underset{\searrow O}{N}} + (C_6H_5AlCl_3)H \longrightarrow (C_6H_5AlCl_3){-}\overset{\nearrow O}{\underset{\searrow ONa}{N}}{-}OH \longrightarrow$$

$$\rightarrow C_6H_5NO_2 + NaOH + AlCl_3 \tag{53b}$$

CONCLUSIONS

It appears that concentrated nitric acid follows a heterolytic dissociation mainly according to the equation:

$$NO_2OH \leftrightarrow NO_2^+ + OH^-$$

The presence of acids stronger than HNO_3 accelerates the heterolysis of nitric acid into NO_2^+ and OH^-. It is for this reason that mixed acid is so effective:

$$HNO_3 + H_2SO_4 \leftrightarrow H_2NO_3^+ + HSO_4^-$$

$$H_2NO_3^+ + H_2SO_4 \leftrightarrow NO_2^+ + H_3O^+ + HSO_4^-$$

In neutral organic solvents (which do not react with the acids) only a second molecule of nitric acid can supply the necessary proton:

$$2HNO_3 \leftrightarrow H_2NO_3^+ + NO_3^-$$

$$H_2NO_3^+ \leftrightarrow NO_2^+ + H_2O$$

It should, however, be pointed out that most of the evidence presented by a number of authors, and chiefly by Ingold and his school in support of the nitronium ion mechanism of nitration, was obtained with homogeneous solutions under conditions that could not be compared directly with the conditions generally applied in industrial nitrations.

The work of Bennett and his co-workers [87] (discussed in detail on the p. 312) was an exception: a 50/50 mixture of di- and tri-nitrotoluene was nitrated by shaking with mixed acids of various compositions for a fixed time. The reaction was then quenched with cold water and the proportion of the dinitrotoluene which has been converted to trinitrotoluene was determined. The conversion, and the reaction rate, approach zero as the mole ratio water: sulphuric acid approaches unity. This is significant, because if this ratio considerably exceeds 1.0 the NO_2^+ ion is spectroscopically undetectable in sulphuric acid-nitric acid-water solutions. Bennett showed that various acid mixtures that gave the same conversion contained practically the same concentration of the NO_2^+ ion, as determined by Raman spectra. Hetherington and Masson [84] had already found that the reaction rate became negligibly small at certain concentrations and that a line drawn through the limiting boundary almost coincides with the boundary of the area of spectroscopic detection of NO_2^+ ions.

However, a few authors offered evidence showing that nitration can also occur with mixtures in which concentrations of the nitronium ion are too weak to be spectroscopically detectable (Lowen, Murray, Williams [116]; Bunton, Halevi, for C-nitration [93], and Urbanski and Hackel [80] for O-nitration). Also Brennecke and Kobe [117] drew attention to the experiments of McKinley and White [118] who found that the acids for mononitration lie outside the nitronium ion envelope.

All this created doubt as to whether the nitronium ion mechanism can be applied to all cases. As will be pointed out later, it seems that the mechanism of the nitration reaction is more complicated and may proceed under the influence of nitrating agents other than the NO_2^+ ion. According to Titov in his early work of 1941, nitration with nitric acid of moderate concentration (60-80% HNO_3) occurs through the action of NO_2 (or N_2O_4) and nitric acid plays only the role of a source of NO_2.

However, Bunton and Halevi [93] have expressed the view that the nitronium ion mechanism is still responsible for C-nitration even in highly aqueous conditions. Bunton, Halevi and Llewellyn [92] in their work described above (p. 38) examined the mechanism of oxygen exchange between nitric acid and water in an aqueous nitric acid medium by using isotopically labelled water. From the identity of the absolute rate of exchange in such a medium with the absolute rate in the same medium used for an aromatic nitration they suggested that the nitronium ion mechanism is responsible for nitration with nitric acid containing for example 60 mole % of water. Banner and Frizel [99b] have also suggested the nitronium ion mechanism for O-nitration of alcohols by nitric acid in aqueous solution.

It should be pointed out that phenols and anilides can be nitrated with very dilute nitric acid. The mechanism of such reactions might differ essentially from that of the reactions of C-nitration in other aromatic compounds, as it most likely passes through the formation of nitroso compounds which are then oxidized to the corresponding nitro compounds. This problem is discussed later (e.g. p. 85, 116).

Since industrial nitration occurs, in most cases, in two-phase system a number of workers have investigated the kinetics in both phases: organic and acid. Hetherington and Masson [84], McKinley and R. R. White [I18], Barduhn and Kobe [119] all reported that nitration of aromatic hydrocarbons takes place only in the acid phase. However, other workers (W. K. Lewis and Suen [120]) have shown, when nitrating benzene, that the reaction rate in the organic phase is an appreciable fraction (10-15%) of that in the acid phase.

As mentioned already (p. 40) it appears that nitration takes place mainly (but not exclusively) in the acid phase.

Taking into consideration that the rate of reaction in the organic phase is negligible compared with that in the acid phase, the following definition of the rate of nitration, R, of toluene in the unit volume of acid phase can be given

$$R = \frac{\text{moles of MNT produced}}{\text{hr x litre of acid phase}}$$

Brennecke and Kobe [117] reported that the rate of nitration of toluene appears to be proportional to the mole fraction of toluene in the effluent organic phase X_T (for acids containing not more than 30 mole % sulphuric and 15 mole % nitric acid). This suggested that the ratio $R:X_T$ is the rate that would be obtained if the organic phase were pure toluene. Kobe came to the conclusion that the mechanism of nitration through the nitronium ion controls the rate of reaction in acids containing more than 30 mole % of sulphuric acid.

The fact that most industrial nitrations take place in a two-phase system necessitated investigations into the influence of mixing on the rate of reaction.

A few authors, e.g. Kobe and his co-workers [117, 119], Orlova [123] have found that the rate of nitration greatly depends on the intensity of agitation of a reacting mixture. This is discussed in a more detailed way in the chapter devoted to the practical principles of nitration, i.e. the technology of the process and apparatus for nitration (pp. 152, 266, 288, 314).

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CHAPTER II

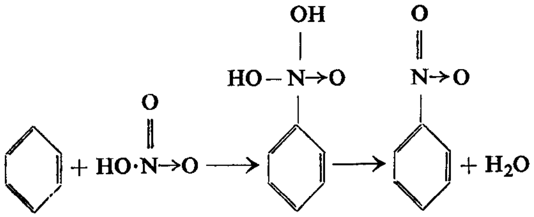
NITRATION THEORIES

THERE are two main theories concerning the nitration of hydrocarbons by means of the nitrating agents described above.

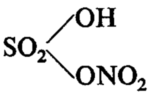
The first theory assumes a two-stage reaction with an addition reaction as the first stage and the second assumes that nitration is a double exchange reaction. At present the second theory has more adherents, since it is based on more recent experimental data.

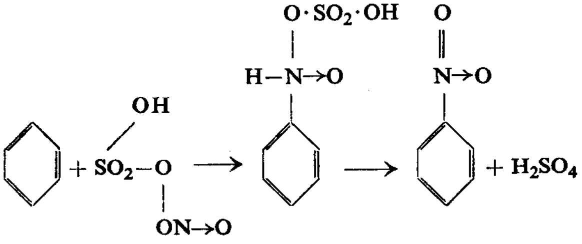
NITRATION AS AN ADDITION REACTION

According to Michael [1], on nitrating aromatic hydrocarbons an intermediate addition product is formed, which has one hydrocarbon hydrogen atom attached to one oxygen atom of nitric acid, and a carbon atom of the aromatic ring directly attached to the nitrogen atom of the acid. The "aldol" formed gives off water in the presence of an excess of nitric or sulphuric acid. The mechanism was depicted by the author as follows:



(1)

Likewise the mechanism of nitration of an aromatic hydrocarbon with nitrosulphuric acid  $SO_2\begin{matrix}\diagup OH\\ \diagdown ONO_2\end{matrix}$ was formulated by Michael as:

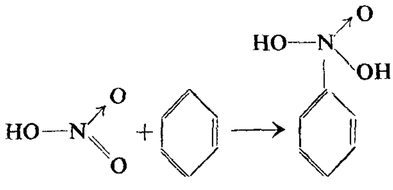


(2)

Here it is not water but sulphuric acid which is given off.

This view Michael confirmed in 1935 when he emphasized [2] that in a molecule of nitric acid the dominating factor, which facilitated the reaction, was the affinity of oxygen for hydrogen and of nitrogen for the aryl group.

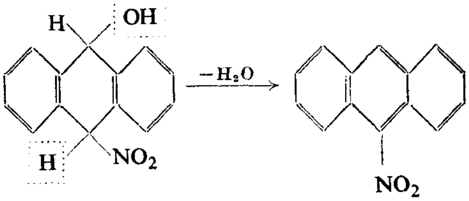
Hence the facility of the transformation:



(3)

However, Giersbach and Kessler [3] supposed that the initial step in the nitration reaction was the addition of two nitric acid molecules to a benzene molecule,

Experimental evidence of the possibility of the formation of products from aromatic hydrocarbons by the addition of nitric acid was provided by Meisenheimer [4]. He found that with anthracene the nitric acid molecule attached itself to the 9 and 10 carbons (of aliphatic character), yielding the product I, which in the presence of sodium hydroxide or acetic anhydride gave off water to form *meso*-nitroanthracene (II) :



I II

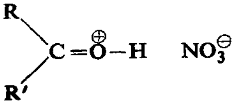
(4)

It has also been found that certain aldehydes, ketones and carboxylic acids esters form well defined products with nitric acid (Reddelien [5]). For example, bemzaldehyde with 60% nitric acid gives a colourless, unstable oil, and cinnamic aldehyde forms fairly stable white crystals, melting at 60-61°C, with 65% nitric acid. Acetophenone, benzophenone, fluorenone, phenanthrenoquinone and camphor give similar addition products.

They are converted to nitro compounds under the influence of nitric acid or acetic anhydride and are decomposed by water to give the initial components.

According to T. Urbanski and Hofman [5a] the ionic oxonium salt structure can be attributed to these compounds:

$$\mathrm{RHC{=}\overset{\oplus}{O}{-}H\qquad NO_3^{\ominus}}\qquad \text{and}$$



$$\mathrm{\begin{matrix}R\\ \end{matrix}\!\!\searrow C{=}\overset{\oplus}{O}{-}H\qquad NO_3^{\ominus}\quad (R, R')}$$

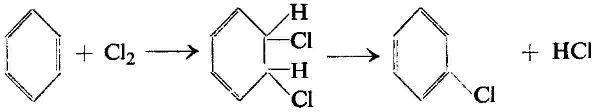
This was based on infra-red absorption spectra which show frequencies of the oxonium ion bond (O^+-H, ca. 2600 cm^{-1}) and of the nitrate ion.

Houben [6] gives the following sequence of transformations for "benzaldehyde nitrate" :

$$C_6H_5CHO.HNO_3 \left\{ \begin{array}{lr} + H_2O \rightarrow C_6H_5CHO + HNO_3 & (a) \\ \text{left in a hermetic vessel} \rightarrow C_6H_5COOH + HNO_2 & (b) \\ + (CH_3CO)_2O \rightarrow C_6H_5CH(OOC.CH_3)_2 + HNO_3 & (c) \\ + H_2SO_4 \rightarrow m\text{-}\ C_6H_4(NO_2)CHO + H_2O & (d) \\ + H_2SO_4 + (CH_3CO)_2O \rightarrow p\text{-}\ C_6H_5(NO_2)CHO + H_2O & (e) \\ + C_{10}H_8 \rightarrow C_6H_5CHO + C_{10}H_7.NO_3 & (f) \end{array} \right.$$

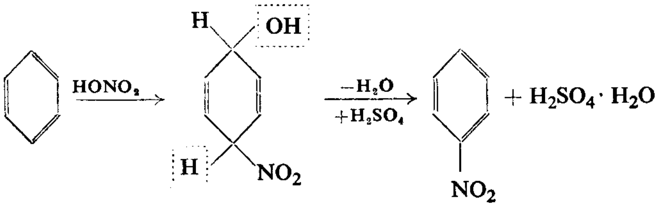
An interesting point is the influence of the compounds which react with an addition compound (reactions d and f) on the position of the nitro group introduced.

Following Thiele's view [7] that any aromatic substitution is preceded by the formation of an addition product Holleman [8] suggested in 1910 that the reaction of nitration, like that of chlorination, consisted in addition, followed by splitting off, according to the following scheme for chlorination:



(5)

A similar scheme for the nitration process was given by Reddelien [5] who expressed the view that nitration of aromatic hydrocarbons with mixtures of nitric and sulphuric acids gave addition products, e.g.

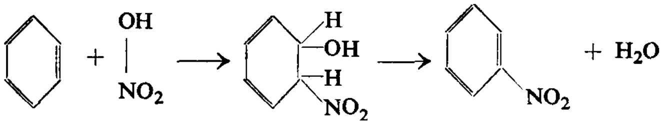


III IV

(6)

The product (III) undergoes decomposition, the group OH being attached to H_2SO_4 as H_2O (IV). The addition product is hydrolysed by water, and mono- or polynitro compounds are formed.

Mainly on the basis of Holleman's hypothesis and studies on the nitration of olefins, Wieland [9,10] assumed the addition of a nitric acid molecule to the double bond, resulting in the formation of a cyclohexadiene derivative (V), followed by the loss of a water molecule:

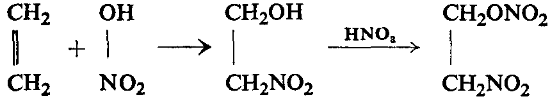


V

(7)

The addition of a nitric acid molecule to the double bond was first studied by Kekulé [11], who obtained an oily, explosive product on treating ethylene with concentrated nitric acid. Wieland [9,10] and Anschütz [12] believed the reaction to proceed principally according to the eqns. (8) and (9).

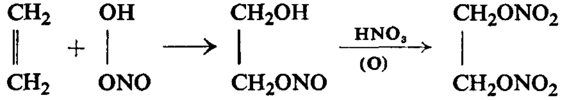
In support of this theory Wieland [10] reported the results of his investigations, carried out in co-operation with Sakellarios, where two products (VI) and (VII) were obtained in the reaction of ethylene with nitric acid:



$$\begin{array}{c}\mathrm{CH_2}\\ \| \\ \mathrm{CH_2}\end{array} + \begin{array}{c}\mathrm{OH}\\ | \\ \mathrm{NO_2}\end{array} \longrightarrow \begin{array}{c}\mathrm{CH_2OH}\\ | \\ \mathrm{CH_2NO_2}\end{array} \xrightarrow{\mathrm{HNO_3}} \begin{array}{c}\mathrm{CH_2ONO_2}\\ | \\ \mathrm{CH_2NO_2}\end{array} \qquad (8)$$

VI

Nitroethyl nitrate



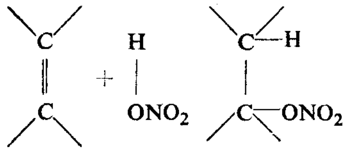
$$\begin{array}{c}\mathrm{CH_2}\\ \| \\ \mathrm{CH_2}\end{array} + \begin{array}{c}\mathrm{OH}\\ | \\ \mathrm{ONO}\end{array} \longrightarrow \begin{array}{c}\mathrm{CH_2OH}\\ | \\ \mathrm{CH_2ONO}\end{array} \xrightarrow[\mathrm{(O)}]{\mathrm{HNO_3}} \begin{array}{c}\mathrm{CH_2ONO_2}\\ | \\ \mathrm{CH_2ONO_2}\end{array} \qquad (9)$$

VII

Glycol dinitrate

In both reactions products were formed which resulted from addition (in the first stage of the reaction) of a nitric acid molecule to the double bond.

Wieland's theory was criticized. Michael and Carlson [2] called in question Wieland's view and proposed a different mechanism:



(10)

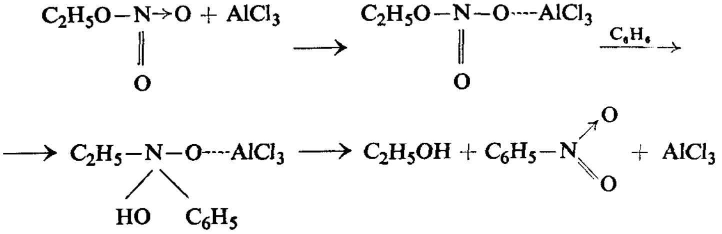
since they found that at temperatures below 0°C concentrated nitric acid adds to olefines, such as isobutylene, trimethylethylene, to yield the nitric esters of the corresponding alcohols. Other objections to the Wieland theory were also put forward by Topchiyev [13]:

(1) The cyclohexadiene derivative (V), formed by addition of a nitric acid molecule, is very unstable and it is difficult to speak about a definite direction of the decomposition reaction of the compound V.

(2) Against the theory of the similarity of the processes of attaching HNO_3 and Br_2 to the double bond is the fact that molecules are attached with different rate. Bromine is attached only with great difficulty (without a catalyst). On the contrary, nitration is very easy to carry out.

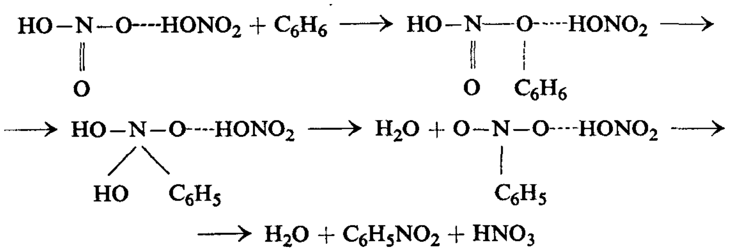
Taking this into account, Tronov [14,15,16] and Nametkin and Zabrodina [16a] advanced another idea, similar to Michael's initial hypothesis. Thus on the basis of Giersbach and Kessler's [16b] experiments Tronov inferred that one of the two HNO_3 molecules reacting with one molecule of benzene acts as a catalyst.

On the basis of Boedtker's experiments [17], who found that benzene was nitrated by ethyl nitrate in the presence of aluminium chloride, Tronov suggested the following mechanism for this process:



(11)

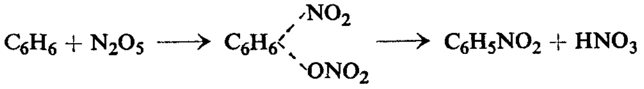
By analogy with this, Tronov gives the following plan for the general mechanism of nitration:



(12)

According to Schaarschmidt [18] the mechanism of nitration with a mixture of nitric and sulphuric acids consists in the formation of nitric anhydride which becomes attached to the aromatic compound. The addition compound is unstable and decomposes, giving a nitro compound and nitric acid. The mechanism of nitration suggested by Schaarschmidt is:

$$2HNO_3 + H_2SO_4 \leftrightarrow N_2O_5 + H_2SO_4.H_2O \tag{13}$$



Unstable nitration product

Hetherington and Masson [19] suggested that nitrobenzene can form complexes with H_2SO_4 and HNO_3 and that the cation, $C_6H_5NO_2H^+$, of these complexes reacts with HNO_3 to form dinitrobenzene:

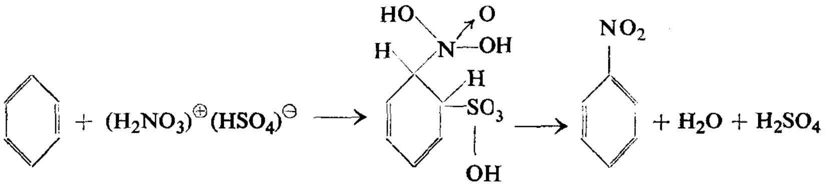
$$H_2SO_4 + C_6H_5NO_2 \leftrightarrow C_6H_5NO_2H^+ + HSO_4^- \tag{14}$$

$$HNO_3 + C_6H_5NO_2 \leftrightarrow C_6H_5NO_2H^+ + NO_3^- \tag{14a}$$

$$C_6H_5NO_2H^+ + H_2O \leftrightarrow C_6H_5NO_2 + H_3O^+ \tag{15}$$

$$C_6H_5NO_2H^+ + HNO_3 \leftrightarrow C_6(NO_2)_2 + H_3O^+ \tag{15a}$$

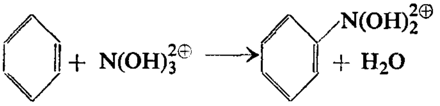
Lauer and Oda [20] assumed the existence of nitracidium sulphate (according to Hantzsch) and suggested that the mechanism of nitration with a nitrating mixture is as follows:



(16)

A similar nitration mechanism was suggested by Vorozhtsov [21]. He also assumed the formation of an addition product of the hydrocarbon with HNO_3 and H_2SO_4, followed by splitting off H_2SO_4 and H_2O.

Usanovich [22] also assumed Hantzsch's cations to be the nitrating agents in a mixture of nitric and sulphuric acids. He believed that in the nitration process the nitracidium cation was attached first accompanied by splitting off water:



(17)

On dilution with water the resulting new cation, $C_6H_5N(OH)_2^{2+}$, gives nitrobenzene:

$$C_6H_5NO_2H_2^{2+} + 2H_2O \rightarrow C_6H_5NO_2 + 2H_3O^+ \qquad (18)$$

In the nitration of aliphatic hydrocarbons the NO_3^- ion reacts:

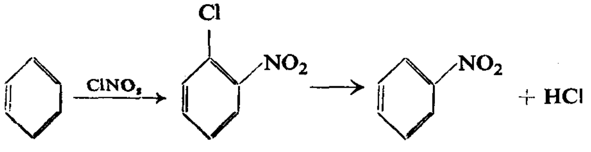
$$R.CH_3 + NO_3^- \leftrightarrow R.CH.NO_2(OH)^- \qquad (19)$$

The anion formed may undergo a hydrolysis process in an acid medium:

$$R.CH_2NO_2(OH)^- + H_3O^+ \rightarrow R.CH_2NO_2 + 2H_2O \qquad (20)$$

In favour of the view, that postulates the formation of an addition product during the first stage of nitration this fact should be known to all who are practically engaged in nitration of aromatic hydrocarbons. Immediately before contacting the nitrating acid (HNO_3 or nitric and sulphuric acids mixture), benzene and toluene give brown coloured products amid nitric acid vapours. On dissolution in the acid these products decolourize at once. It is quite possible they arc addition products formed by nitric acid vapours with the hydrocarbon.

The existence of similar addition products must be mentioned here. Steinkopf and Kühnel [23] observed that benzene reacted with nitryl chloride at room temperature under pressure to yield 1-chloro-2-nitrocyclohexadiene, which on heating released a molecule of hydrogen chloride giving nitrobenzene:



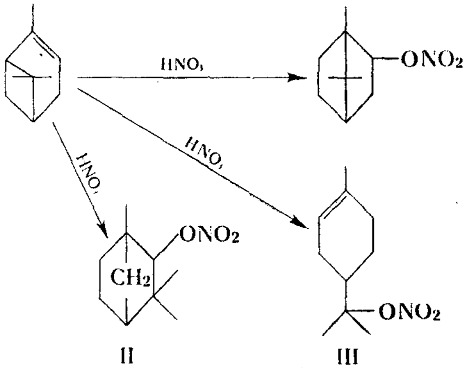
(21)

Thus, there is evidence that such addition is probable and it seems to confirm the basic scheme of Thiele-Holleman-Wieland, assuming that under certain conditions substitution with the NO_2 group may be preceded by the formation of addition products.

Although this view was replaced by the conception of the nitration reaction as double exchange reaction, it seems that the mechanism of the nitration reaction is rather a complicated one and under various conditions may proceed differently. The mechanism which includes addition may also exist, especially at low temperatures, and may not necessary proceed under the influence of the nitronium ion. It seems that nitric acid in the form of HO-NO_2 can be the nitrating agent acting through the addition mechanism.

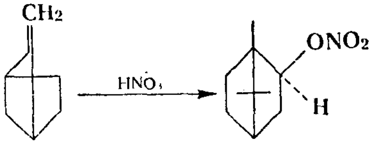
Studies of the nitration of terpenes are of interest too, as they provide evidence for the possibility of attaching a HNO_3 molecule to the double bond. Konovalov [24] obtained nitro derivatives from menthene, camphene, pinene and bornylene on acting with nitric acid. Bouveault [25] was able to prepare an addition product of camphene and HNO_3. He obtained an oily product with a structure that could not be well defined. The reaction of addition of nitric acid to the double bond was studied in detail by Sucharda [26]. He found that on acting on pinene with nitric acid containing 33% of KNO_3 instead of with pure nitric acid, or by introducing nitric acid vapours diluted with dry air, nitric acid esters were obtained in over 70% yield. When reduced with zinc dust in the presence of ammonia, the esters were converted to the corresponding alcohols.

Using both methods Sucharda obtained: borneol (I), fenchol (II) and terpineol (III) nitrates :



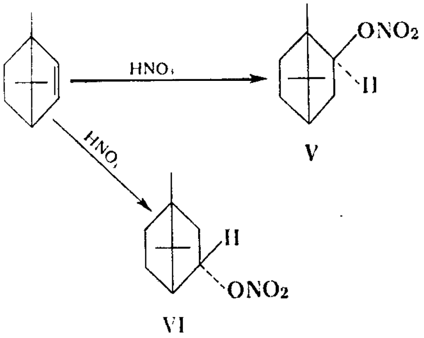
II III

H. Kuczynski and L. Kuczyliski [27] extended Sucharda’s observations in their studies on other terpene hydrocarbons. They obtained isoborneol nitrate (IV) on reacting camphene with concentrated nitric acid (without KNO_3):



IV

From bornylene they obtained isoborneol (V) and epiborneol (VI) nitrates:

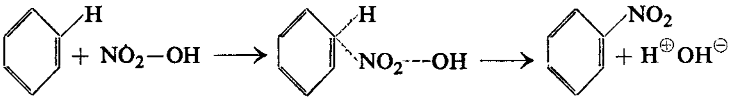


H. Kuczynski and L. Kuczynski have also studied the action of nitric acid on β– and δ– fenchene, limonene, sylvestrene and other terpene hydrocarbons.

It has also been shown that the addition of nitric acid molecules to olefins is not the only possible reaction of olefins with HNO_3. Formation of nitro-olefins, i.e. ordinary nitration by substitution, is also likely. This is discussed later (p. 81).

NITRATION AS A DOUBLE EXCHANGE REACTION

At present it is generally accepted that the nitration reaction is a double exchange reaction. The nitro group becomes attached to one of the carbons in an aromatic ring, while simultaneously an atom of hydrogen initially connected with an atom of carbon, is split off as a proton:

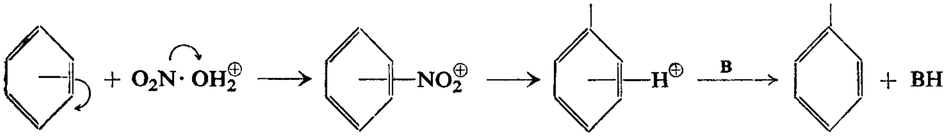


(22)

A nitration mechanism formula of this type was suggested by Ingold [28] in 1935.

In 1946, Dewar [29] gave the following mechanism for the double exchange with the nitracidium ion taking part:

(23)



B is a proton acceptor (e.g. the OH^- or HSO_4^- ions).

Benford and Ingold [30] pointed out in 1938 that the efficiency of bromination with a brominating agent of the general formula X-Br depended on the affinity of X for the electrons of the X-Br bond. It is known, for example, that Cl.Br is a better brominating agent than Br.Br. Likewise the efficiency of a nitrating agent, $X\text{-}NO_2$, depends on the affinity of X for electrons.

A still more powerful brominating agent is the free Br^+ ion, which is probably formed in the presence of ferric bromide used as a bromination catalyst:

$$FeBr_3 + Br_2 \rightarrow FeBr_4^- + Br^+$$

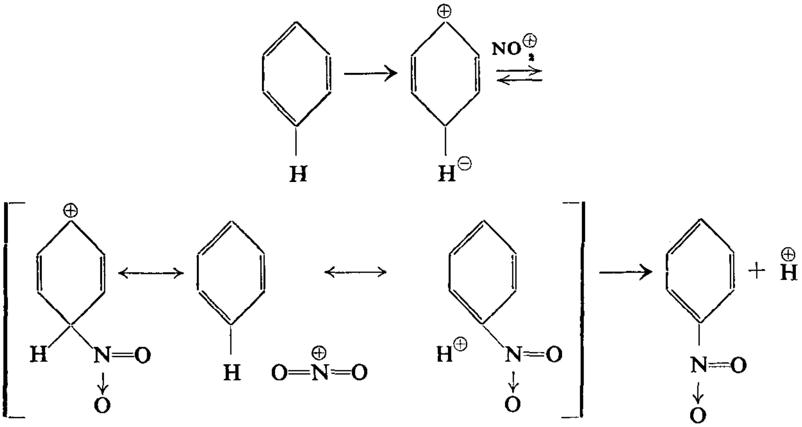
By analogy it is to be expected that the NO_2^+ is the most powerful nitrating agent.

Gillespie and Millen [31] arranged various nitrating agents according to increasing nitration power :

$C_2H_5O.NO_2$	ethyl nitrate
$HO.NO_2$	nitric acid
$CH_3COO.NO_2$	acetyl nitrate
$NO_3.NO_2$	nitric anhydride
$Cl.NO_2$	nitryl chloride
$H_2O.NO_2^+$	nitracidium ion
NO_2^+	nitronium ion

This order seems to require some alteration. For example, nitryl chloride has been found to be a definitely weaker nitrating agent than nitric acid and should have been placed before it.

On the basis of the numerous physico-chemical investigations referred to above, we assume that in the nitrating mixture HNO_3-H_2SO_4-H_2O the nitronium ion is present, it being the essential nitrating agent. Hence Titov [32] suggested in 1941 the following nitration mechanism where nitronium ion forms intermediate complex structures with aromatic compounds (in brackets):



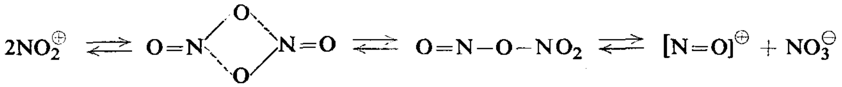
(24)

Ingold and his co-workers [33] and Bennett and co-workers [34-36] believed that the reaction rate depends on the concentration of the nitronium ions, NO_2^+. They suggested the following summarized nitration mechanism :

$$R.H + NO_2^+ + B \rightarrow R.NO_2 + HB \quad (25)$$

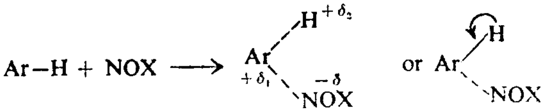
where B is a proton acceptor, for example HSO_4^- or OH^- ions.

Or the basis of the results of his own experimental studies, Titov [37] in 1947 accepted this view, but at the same time he pointed out that the nitration reaction occurred in a more complex way than that suggested by Ingold. The nitrating agents according to Titov were all the molecules and ions in equilibrium, viz.: NO_2^+, $NO\text{-}ONO_2$ and NO^+ :



(26)

These agents have both nitrating and nitrosating properties. Titov believed the nitration promoting energy was that generated by the transfer of electrons from the aromatic compound to nitrogen atoms of a nitrating or nitrosating agent according to the general formula NOX:



(27)

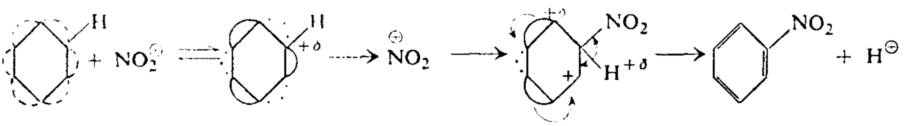
The difference in the electron affinities, Δ E, approximately equal to k δ, necessary for the formation of the intermediate complex, depends to a great extent on the degree of steric accessibility and coordinative unsaturation of the nitrating and nitrosating agents.

Since according to the experimental data, the coordination number of nitrogen in its oxygen compounds does not exceed 3, the nitrogen atom in the nitric acid molecule is coordinatively saturated and has only slight electrophilic reactivity. This, according to Titov, makes the formation of addition products of nitric acid with aromatic compounds difficult.

Contrary to this nitrogen compounds with the coordination number 1 or 2 (thus, NO_2^+, NO^+ ions and $ONONO_2$), may exhibit their electrophilic reactivities and combine with the corresponding nucleophilic atoms of aromatic compounds.

To make it clear that splitting off a proton has no bearing on the rate of nitration a mechanism should be presented where the nitration reaction proceeds in, two steps, as pointed out by Melander [38] (p. 37).

Dewar's diagram eqn. (23) (see p. 60) already gives this idea, the binding of the proton by the acceptor B being the second step reaction. Titov [39] suggested recently a scheme which would clearly show the step-wise mechanism:



(28)

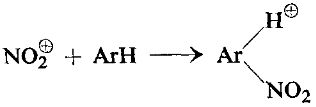
Here aromatic bonds are designated with dotted curved lines. Plain curved lines are π– bonds, three dots signify weaker π– bonds (as in 2,3-butadiene), the dotted arrow (->) represents shifting of π– electrons into the cation field, and the curved arrow (↷)) the displacement of electrons. These denote the most important forms of the conjugations.

According to Ingold nitration is the simplest form of electrophilic substitution.

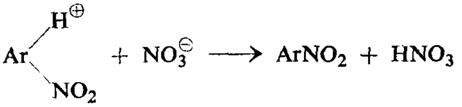
Recently Ingold and his co-workers [40] summarized the results of their investigations [41-48] into the three forms of nitration: C-, O- and N- nitration. The nitronium ion is formed in two stages, the first of which (a) - protonation -is always fast:

$$HNO_3 + HNO_3 \leftrightarrow H_2NO_3^+ + NO_3^- \qquad \text{(fast)} \qquad \text{(a)}$$

$$H_2NO_3^+ \leftrightarrow NO_2^+ + H_2O \qquad \text{(slow)} \qquad \text{(b)}$$

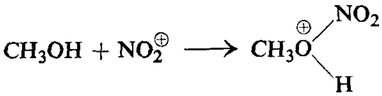


$$NO_2^{\oplus} + ArH \longrightarrow Ar\begin{matrix} H^{\oplus} \\ NO_2 \end{matrix} \qquad \text{(slow)} \qquad \text{(c)}$$

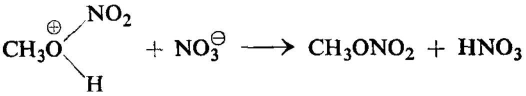


$$Ar\begin{matrix} H^{\oplus} \\ NO_2 \end{matrix} + NO_3^{\ominus} \longrightarrow ArNO_2 + HNO_3 \qquad \text{(fast)} \qquad \text{(d)}$$

If O- or N- substitution takes place, the reactions (a) and (b) proceed in the same way. In O- nitration, the subsequent reactions take place according to the following scheme :

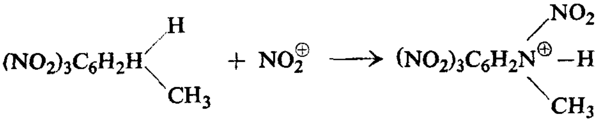


$$CH_3OH + NO_2^{\oplus} \longrightarrow CH_3\overset{\oplus}{O}\begin{matrix} NO_2 \\ H \end{matrix} \qquad \text{(slow)} \qquad \text{(c')}$$

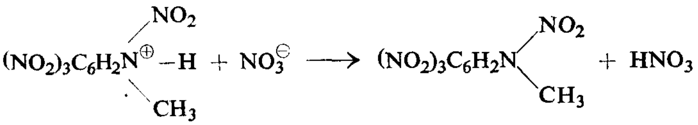


$$CH_3\overset{\oplus}{O}\begin{matrix} NO_2 \\ H \end{matrix} + NO_3^{\ominus} \longrightarrow CH_3ONO_2 + HNO_3 \qquad \text{(fast)} \qquad \text{(d')}$$

Ingold gives the following examples of N-nitration reactions:



$$(NO_2)_3C_6H_2N\begin{matrix} H \\ CH_3 \end{matrix} + NO_2^{\oplus} \longrightarrow (NO_2)_3C_6H_2\overset{NO_2}{\underset{CH_3}{N^{\oplus}}}-H \qquad \text{(slow)} \qquad \text{(c'')}$$



$$(NO_2)_3C_6H_2\overset{NO_2}{\underset{CH_3}{N^{\oplus}}}-H + NO_3^{\ominus} \longrightarrow (NO_2)_3C_6H_2N\begin{matrix} NO_2 \\ CH_3 \end{matrix} + HNO_3 \qquad \text{(fast)} \qquad \text{(d'')}$$

In all these diagrams splitting off the proton is the last stage of the reaction.

ORIENTATION OF NITRO GROUPS

The orientation of a nitro group entering an aromatic ring depends first of all on the substituent already present in the ring and to a lesser degree on the composition of the nitrating acids, the nitrating conditions, etc. It is well known that the nitro group itself directs substituents to the *meta* position.

The problem of the orientation of nitro groups is connected with that of nitration kinetics. Nitration kinetics have already been discussed in connection with the composition of nitrating mixtures, especially with regard to the presence and the role of nitronium and other ions in the nitration process. Now nitration kinetics will be considered from another viewpoint-that of the influence of various substituents in promoting or inhibiting further substitution.

A great deal of research work has been carried out with the object of studying the orientation of nitro groups introduced into an aromatic ring. The most extensive investigations are those by Holleman [49-55], who in the period 1895-1924 carried out numerous experiments and systematized the data obtained.

TABLE 2

Group present on the ring	Composition of the product		
	% ortho-	*% meta-*	*% para-*
F	12.4	trace	87.6
Cl	30.1	trace	69.9
Br	37.6	trace	62.4
I	41.1	trace	58.7
CH_3	58.8	4.4	36.8
CH_2Cl	40.9	4.2	54.9
$CHCl_2$	23.3	38.8	42.9
CCl_3	6.8	64.5	28.7
$COOC_2H_5$	28.3	68.4	3.3
COOH	18.5	80.2	1.3
NO_2	6.4	93.2	0.25

Holleman [55] gives the following data on the composition of the nitration products obtained in the nitration of different monosubstituted benzene derivatives with mixtures of nitric and sulphuric acids (Table 2). As appears from the data shown below, the substituent already present affects the orientation of the group which is being introduced. It is evident that nitration can be influenced by the steric factor. For exampl: tert.-butylbenzene is mainly nitrated in *para* (72.7%) and to a much lesser extent in *ortho* (15.8%) positions (H. C. Brown and Nelson [88]).

TABLE 3

Temperature, °C	Composition of the product		
	% ortho-	% para-	% meta-
-30	55.6	41.7	2.7
0	56.0	40.9	3.1
+30	56.9	39.9	3.2
+60	57.5	38.5	4.0

The influence of the nitration temperature on the orientation of a nitro group is in certain cases rather marked. When nitrating toluene with a mixture of nitric and sulphuric acids at -5°C, Pictet [56] observed that more para-isomer was obtained than at the temperature of 0°C.

Holleman and Arend [49] gave more detailed data, showing the influence of temperature on the composition of the product obtained in the mononitration of toluene with a mixture of nitric and sulphuric acids (Table 3).

Similar results have been obtained in the nitration of chlorobenzene, as shown in Table 4.

TABLE 4

Temperature, °C	Composition of the product	
	% ***ortho-***	% ***para-***
0	30.1	69.9
-30	26.9	73.1

As for naphthalene, Pictet [56] found that nitration at temperatures from -50 to -60°C mostly resulted in the formation of 1,5-dinitronaphthalene with a certain amount of the 1,3-isomer, while at a temperature higher than room temperature 1,5-dinitronaphthalene is formed along with l,8-isomer.

Bradfield and B. Jones [57] applied the Arrhenius equation, known from chemical kinetics, to the reaction of substituting various benzene derivatives by the nitro group (or by chlorine) at different temperatures:

$$k = nA\exp\left(-\frac{E}{RT}\right)$$

where for each isomer:

k - rate constant for the substitution reaction,

E - activation energy,

A - coefficient independent of temperature,

T - absolute temperature,

R - gas constant,

n - number of equivalent substitutions possible (for example, in the conversion of a monosubstituted into an ortho-disubstituted derivative n = 2, into a meta-disubstituted derivative, n = 2, and into the para-disubstituted derivative n = 1).

The number of isomers formed in a substitution reaction at a given temperature may be calculated if the composition of the substitution product, obtained at a different temperature is known. The equations have to be worked out for each isomer, in which k_o, A_o, E_o, k_m, A_m, k_m, k_p, A_p, E_p are the values, corresponding to the *ortho-*, *meta-* and *para-* isomer respectively.

The procedure of Bradfield and B. Jones was applied later by W. W. Jones and Russel [58] to their experiments on the nitration of toluene (their work will be further discussed later on p. 274). The results they obtained established the rule: a lower nitration temperature causes an increase in the quantity of *para-* nitrotoluene formed and reduces the amounts of *ortho-* and *meta-* isomers.

The nature and composition of the nitrating agent distinctly affects the composition of the nitration products.

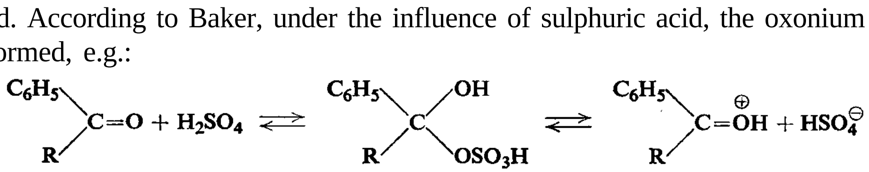
Noelting and Forel [59] stated that an increase in HNO_3 concentration in the nitrating mixture increases the amount of *para-* nitro compound produced. Thus, for example, in nitrating toluene with a mixture of nitric and sulphuric acids they obtained a product containing 60% of *p*- nitrotoluene, while in nitration with nitric acid alone the *para*- isomer content was 66%.

Baker and his co-workers [60,61] investigated the influence of the sulphuric acid concentration in nitrating mixtures on the *meta*- nitro derivatives of the following compounds: benzaldehyde, benzophenone and ethyl benzoate. The content of a *meta*- nitro derivative increases with the increase in acidity of the solution. For example, in nitration with a nitrating mixture containing 80% sulphuric acid the yield of *m*- nitrobenzaldehyde is 83.9%. When nitrated with a mixture containing oleum (7.3% of free SO_3), benzaldehyde gives *m*- nitrobenzaldehyde in 90.8% yield. According to Baker, under the influence of sulphuric acid, the oxonium ion is formed, e.g.:

TABLE 5

NITRATION OF ANILINE AND ANILIDES

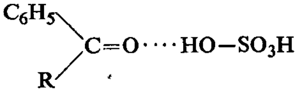
Nitrated compound	Composition of the product		
	% *ortho-*	% *meta-*	% *para-*
	With nitric acid		
Aniline nitrate	4	40	56
Acetanilide	42		58
Benzanilide	40		60
Formanilide	35	-	65
Chloroacetanilide	27	-	73
Oxanilide	15	-	85
	12	-	88
With a solution of 94% nitric acid in the concentrated sulphuric acid			
Aniline	1	49	50
Acetanilide	8	-	92
Benzanilide	7	-	93
Formanilide	6	-	94
Chloroacetanilide	4	-	96
Oxanilide	2	-	98
	2	-	98
With a solution of 80% nitric acid in anhydrous acetic acid			
Aniline	36	-	64
Acetanilide	30	-	70
Benzanilide	28	-	72
Formanilide	26	-	74
Chloroacetanilide	25	-	75
Oxanilide	21	-	79
	16	-	84



$$\begin{matrix}C_6H_5\\R\end{matrix}\!\!>C{=}O + H_2SO_4 \rightleftarrows \begin{matrix}C_6H_5\\R\end{matrix}\!\!>C<\!\!\begin{matrix}OH\\OSO_3H\end{matrix} \rightleftarrows \begin{matrix}C_6H_5\\R\end{matrix}\!\!>C{=}\overset{\oplus}{O}H + HSO_4^{\ominus} \qquad (29)$$

The oxonium group directs mostly to the *meta* position.

Gillespie and Millen [31] believed that sulphuric acid in an intermediate addition product is linked to the carbonyl group by a hydrogen bond:



K. Lauer [62] obtained the results (given in Table 5) by nitrating aniline and anilides with nitric and with mixtures of nitric and sulphuric or acetic acids at 20°C, over 24 hr.

It can be seen from the results referred to and also from the earlier data of Holleman and his co-workers [53] that aniline acylation has a decisive influence on the orientation of the nitro group.

When nitrating *p*- cresol, Holleman [51] found that according to whether *p*- cresol was reacted alone or as the *p*- cresol carbonic ester different isomers were obtained (Table 6).

TABLE 6

Nitrated compound	Composition of the product	
	% 2-nitro	% 3-nitro
p- Cresol	trace	close to 100
p- Cresyl carbonate	96.3	3.7

Holleman compared the data obtained by Pictet and Khotinsky [63] in the nitration of toluene with acetyl nitrate with those obtained by other authors in the nitration of toluene with a conventional nitrating mixture. The results are tabulated below (Table 7).

TABLE 7

Nitrating agent	Composition of the nitration product	
	% ***ortho-***	% ***para-***
Acetyl nitrate	88	12
Nitric and sulphuric acid mixture	55	40

Martinsen [64] in his studies on nitration kinetics determined the influence of substituents on the rate of the reaction. He classified them according to their influence on the reaction rate, comparing it with that of chlorine, which in some cases (as compared with hydrogen) can lower, while in others raise the rate:

$$NO_2 > SO_3H > COOH > Cl < CH_3 < OCH_3 < OC_2H_5 < OH$$

decreasing the reaction rate — increasing the reaction rate

It is interesting to know that the substituents which decrease the reaction rate direct towards the *meta* position while those increasing it direct towards the *ortho* and *para* positions.

The rule was checked by Tronov and Ber [15] when nitrating aromatic compounds with nitric acid in nitrobenzene. They found there was no simple correlation between the influence of a substituent on the reaction rate and its orienting activity. The rule is true only for the groups with strong orienting activity (e.g. NO_2, CN, CH_2CN, C_6H_5CO).

Ingold [65] gave the following order, representing activating properties of substituents in the nitration of an aromatic ring:

$$CH_3 > H > F, I > Cl, Br > COOC_2H_5 > SO_3H > NO_2$$

The introduction of several groups intensifies the action of the substituents. Thus Tronov and Ber have found that *o*-, *m*-, and *p*- xylene are nitrated 1.6-1.9, 4.5-4.9 and 5.7-10.5 times faster respectively than toluene. According to Ingold, *p*- dichlorobenzene is nitrated more slowly than chlorobenzene.

Striking data for the deactivating properties of nitro groups have been provided by Westheimer and Kharasch [65a]. They are related to the known fact that the nitration of nitrotoluene proceeds much faster than that of dinitrotoluene.

Tronov, Kamay and Kovalenko [66] have measured the rate of nitration of aromatic hydrocarbons and their halogenides with a mixture of nitric and acetic acids. The compounds examined were arranged according to increasing rate of nitration the relative rate is given in brackets, taking 1 for benzene:

$$C_6H_5Cl\ (0.15) < C_6H_5Br\ (0.25) < C_6H_5CH_2Cl\ (0.4) < m\text{-}\ CH_3C_6H_4Cl(0.5) < C_6H_6\ (1) <$$

$$< p\text{-}\ CH_3C_6H_4Cl(1.15) < o\text{-}\ CH_3H_4Cl(1.2) < m\text{-}\ \text{xylene}\ (7) < \text{mesitylene}\ (2.5)$$

If there are two substituents on the ring directing the NO_2 group into different positions more isomers may of course, be formed. Holleman [55] analysed minutely the problem as to which isomers were obtained in such cases. He established that their position, or positions, depend on the effect of separate groups on the reaction rate.

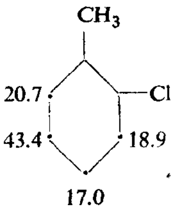
He arranged ***ortho-*** and *para-* orienting groups, according to their decreasing substitution rates, as follows :

$$OH > NH_2 > I > Br > CI > CH_3$$

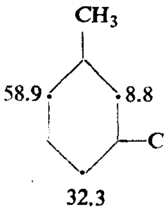
and did likewise for meta-orienting groups:

$$COOH > SO_3H > NO_2$$

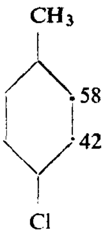
When nitrating aromatic compounds containing more than one substituent, the position of a new entrant group may be predicted from the number of isomers obtained by nitrating the compound with each of the substituents taken separately. Wibaut [67] studied this problem in detail when nitrating chlorotoluenes. He found that all possible isomers could be formed from *o*- chlorotoluene (formula I). The figures in different positions give the percentage of the corresponding isomers. By nitrating *m*- chlorotoluene, three isomers were obtained (II) and by nitrating *p*- chlorotoluene, two isomers (III):



I



II



III

From these data Wibaut calculated the ratio of the substitution rate influenced by the CH_3 and Cl groups to be:

$$CH_3 : Cl = 1 : 1.475$$

To obtain the ratio of nitration rates when the CH_3 or Cl group was present alone in a nitrated compound, Wibaut nitrated a mixture of toluene and chlorobenzene with only a small quantity of concentrated nitric acid. It was found that contrary to all expectations based on earlier observations, toluene was nitrated much faster than chlorobenzene. From this it must be concluded that the ratio of the nitration rates influenced by the two groups present together differed completely from that when only one of the groups was present in the ring.

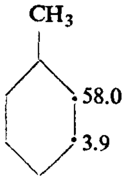
Taking that into account, Holleman [55] calculated which isomers were formed when nitrating bromotoluenes. These calculations were based on the following experimental data of his own:

(1) the ratio of the isomeric nitrotoluenes, resulting from the nitration of toluene,

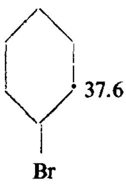
(2) the ratio of the isomeric bromonitrobenzenes, resulting from the nitration of bromobenzene,

(3) the ratio of the substitution rates influenced by the bromine and the methyl group present in the benzene ring simultaneously. This was calculated by Holleman from the ratios: Cl : Br = 1 : 0.88 (Holleman [54]) and CH_3 : Cl = 1 : 1.475 (given by Wibaut), from which he obtained CH_3 : Br = 1 : 1.3.

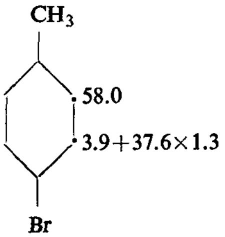
Since toluene, when nitrated, yields the ***ortho-*** and *meta-* isomers in the quantities shown in diagram IV, and bromobenzene in those shown in diagram V, for *p-* bromotoluene the quantities can be calculated. They are shown in diagram VI.



IV

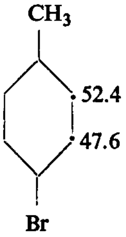


V

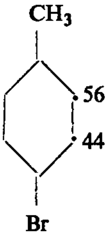


VI

The percentage is shown in diagram Via. Diagram VIb shows the values found experimentally. It can be seen that they differ only slightly from the calculated ones:



VIa

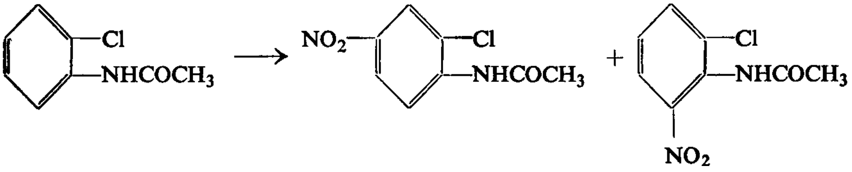


VIb

Holleman points out that such good agreement between the calculated and experimental values is not always the case. Moreover, instances are known of deviations from the substitution rules. According to Holleman [55] they may be ascribed in many instances to insufficient accuracy in the experimental data.

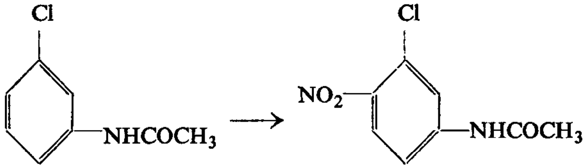
Marked deviations were observed when the nitro group was introduced into benzene derivatives with three substituents, e.g. into 2,3-dichloroacetanilide (Holleman and Hollander [52]).

Earlier Lobry de Bruyn [68] found that the nitration of *o*- and *m*- chloroacetanilides (VII) and (X) gave the products VIII, IX and XI, respectively:



(30)

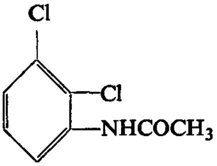
VII VIII 59% IX 39%



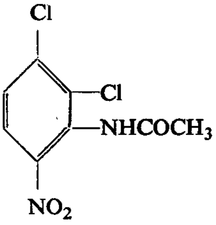
(31)

X XI 56%

From this Holleman inferred that in the nitration of dichloroacetanilide (XII) the nitro group should enter the 6- position, yet he obtained the substitution almost exclusively in 4- position (XIII)

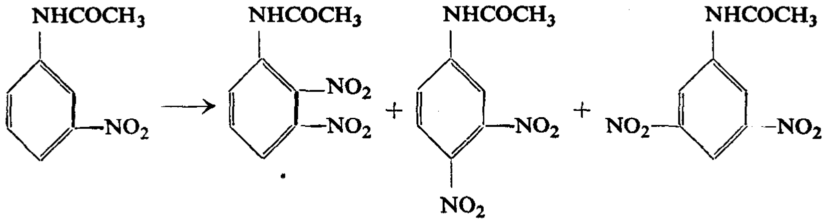


XII



XIII

Vorozhtsov [21] referred to the nitration of *m*- nitroacetanilide (XIV) as an example of inconsistency between the results obtained and predicted, viz.:

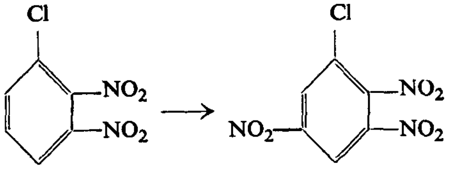


(32)

XIV XV 50% XVI 30% XVII 6%

A characteristic feature of the reaction is a complete lack of *meta* orientation to the nitro group. However, this is a rather complicated case of nitration accompanied by Bamberger rearrangement (p. 41 and Vol. III).

Holleman [47] also gave an example of an anomaly in the nitration of chloro-2,3-dinitrobenzene (XVIII). Instead of the third nitro group entering into the 4- or 6 positions as expected, which would be consistent with the orienting action of Cl and of one of the NO_2 groups, he obtained compound XIX, with the third nitro group in the 5- position:



(33)

XVIII XIX

Among more recent investigations the experiments of Hammond, Medic and Hedges [69] deserve special attention. They explain the influence of the medium on orientation when nitrating 2,5-dichloro- and 2,5-dibromo-nitrobenzene. Substitution into all three free positions takes place and derivatives *ortho-*, *meta-* and *para-* to the nitro group are formed. The yield of the *ortho-* derivative may vary from 11.0 to 35.0% while of the yield the *meta-* derivative amounts to 45.7%. The quantities of the different isomers depend on the nitrating agent. For example, in the nitration of 2,5-dichloronitrobenzene the results obtained have been shown in Table 8. The modern approach to substitution rules consists in molecular orbital calculations [89].

TABLE 8

NITRATION OF 2,5-DICHLORONITROBENZENE

Nitration at 100°C with	*% ortho-*	*% meta-*	*% para-*
Fuming sulphuric acid and sodium nitrate (6%)	14.5	53.0	32.5
96.2% sulphuric acid and sodium nitrate (6%)	21.4	50.8	27.7
96.2% sulphuric acid and sodium nitrate (15%)	35.0	45.7	19.3
Nitric acid and 60% perchloric acid (2%)	33.1	45.1	21.1

A number of authors have studied substitution with the nitro group in benzene derivatives containing *ortho-para* directing substituents, when nitric acid with acetic anhydride was used. The experiments led to the conclusion that replacement of water in the nitrating mixtures by acetic anhydride produces an increase of the ratio of *ortho-* to *para-* isomers.

This was observed in the nitration of acetanilide (Holleman, Hertogs and van der Linden [53]; Arnall [70]), propionanilide (Arnall [70]), anisol (Griffiths, Walkey and Watson [71]; Halverson and Melander [72]). The effect was much less pronounced when toluene was nitrated (Hollernan, Vermeulen and de Mooy [54]).

Recently Paul [73] nitrated chloro- and bromobenzene with a solution of nitric acid in acetic anhydride with the addition of a catalytic quantity of sulphuric acid. The result was contrary to that observed earlier: the proportion of *para-* isomer was much higher than in the instance of nitration with 90% nitric acid, e.g. acetic anhydride containing 2 M HNO_3 and 0.04 M H_2SO_4 nitrated chlorobenzene to yield o- and p-chloronitrobenzenes in the proportion of 10:90. When 90 per cent nitric acid was used alone Holleman and Bruyn [50] obtained the isomers in the proportion 30:70. Bromobenzene gave the figures 25:75 and 38:62 respectively. According to Paul, the result depends on dipole moments: (1) of substituents attached to the ring (prior to nitration) and (2) of the solvent (such as acetic anhydride).

TABLE 9

RELATIVE REACTIVITY TOWARDS NITRATION

Compound	Relative reactivity		
	ortho	***meta***	***para***
$C_6H_5.H$	1	1	1
$C_6H_5.CH_3$	43	3	55
$C_6H_5.COOC_2H_5$	0.0026	0.0079	0.0009
$C_6H_5.Cl$	0.030	0.000	0.139
$C_6H_5.Br$	0.037	0.000	0.106

Among other researches, those carried out by Ingold and his co-workers [74,75] are of considerable importance. They have determined the relative reactivities of the various *ortho, meta* and *para* positions in several substituted benzenes by competitive nitration. Relative rates of nitration were determined in experiments in which benzene and a substituted benzene derivative were nitrated together, an insufficient quantity of nitric acid being used. The relative quantities of the products: $C_6H_5NO_2$ and $X.C_6H_4.NO_2$ gave the relative rates of nitration of benzene and of $C_6H_5.X$. When these results were combined with the relative quantities of *o-*, *m-* and *p-* isomers formed, it was possible to arrive at figures representing the relative reactivity of each of the possible substitution positions (Table 9).

The results show that the methyl group is a typical *ortho-para* directing group. The relative reactivity of all three positions is greater than that of benzene. This is in accordance with the known electron-repelling effect of the methyl group.

The ester group lowers the reactivity of all three positions, but especially that of the *ortho* and *para* positions, in accordance with the known electron-attracting effect of the group.

On the basis of these experiments, the conclusion could be drawn that nitration is not only an electrophilic reaction, but that the orientation of the product is controlled by the selective activation and deactivation of various substitution positions.

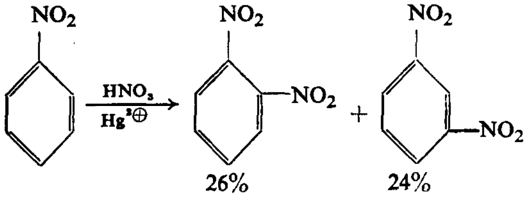
Ingold also examined the directing influence of a positively charged group $-N(CH_3)_3^+$. In nitration this group directs exclusively into the *meta* position. When, however, the positive charge is separated by $(CH_2)_n$ groups, the amount of *meta* substituted product rapidly diminishes as *n* increases. Thus:

$C_6H_5N(CH_3)_3$	100% *meta-*
$C_6H_5CH_2N(CH_3)_3$	88%
$C_6H_5CH_2N(CH_3)_3$	19%
$C_6H_5CH_2CH_2CH_2N(CH_3)_3$	5%

Similarly the ***meta-*** directing force of the nitro group is rapidly diminished when it is separated from the ring:

$C_6H_5NO_2$	93% *meta-*
$C_6H_5CH_2NO_2$	67%
$C_6H_5CH_2CH_2NO_2$	13%

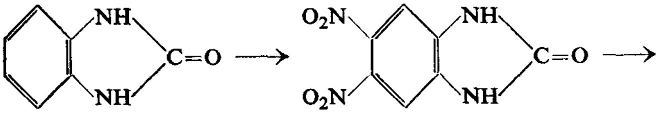
Ogata and Tsuchida [76] found in 1956 that the orienting activity of the nitro group may be partly changed in the presence of mercury ions. Thus, from nitrobenzene fairly considerable quantities of *o*- dinitrobenzene are obtained Blong with *m*- dinitrobenzene :



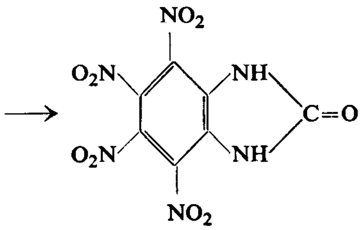
(34)

Other instances of anomalous substitution under the influence of substituents already present on the ring are also known.

Thus, for example, Kym and Ratner [77] found that benzimidazolone (XX) is readily nitrated to the 5,6-dinitro derivative (XXI). According to the experiments of Efros and Yeltsov [78] the compound obtained may undergo further nitration to the tetranitro derivative (XXII) having all nitro groups placed adjacent to one another (see also p. 552):



XX XXI



(35)

XXII

It should be borne in mind that since the advent of chromatography, it is now possible to separate and identify the constituents of complex mixtures which formerly presented some difficulty. It therefore seems desirable that some of the existing data on the composition of nitration products, particularly those obtained in earlier studies should be re-examined using up to date techniques.

Finally attention must be drawn to the fact that the orienting effect of the nitro group in nucleophile and radical reactions usually differs from that in electrophilic reactions, and instead of *meta* orientation, *ortho* or *para* orientation takes place. The corresponding observations are referred to in chapters dealing with nucleophile and radical substitutions of nitro compounds (pp. 204, 207 and 212 respectively).

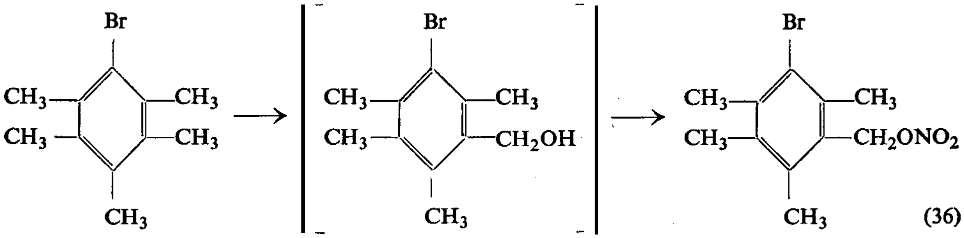
A monographic description of aromatic nitration and modern approach to substitution rules was recently given by de la Mare and Ridd [78a].

SIDE REACTIONS IN THE NITRATION PROCESS

A nitration reaction is always accompanied by side reactions which depend on such different factors as the nature of the substance being nitrated, the composition of the nitrating acid and the general nitration conditions.

Thus, oxidation reactions occurring along with a nitration reaction are particularly strong, whenever the aromatic ring is liable to such a reaction (e.g. oxidation of phenol to oxalic acid, oxidation of methyl groups in benzene homologues to hydroxymethyl and carboxyl group, oxidation of naphthalene to phthalic acid etc.).

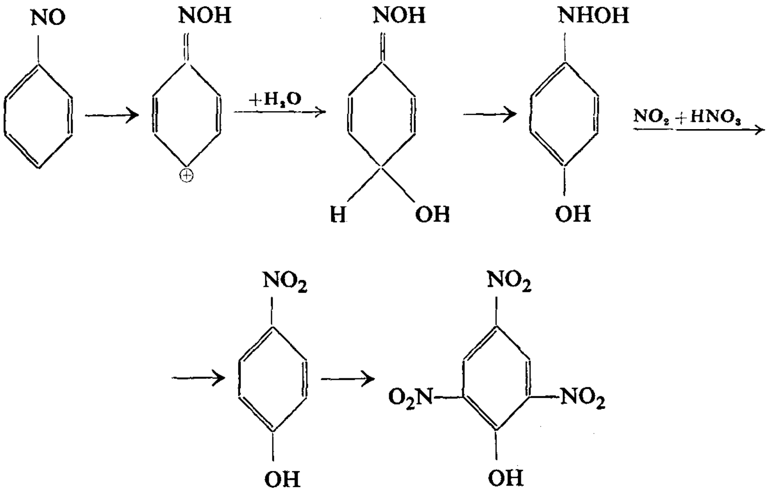
According to Nightale [79] the action on polyalkylbenzene of concentrated nitric acid (d = 1.5) leads to oxidation of an alkyl group to yield an alcohol and possibly a nitrate, e.g.:



(36)

An aromatic nucleus not yet substituted with the nitro group is also readily oxidized to form phenols. That is the reason why certain quantities of nitrophenols are formed when nitrating benzene to nitrobenzene, and certain nitrocresols when nitrating toluene. Since the phenolic group thus introduced then promotes the introduction of the nitro groups, the number of the latter may be relatively large. Thus, in the nitration of naphthalene to nitronaphthalene, 0.5-3.5% of 2,4-dinitro-α– naphthol is formed (Fierz-David and Sponagel [80]). Titov [39] found dinitrophenol and picric acid in the products resulting from the nitration of benzene, trinitro-m-cresol in the products of the nitration of toluene and trinitro-m-chlorophenol in the products of nitrating chlorobenzene.

Titov believes that phenols are formed from hydrocarbons under the influence of the nitrosyl ion, NO^+ A nitroso compound forms first, which then undergoes a rearrangement :



(37)

Another scheme of Titov [32,39] suggests that the mechanism of oxidation operates through the formation of an aryl nitrate, which is the result of attaching NO_2^+ through the oxygen atom:

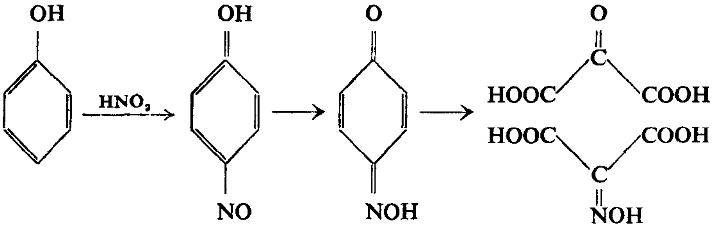
$$\mathrm{Ar{-}H + O{=}N^+{=}O \rightarrow Ar{-}O{-}N{=}O + H^+} \tag{38a}$$

$$\mathrm{Ar{-}O{-}N{=}O + H^+ \rightarrow Ar{-}OH + NO^+} \tag{38b}$$

A similar hypothesis was suggested by Bennett [35] in 1945.

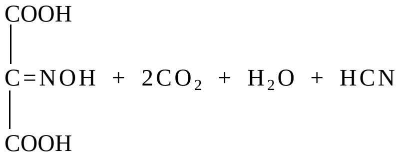
Oxidation followed by decomposition of the molecule may result in the formation of nitrated aliphatic compounds, as for example tetranitromethane and chloropicrin in the nitrations of toluene or chlorobenzene respectively.

Along with nitration processes, isomerization processes may take place which in turn may lead to various fairly complex reactions. As a result such products as CO_2, CO, NH_3 are formed. Such reactions are particularly notable in the nitration of phenols. Their mechanism has been explained by Seyevetz [81] in the following way. A phenol undergoes nitrosation under the influence of nitrous acid present in the nitrating acid. Nitrosophenol isomerizes to quinone oxime, which oxidizes at the double bonds to form mesoxalic acid and its oxime:



(39)

The oxime decomposes giving off hydrogen cyanide:



$$\begin{array}{l}\mathrm{COOH}\\ |\\ \mathrm{C{=}NOH}\\ |\\ \mathrm{COOH}\end{array} \quad + \; 2CO_2 + H_2O + HCN$$

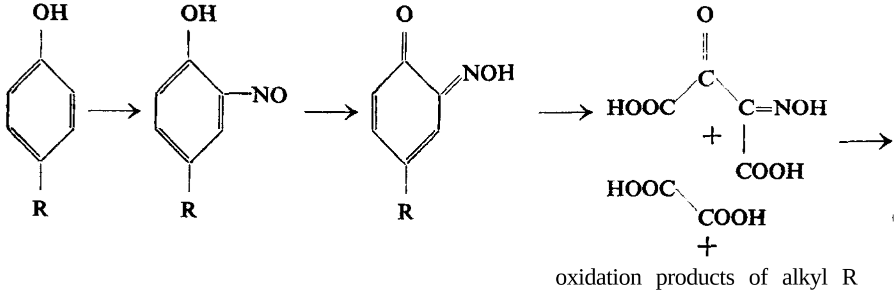
As is well known, hydrogen cyanide hydrolyses to form formic acid and ammonia, the formic acid being readily decomposed in concentrated acid with the evolution of CO:

$$HCN \rightarrow HCOOH + NH_3$$

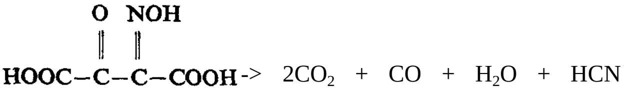
$$\downarrow H_2SO_4$$

$$H_2O + CO$$

If the *para* position on the phenol nucleus is occupied, *o*- quinone oxime is formed and the reaction proceeds in a similar way, but with the formation of oxalic acid and dioxysuccinic acid oxime, which then decomposes, giving off HCN:



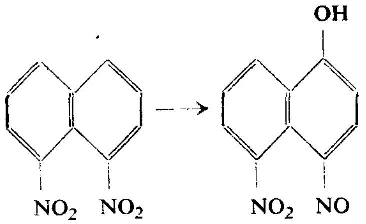
(40)



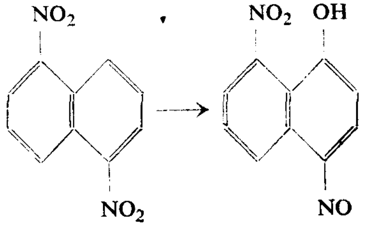
$$\mathrm{HOOC{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}\overset{\overset{\displaystyle NOH}{\|}}{C}{-}COOH} \rightarrow 2CO_2 + CO + H_2O + HCN$$

Similarly the nitration of dimethylaniline yields *p*- nitroso derivative, which undergoes similar reactions, to form HCN.

According to Seyewetz [81] not only phenols can undergo such a reaction in the nitration process. This opinion is based on Graebe's observation [82] that nitronaphthalenes isomerize to nitrosonaphthols under the influence of fuming sulphuric acid :

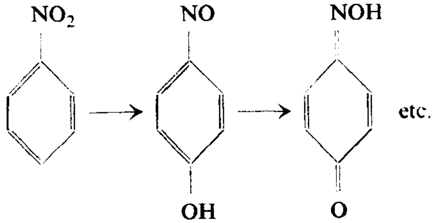


(41)



(42)

On this ground Seyewetz assumes that all nitro compounds with a free *para* or *ortho* position can isomerize in the following way:

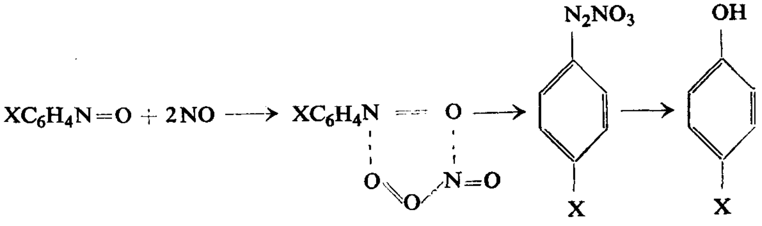


(43)

Indeed Pascal [83] found that in the waste acid from the nitration of naphthalene to dinitronaphthalene, the NH_3 content amounted to 0.001-0.002%, based on the naphthalene used for nitration.

During the nitration of aromatic compounds a certain amount of diazo compounds as by-products can also be formed. This for the first time was described by Weselsky as early as in 1875 [84] in the case of nitration of phenols with nitrogen dioxide and of nitration of aromatic hydrocarbons by Titov and Baryshnikova [85].

Titov [39] explained the reaction as the result of reaction of nitroso compounds with NO:



I II

The diazo compound (I) can next be transformed into the phenol (II) (see also [18a]).

In some experimental conditions aromatic hydrocarbons, particularly those with alkyl side chains can form dark coloured, reddish-brown by-products on nitration. They are often formed when the quantity of nitration acid is inadequate. An excess of nitrating mixture above the theoretical quantity prevents the formation of these products.

According to Battegay [86] benzene can give the dark coloured substances in the presence of nitrogen dioxide and sulphuric acid. He postulated the existence of a complex product of the general formula

$$(C_6H_6)_x(ONOSO_3H)_y(H_2SO_4)_z$$

Orlova and Romanova [87] established that toluene yields a dark coloured complex of the composition:

$$C_6H_5CH_3.2ONOSO_3H.3H_2SO_4$$

The following are factors which favour the formation of the complex: high temperature, and a high content of nitrogen oxide in the nitrating mixture. The complex can be destroyed by an excess of nitric acid when the concentration of nitrating mixture is high enough and nitrotoluenes result from this destruction. If the quantity of nitric acid is too low, the complex is liable to decomposition with foaming and formation of tarry matter, which is the product of both: nitration and oxidation.

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CHAPTER III

NITRATION AGENTS AND METHODS MORE RARELY USED

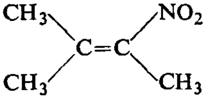
Nitration with concentrated nitric acid or its mixture with sulphuric acid has already been described and several examples will be given in those chapters dealing with the preparation of nitro compounds. Methods more rarely used which have already been applied in practice or may be in future, are described in this chapter.

They are concerned both with using less common nitrating agents and with nitrating substances which do not yield products of great practical importance (at least at present). Such, for example, is the nitration of olefins or acetylenes.

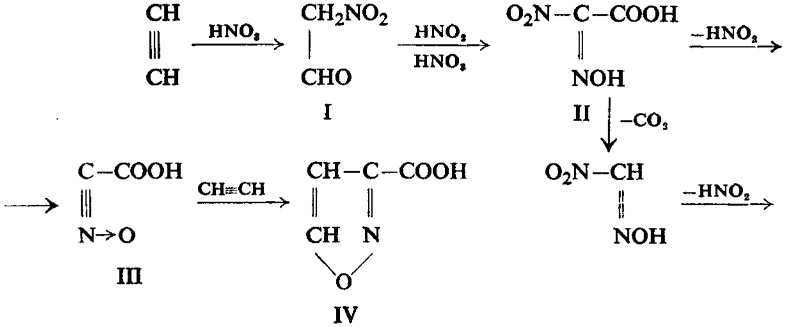
NITRATION OF ALKENES AND ALKYNES WITH CONCENTRATED NITRIC ACID

Some instances of the nitration of olefins havea heady been described in dealing with the problem of adding a molecule of nitric acid to a double bond. Besides adding concentrated HNO_3 to olefins, true nitration of olefins through electrophilic substitution can take place to yield nitroolefins. As early as in 1839 E. Simon [1], on cautious nitration of styrenes, obtained “nitrostyrene”, which, according to Alekseyev [2], proved to be *o*- nitrostyrene. Lipp [3] in 1913 also found that the action of nitrous acid on camphene resulted in the formation of ω– nitrocamphene, along with addition products. In 1878 Haitinger [4] found that the nitration of isobutylene with anhydrous nitric acid led to several products, among which was nitroisobutylene $(CH_3)C_2{=}CHNO_2$, in 10% yield.

In 1935, Michael and Carlson [5] reported that with fuming nitric acid trimethylethylene gave crystalline 3-nitro-2-methyl-2-butylene in 20% yield:



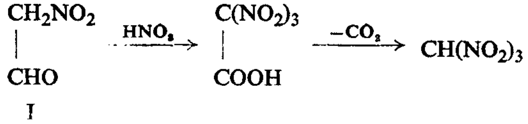
More recently Petrov and Bulygina [6] investigated in detail the conditions under which several olefins can be nitrated. They found that good yields could be obtained with concentrated nitric acid reacted with olefins at *ca.* 60°C, and with less concentrated at a slightly higher temperature, i.e. 80-90°C. Nitration was also possible with 20% nitric acid, containing nitric dioxide when reacted at 70°C. Probably, according to Titov’s theory (p. 88, 118) nitric dioxide is the nitrating agent, while the role of nitric acid is to regenerate the NO_2 radical. The course of the reaction between acetylene and nitric acid is much more complicated. By passing acetylene through fuming nitric acid at ordinary temperature in 1901 Baschieri [7] and in 1902 Mascarelli and Testoni [8] obtained, besides nitroform, $CH(NO_2)_3$, two other crystalline compounds: an acid $C_4H_3O_3N$ and an explosive, $C_4H_2O_7H_6$ [9]. A thorough investigation of these substances was carried out by Quilico and Freri in numerous papers published between 1929 and 1932 [10,11]. They recognized that these compounds were all isoxazole derivatives (II) and they established their structure and mechanism of formation. The following is the scheme drawn up by Quilico [10] and Quilico and Simonetta [12] in 1946. It is closely related to the classic interpretation by Wieland [13,14] of the formation of fulminic acid from ethanol, nitric acid and mercuric nitrate (Vol. III):



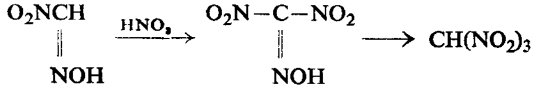
(1)

Here, isoxazole-3-carboxylic acid (IV)-the main product of the reaction-is formed from nitrile oxide (III) on adding acetylene to it.

The formation of nitroform is presented by Quilico as follows:



$$\underset{\text{I}}{\begin{array}{c}CH_2NO_2\\|\\CHO\end{array}} \xrightarrow{HNO_3} \begin{array}{c}C(NO_2)_3\\|\\COOH\end{array} \xrightarrow{-CO_2} CH(NO_2)_3 \qquad (2)$$

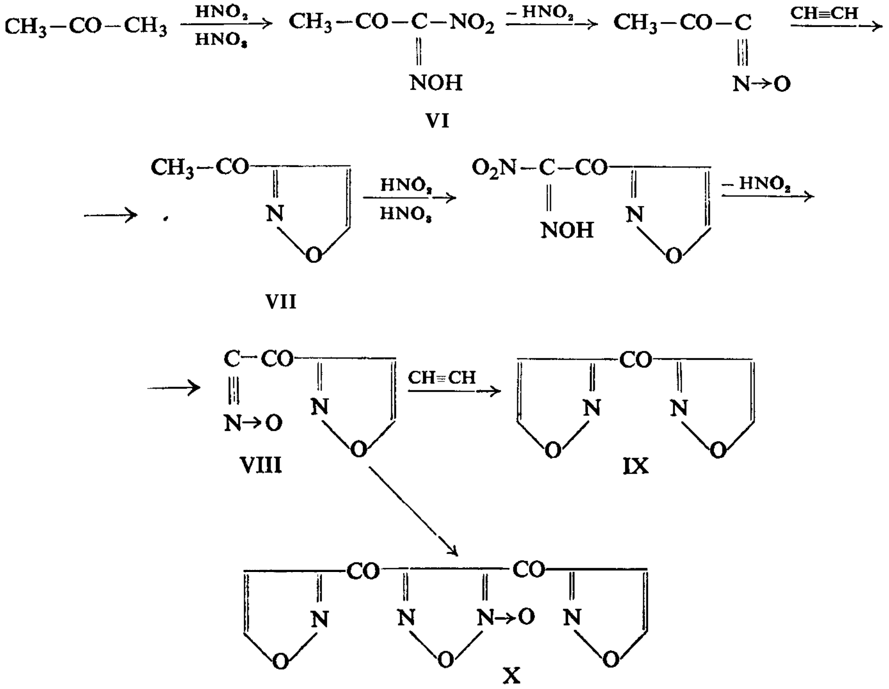


$$\begin{array}{c}O_2NCH\\\|\\NOH\end{array} \xrightarrow{HNO_3} \begin{array}{c}O_2N-C-NO_2\\\|\\NOH\end{array} \longrightarrow CH(NO_2)_3 \qquad (3)$$

From compound III the loss of CO_2 could lead directly to the formation of fulminic acid (V) which in Wieland's scheme would take its origin from (II) through loss of CO_2 and HNO_2.

In the presence of mercuric nitrate, a high yield of tetranitromethane is obtained through the intermediate formation of nitroform. This reaction is dealt with on p. 594 (manufacture of tetranitromethane).

Experimental support for this mode of formation of the isoxazole derivative (IV) was found in 1946 by Quilico and Simonetta [12]. They obtained V from acetylene and the ethyl ester of II reacted at room temperature in nitric acid solution. 3,3-Diisoxazolylketone (IX) is formed in a similar way from acetylene, acetone and nitric acid, according to Quilico and Freri [10] and Quilico and Simonetta [12]:



(4)

Acetyl methyl nitrolic acid (VI) is the well known product of the reaction of HNO_3 on acetone. After loosing HNO_2 it condenses with acetylene to yield 3-acetylisoxazole (VII). Through the same sequence of reactions it eventually forms IX. Dimerization of the nitrile oxide (VIII) yields diisoxazoylfuroxane (X).

All the isoxazole derivatives formed from acetylene belong to the 3-mono-substituted series (Quilico [12a]).

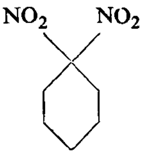
On the formation of furoxane derivatives see also Wieland's work on the action of N_2O_3 on unsaturated compounds p. 101.

NITRATION WITH DILUTE NITRIC ACID

Konovalov [15] nitrated aliphatic hydrocarbons in sealed tubes at 120-130°C, using dilute nitric acid of concentration 6.5-19%. From normal hydrocarbons he obtained secondary nitro compounds in yields varying from 40% (2-nitrohexane from hexane) to 49-50% (2-nitrooctane from octane). Aromatic hydrocarbons with an aliphatic substituted group when nitrated under the same conditions gave nitro derivatives with a nitro group in the side chain. For example, ethylbenzene, when nitrated with 12.5% nitric acid at 105-108°C, gives phenylnitroethane in 44% yield. The optimum yield is obtained with 13% acid.

Cycle-polymethylenic hydrocarbons can also be nitrated with dilute nitric acid (e.g. Wichterle [15a]).

Grundman and Haldenwanger [70] nitrated cyclohexane with nitric acid (34% HNO_3) at 122°C under 4 atm pressure. Nitrocyclohexane and gem-dinitrocyclohexane (I) resulted (m. p. 218°C).



I

Aromatic hydrocarbons, e.g. benzene, are not nitrated with dilute nitric acid.

On the contrary, olefins can readily be nitrated to nitroolefins by means of 12.5% nitric acid as shown by Konovalov [15].

The tertiary carbon (>CH) is nitrated most readily, the secondary one ($-CH_2$) with some difficulty, and the primary one ($-CH_3$) with greater difficulty. Oxidation products, as for example acids, are formed along with nitro compounds.

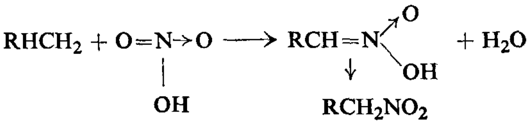
These classical studies were continued by Markovnikov [16] in 1898 and Nametkin [17] in 1908. The principal conclusions of Nametkin are:

(1) Within certain limits the nitration yield does not depend on the concentration of nitric acid, but on the quantity of the acid; for example, the same yields are obtained with 47.5% nitric acid (sp. gr. 1.3) as with 13.5% nitric acid (sp. gr. 1.075).

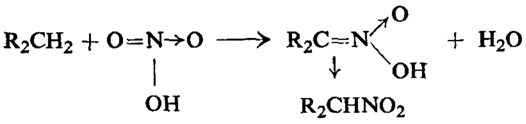
(2) The nitration rate depends on temperature, pressure and the concentration of the acid. The higher the temperature and pressure and the stronger the acid, the higher the reaction rate.

(3) The quantity of nitric acid used for nitration affects the direction of the reaction. A long run treating with an excess of nitric acid at a high temperature enhances the formation of oxidation products.

Nametkin presents the nitration mechanism as follows:



$$\mathrm{RHCH_2} + \mathrm{O{=}\underset{\displaystyle |\atop \displaystyle OH}{N}{\to}O} \longrightarrow \underset{\displaystyle \downarrow\atop \displaystyle \mathrm{RCH_2NO_2}}{\mathrm{RCH{=}N}}\begin{smallmatrix}\nearrow \mathrm{O}\\ \searrow \mathrm{OH}\end{smallmatrix} + \mathrm{H_2O} \qquad (5)$$



$$\mathrm{R_2CH_2} + \mathrm{O{=}\underset{\displaystyle |\atop \displaystyle OH}{N}{\to}O} \longrightarrow \underset{\displaystyle \downarrow\atop \displaystyle \mathrm{R_2CHNO_2}}{\mathrm{R_2C{=}N}}\begin{smallmatrix}\nearrow \mathrm{O}\\ \searrow \mathrm{OH}\end{smallmatrix} + \mathrm{H_2O} \qquad (6)$$

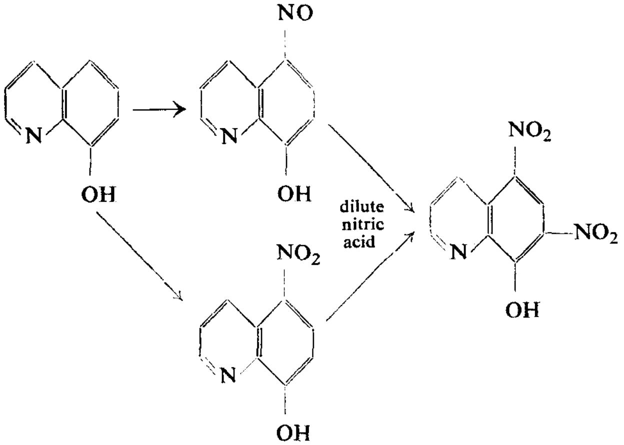
The author believes the labile forms with the -C=N bond are obtained as intermediates and subsequently they isomerize to form nitro compounds.

Phenols can be nitrated with very dilute nitric acid. Thus, Cumming, Hopper and Wheeler [18] reported that phenol can be converted into nitrophenol by

3% nitric acid, while 4% acid converts methyl- and ethyl-acetanilide into the corresponding dinitro derivatives. In 1958 T. Urbanski [19] found that 8-hydroxyquinoline can be converted to the 5,7-dinitro compound by boiling with 8% nitric acid and more recently he and Kutkiewicz [20] have found that the same result can be obtained by prolonged boiling with nitric acid of concentrations as low as 0.5%. However, the reaction occurred only after a certain induction period which ended by evolution of nitrous fumes. When $NaNO_2$ was added to the nitric acid, the reaction started almost immediately. The nitration of 8-hydroxy-5-nitrosoquinoline leads readily to formation of the same nitration product without the induction period.

The introduction of the 5-nitro group can easily be explained by nitrosation of 8-hydroxyquinoline in position 5 and subsequent oxidation of the nitroso compound. No similar explanation can be given with regard to the mechanism of the introduction of the second nitro group, in position 7, as no nitrosation of nitrophenols is known and the formation of "8-hydroxy-5-nitro-7-nitrosoquinoline", does not seem to be possible. The formation of "5,7-dimtroso-8-hydroxyquinoline" as an intermediate is also improbable because no instance of the introduction of two nitroso groups into a monophenol is known. Thus nitration most likely procedes through the formation of the 5-nitroso derivative only.

It has also been found that 5-nitro-8-hydroxyquinoline can be nitrated with 1% nitric acid to yield 5,7-dinitro-8-hydroxyquinoline. This excludes nitrosation as an intermediate step for the reason given above:



(7)

The introduction of the nitro group into position 7 would support the view already expressed (p. 48) that the NO_2^+ ion is not the only nitrating agent.

Slavinskaya [21] in 1957, found that phenol can be nitrated to *o*-, *p*- and 2,4-dinitrophenol using nitric acid dissolved in ethyl nitrate at a concentration as low as 0.5% HNO_3. Phenetole and naphthalene can also be nitrated with this solution to yield mononitro products. The presence of NO_2 was essential for successful nitration at such a low concentration of HNO_3.

ELECTROLYTIC NITRATION

Electrolytic nitration was first proposed by Triller [22] in 1897. This author pointed out that with nitric acid of concentration 52% HNO_3 at 80°C α– nitronaphthalene free from dinitronaphthalene can be obtained at the anode. With nitric acid of concentration 65% HNO_3 dinitronaphthalene is obtained. Fichter and Plüss [23] checked the Triller's patent in 1931 by carrying out simultaneous experiments with ordinary and electrolytic nitration. They found that the electrolytic method did indeed provide higher yields of α– nitronaphthalene. But the authors believed this was due not to a higher concentration of nitric acid (or more exactly of NO_3^- ions) at the anode, but rather to a rise of temperature over this area. Contrary to this view, Calhane and Wilson [24] came to the conclusion that it was the formation of a layer of high concentration around the anode that accounted for the increase in the yield.

Kirk and Brandt [25] nitrated toluene with a mixture of nitric and sulphuric acids both by the usual method and by the simultaneous use of the electrolytic method and found that with the latter technique higher yields could be obtained. Atanasiu and Belcot [26,27] treated aromatic hydrocarbons with a much dilute nitric acid (at a concentration insufficient for nitration) and, due to the electrolysis, which they carried out simultaneously, they succeeded in obtaining nitration in the anode area. In studying the reaction they observed particularly vigorous oxidation processes.

Edwards [28] carried out experiments in 1950 comparing the nitration of toluene under ordinary conditions with that combined with simultaneous electrolysis and found that higher yields of nitro compounds resulted when electrolysis was applied.

NITRATION WITH NITRIC ACID VAPOUR

The nitration of aliphatic hydrocarbons may be accomplished in the vapour phase, at 410-430°C, using nitric acid vapour. A number of papers describing this method of nitration were published by Hass and co-workers [29] between 1936 and 1940.

Under the influence of a high temperature during the reaction the hydrocarbon chain is split off to give shorter ones and such compounds as nitromethane and nitroethane are formed. For example, the authors obtained the following products in the nitration of n-pentane at 400°C:

nitromethane	1.1%
nitroethane	7.2%
1-nitropropane	13.8%
1-nitrobutane	12.5%
1-nitropentane	20.6%
2-nitropentane	20.8%
3-nitropentane	23.0%

Higher temperature enhances the formation of nitroparaffins with shorter chains.

This is seen clearly in Table 10, which shows the results of nitration of butane at various temperatures.

TABLE 10

COMPOSITION OF THE PRODUCTS OF THE BUTANE NITRATION AT VARIOUS TEMPERATURES

Temperature °C	Nitromethane %	Nitroethane %	1-Nitropropane %	2-Nitropropane %	1-Nitrobutaue %
395	2.1	12.7	4.9	4.9	30.5
393	6.0	19.0	7.0	41.0	27.0
445	5.9	18.2	6.5	37.0	31.8
450	9.0	25.0	7.0	28.0	31.0

Apart from this, at higher temperatures the amount of primary nitropropane increases as compared with the secondary derivative.

Similar experiments have been carried out by Grundmann [30]. He found 160-180°C to be the best temperature for the reaction. The products of nitration of long-chain paraffins were mono- and polynitro compounds.

Thus n-dodecane was nitrated at 180-190°C to yield the products shown in Table 11.

TABLE 11

NITRATION OF n-DODECANE

Mol. ratio n-dodecane:HNO_3	Products			
	Unreacted n-dodecane	Mononitro dodecane	Polynitro dodecane	Fatty acids
2:1	58	36	5	1
1:1	43	40	15	2
1:2	33	25	38	4
1:4	24	4	47	25

Hass and Alexander [31] and G. B. Bachman, Hass and Addison [32] described the positive influence of oxygen on the yield in gas-phase nitration. Bachman and his co-workers also discovered that the addition of halogens had a positive effect on the yield of the nitration.

Hass and Shechter [33] have formulated thirteen general rules governing the vapour-phase nitration of paraffins (and cycloparaffins). Here they are in a summarized form :

(1) Polynitro compounds can probably be formed only from paraffins of fairly high molecular weight.

(2) Any hydrogen atom in the hydrocarbon is capable of replacement by a nitro group, and the ease of replacement is: tertiary > secondary > primary group. As the temperature rises, however, the ease of replacement tends to become equal.

(3) Any alkyl group present in the paraffin can be replaced by a nitro group, i.e. chain fission takes place. Thus, isopentane yields nine nitroparaffins. The fission reaction increases as the temperature rises.

(4) Oxidation always accompanies nitration, resulting in the formation of nitro compounds and a mixture of acids, aldehydes, ketones, alcohols, nitrites, nitroso compounds, nitroolefins, polymers, carbon monoxide and carbon dioxide. Catalysts such as copper, iron, platinum oxide, etc., accelerate oxidation rather than nitration.

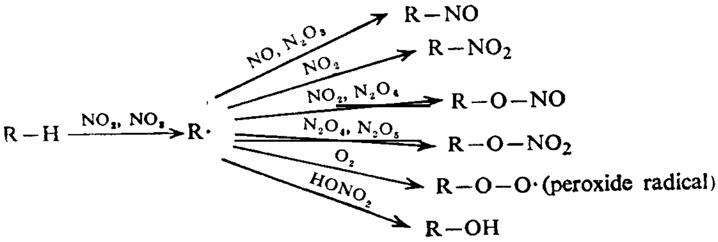
When considering the mechanism of nitration of paraffin hydrocarbons with nitric acid Titov [34] assumed in his papers dating from 1937 to 1948 that nitrogen oxides, NO_2 and NO, were the nitrating agents for aliphatic chains. The role of nitric acid would consist in regeneration of nitrogen oxide by oxidation of the lower nitrogen oxides formed during the reaction. Moreover, Titov assumed the nitration reaction to be a free radical one. In the first stage, a hydrocarbon is converted into a free radical under the influence of a nitrating agent:

$$RH + NO_2 \rightarrow R. + HNO_2 \tag{8}$$

Subsequently, a free radical reacts with nitrogen oxides, also in the form of free radicals to form a nitro compound, nitroso compound or nitrite:

$$\begin{gathered} R. + .N{=}O \rightarrow \underset{\text{Nitroso compound}}{RNO} \\ R. + .NO_2 \rightarrow \underset{\text{Nitro compound}}{RNO_2} \\ R.+ .ONO \rightarrow \underset{\text{Nitrite}}{RONO} \end{gathered} \tag{9}$$

Since Titov believed that the NO_3 radical might also be present in the vapour phase, he gave the following overall scheme for the reaction of NO_2 and NO_3 with a hydrocarbon RH, and for the reactions of NO, NO_2, N_2O_4, N_2O_3, N_2O_5, HNO_3 and O_2 with a free radical R:



It can be seen that nitrites and nitrates, peroxides and alcohols are formed along with nitroso and nitro compounds. The nitroso compounds (secondary) isomerize to give oximes. The nitrites give lower aldehydes, ketones and lower radicals which form lower nitro compounds. The alcohols oxidize to aldehydes and ketones, and the latter to acids, which may yield esters with alcohols. The nitrates may give off a HNO_3 molecule to form olefins, and the latter may give dinitro compounds, etc. The nitroso compound formed may subsequently give a dinitro derivative (Ponzio [35]); for example:

$$C_6H_5CH_2NO \rightarrow C_6H_5CH{=}NOH \xrightarrow{N_2O_4} C_6H_5OH(NO_2)_2 \qquad (10)$$

Titov's experiments have shown that the nitration of alkyl-aromatics may lead not only to formation of ω– nitro compounds, but of ω– dinitro compounds as well.

McCleary and Degering [36] present a different mechanism for the nitration of paraffins with the nitric acid vapour, although like Titov they also assume the formation of free radicals:

$$RH + (\text{oxidizing agent}) \rightarrow R. + .H$$

$$R. + HONO_2 \rightarrow RNO_2 + .OH$$

$$RH + .OH \rightarrow R. + H_2O \text{ etc.} \qquad (11)$$

Yet another mechanism (11) with free radicals taking part has been suggested by Boord [37]:

$$HONO_2 \rightarrow HO. + .NO_2$$

$$RH + HO. \rightarrow R. + H_2O$$

$$R. + \text{-}NO_2 \rightarrow RNO_2 \qquad (12)$$

By analogy with the chlorination mechanism, in which we assume a chain reaction, Boord also suggests another chain mechanism with repeating links. He assumes that nitric acid undergoes decomposition at a high temperature to form nitric anhydride :

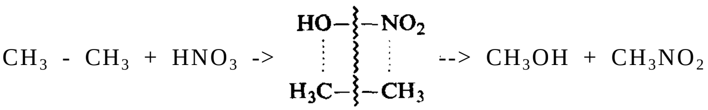
$$2HONO_2 \rightarrow NO_2\text{-}O\text{-}NO_2 + H_2O$$

$$NO_2\text{-}O\text{-}NO_2 \rightarrow .NO_2 + .ONO_2$$

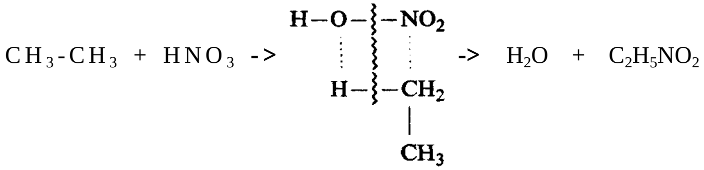
$$RH + .ONO_2 \rightarrow R. + HONO_2$$

$$R. + NO_2\text{-}O\text{-}NO_2 \rightarrow RNO2 + .ONO2 \qquad (13)$$

However, Hass and Riley [38] assume that the nitration of aliphatic hydrocarbons proceeds through the formation of addition products which subsequently undergo a breakdown which may (in the case where a certain kind of the addition product is formed) involve the rupture of C-C bonds:



$$CH_3 - CH_3 + HNO_3 \rightarrow \begin{matrix} HO - & NO_2 \\ H_3C - & CH_3 \end{matrix} \dashrightarrow CH_3OH + CH_3NO_2 \qquad (14)$$



$$CH_3\text{-}CH_3 + HNO_3 \rightarrow \begin{array}{l} H-O-NO_2 \\ H-CH_2 \\ \quad\;\; | \\ \quad\; CH_3 \end{array} \rightarrow H_2O + C_2H_5NO_2 \qquad (15)$$

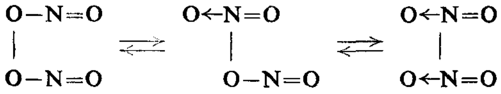
The nitration theory, which assumes that a free radical takes part, seems to be more probable than the addition theory and is in better agreement with the experimental data. An interesting piece of evidence for the participation of free radicals in the reaction was given by McCleary and Degering [36], who obtained a mixture of nitroethane and ethyl nitrate when nitrating tetraethyl lead with nitric acid in an atmosphere of CO_2, at 150°C. It is probable that the reaction proceeds as follows:

$$\begin{array}{c} (C_2H_5)_4Pb \rightarrow Pb + 4C_2H_5. \\ C_2H_5. + HONO_2 \rightarrow C_2H_5NO_2 + OH. \\ C_2H_5. + OH. \rightarrow C_2H_5OH \\ C_2H_5OH + HONO_2 \rightarrow C_2H_5ONO_2 + H_2O \end{array} \qquad (16)$$

NITROGEN DIOXIDE

As is well known, nitrogen dioxide exists as the dimer N_2O_4, at low temperatures, and as the monomer, NO_2, at high temperatures. Its boiling point is 21°C, and its density at 0°C $d = 1.49$ g/cm^3.

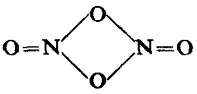
On the basis of the observation that the addition of nitrogen dioxide to compounds with double bonds yields not only nitro compounds, but nitrous acid esters as well (p. 99). Schaarschmidt [38a,39,40] expressed the view that nitrogen dioxide exists in three forms which are in equilibrium. This may be represented in modern symbols in the following way:



(a) (b) (c)

the equilibrium being shifted towards the (c) form.

More recent thermochemical studies (Giauque and Kemp [41]), and spectral work (Millen [42]), as well as determination of the dielectric constant (Addison and Lewis [43]), indicate that formula (b) seems to be the most probable. Formula (d) is possible, but less probable.



(d)

The stereo-structure, including bond distances and bond angles of vapour phase NO_2 (Fig. 17), was investigated by Maxwell and Mosley [44] in 1940 by electron diffraction and the stereo-structure of solid N_2O_4 (Fig. 18) was determined in 1949 by X-ray analysis by Broadley and J. M. Robertson [45].

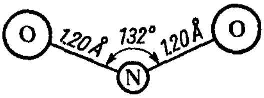


FIG. 17. Bond distances and angles of nitrogen dioxide (Maxwell and Mosley [44]).

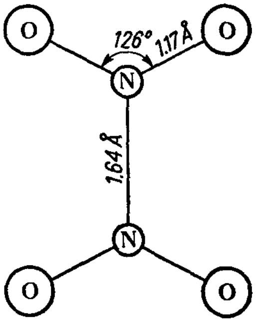


FIG. 18. Bond distances and angles of dinitrogen tetroxide (Broadley and Robertson [45]).

The ability of N_2O_4 to react in various ways suggested that the substance can also undergo heterogeneous dissociation in various ways. Three modes of ionization of N_2O_4 in dilute solutions are known. In water NO_2^- and NO_3^- are produced, in strong acids, such as sulphuric acid, NO^+ and NO_2^+ are formed, and under other conditions intermediate ionization leads to formation of NO^+ and NO_3^-. Clusius and Vecchi [46] found, when dissolving tetramethylammonium nitrate $(CH_3)_4N^+ \, {}^{15}NO_3^-$ labelled with ^{15}N isotope in N_2O_4, that complete exchange of the ^{15}N isotope took place according to the equation:

$$N_2O_4 \leftrightarrow NO^+ + NO_3^- \qquad (17)$$

N_2O_4 in nitric acid solutions dissociated in the same way, as Goulden and Millen [47] found, when examining Raman spectra of such solutions.

Millen and Watson [48] confirmed this observation by examining the infra-red spectra of the same solutions. Very recently Goulden, Lee and Millen [48a] examined the electrical conductances of solutions of dinitrogen tetroxide in nitric acid and came to the conclusion that N_2O_4 is subjected to nearly complete ionization according to eqn. (17).

There is no evidence that the heterolytic dissociation may have the form (18) which was accepted in earlier days:

$$N_2O_4 \leftrightarrow NO_2^+ + NO_2^- \qquad (18)$$

However, a homolytic dissociation into free radicals NO_2 is possible:

$$N_2O_4 \quad \leftrightarrow \quad 2NO_2 \tag{19}$$

This has been confirmed by experiments on the addition of N_2O_4 to asymmetrically substituted olefins (Shechter and Conrad [49]). The most recent review of the chemistry of nitrogen dioxide is that of Gray and Yoffe [50] published in 1955.

The experiments of Falecki, Mint, Slebodzinski and T. Urbanski [185a] mentioned below also suggest that under the action of γ– radiation dinitrogen tetroxide is split mainly into ions NO_2^+ or (even more likely) into free radicals $.NO_2$ (according to eqn. 19).

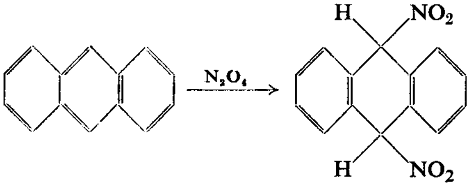
NITRATION WITH NITROGEN DIOXIDE ALONE

Aromatic compounds

The nitration of aromatic compounds with nitrogen dioxide was mentioned by Hasenbach [51] as early as 1871. He observed that when treating benzene with N_2O_4 ($N_2O_4 \leftrightarrow 2NO_2$) at room temperature for 7 days, nitrobenzene was formed along with oxalic acid. Leeds [52] also found picric acid in the reaction products. On treating toluene with N_2O_4 he obtained nitro derivatives of phenols and benzoic acid apart from nitrotoluenes. Naphthalene was nitrated similarly to give nitro and hydroxynitro derivatives.

When nitrating anthracene with N_2O_4 at a temperature of 10-15°C Liebermann and Lindermann [53] obtained nitro derivatives of this hydrocarbon.

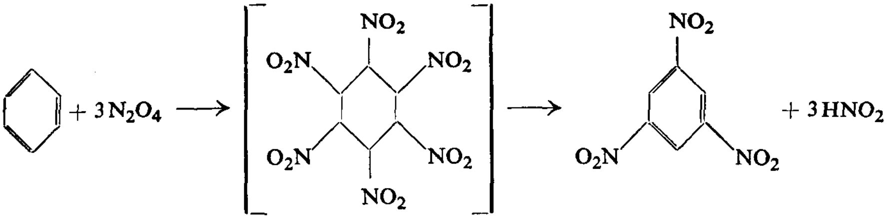
Meisenheimer’s observation [54], in 1904, that anthracene combined with nitrogen dioxide to form meso-dihydrodinitroanthracene, was of special importance :



(20)

It inspired Wieland [55] in 1921 to investigate the possibility of nitrating aromatic compounds with nitrogen dioxide.

When studying the action of nitrogen dioxide on benzene at 80°C Wieland found 1,3,5-trinitrobenzene and picric acid were present along with oxidation products (oxalic acid, CO_2). Nitrobenzene was not obtained in the reaction and a large quantity of benzene remained unconverted. Wieland tried to explain this by assuming that in the first stage of the reaction six molecules of NO_2 combine with benzene just as chlorine or bromine do under the influence of light. The hexanitrocyclohexane thus formed gives off three HNO_2 molecules to form 1,3,5-trinitrobenzene :



(21)

As a result of nitrating phenol by means of N_2O_4 at a low temperature, a mixture of *o*- and *p*- nitrophenol was obtained.

The ability of nitrogen dioxide to form addition products with aromatic compounds has been proved with polycycloketones. Thus, Lukin and Dashevskaya [56] found that benzanthrone formed an addition product with two NO_2 molecules. There is no doubt that the presence of carbonyl groups affects the ability to form addition products just as it does in the addition of nitric acid (pp. 54-55).

It has been found recently that nitrogen dioxide forms addition products with compounds having an ether bond in the molecule (i.e. oxygen, which readily yields oxonium compounds) and for example, with ethyl ether, $N_2O_4.2(C_2H_5)_2O$ (m. p. -74.8°C), and with dioxane, tetrahydrofuran and tetrahydropyran (Rubin, Sisler and Shechter [57]).

Battegay and Kern [58] treated methylaniline with nitrogen dioxide and obtained *p*- nitro-N-nitrosomethylaniline or, with nitrogen dioxide in excess, 2,4-dinitromethylaniline. From dimethylaniline *p*- nitroso- and *p*- nitrodimethylaniline have been obtained, and with an excess of nitrogen dioxide, 2,4-dinitrodimethylaniline. Similar results have been obtained by Schaarschmidt, Balcerkiewicz and Gante [39].

Extensive studies on the nitration of aromatic compounds with nitrogen dioxide have been carried out by Shorygin and Topchiyev [59] and later, since 1939, by Topchiyev [60]. Here are the most important results of their investigations.

(1) Benzene and naphthalene are nitrated with nitrogen dioxide at 18-20°C to yield mononitro derivatives. At 60°C polynitro compounds are obtained as well. Ultra-violet irradiation does not affect the nitration yield.

(2) Nitration of aromatic hydrocarbons with a side chain gives mononitro compounds with the nitro group attached either to the ring or to the side chain, with a predominance of the former. For example, from toluene at temperature 14-15°C, 46% of nitrotoluenes and 9% of phenylnitromethane were obtained. The nitration yield seems to increase under the influence of ultra-violet radiation. For example, from *m*- xylene, 81% of nitro compounds were obtained without applying irradiation, and 99% when using it.

(3) Phenols are nitrated readily to di- and tri-nitro derivatives.

(4) The nitration of amines results partly in the formation of ring nitrated compounds and partly in formation of nitro derivatives of phenols. For example from aniline small quantities of *p*- nitroaniline were obtained along with 2,4-dinitrophenol as the principal product.

(5) Heterocyclic compounds are more difficult to nitrate. For example, from quinoline 11% of mononitroquinoline was obtained at 95-100°C, while at 155-160°C 10-12% of dinitroquinoline could be obtained; from pyridine 6% of nitropyridine was obtained at 115-120°C.

Aqueous solution of N_2O_4 has both a nitrating and a nitrosating action.

N-nitrosation and simultaneous C-nitration of secondary aromatic amines by aqueous solution of N_2O_4 has been studied by Stoermer [61] and Ruff and Stein [62]. Thus N-methylaniline yielded N-methyl-n-nitroso-p-nitroaniline.

Paraffin hydrocarbons

T. Urbanski and Slori [63] in a series of experiments described in preliminary notes between 1936 and 1938 found that normal paraffin hydrocarbons from ethane to n-nonane can be nitrated with nitrogen dioxide in the gaseous phase to give good yields. The authors have nitrated normal hydrocarbons using nitrogen dioxide in large excess. They found the temperature necessary for obtaining the best yield was the lower, the longer the hydrocarbon chain. At the same time they observed that the reaction yields rise with the chain length. The principal yields obtained by the above mentioned authors are shown below in Table 12.

TABLE 12

RELATION BETWEEN THE CHAIN LENGTH OF PARAFFIN HYDROCARBONS AND THE YIELD OF NITRATION PRODUCT

Hydrocarbon	Temperature (minimum), °C	Yield up to % (by weight)
Ethane	250	10
Propane	220	20
n-Butane	200	25
n-Pentane	200	30
n-Hexane	200	35
n-Heptane	200	40
n-Octane	200	40
n-Nonane	180	60

Apart from nitration products some oxidation products such as aldehydes and fatty acids were also obtained. Nitrolic acids were also present in the products.

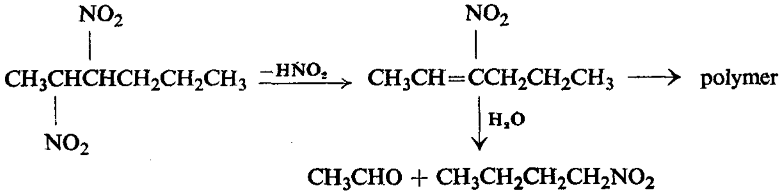
Detailed experiments on nitration of n-hexane with nitrogen dioxide in the vapour phase were recently carried out by Slebodzinski, T. Urbanski *et al.* [64]. They nitrated n-hexane using the molar ratio

$$\frac{\text{hydrocarbon}}{NO_2} = \frac{1}{10} \text{ to } \frac{5}{1}$$

At 300°C the yield of a mixture of nitro compounds was 24-42% by weight. 27-39% of this mixture was composed of lower nitroparaffins (nitromethane, nitroethane, l- and 2-nitropropane). Nitrohexanes (mainly 2- and 3-nitrohexanes with a small proportion of 1-nitrohexane) formed 50-60% by weight. This result would confirm the view expressed by Hass [33] and Asinger [65] on the statistical distribution of NO_2 groups in the course of nitration of long chain paraffins. A large proportion (ca. 10%) of aldehydes mainly formaldehyde and acetaldehyde and fatty acids was also found among the volatile products.

A non-volatile oily fraction which did not distil under 10 mm Hg was also formed with a yield of 10-22% by weight. This is a mixture difficult to identify, composed of various compounds of a relatively high content of nitrogen suggesting the presence of dinitroparaffins.

The authors found that dinitro compounds are readily decomposed at high temperature. This would probably proceed through nitro-olefin formation according to the scheme:



$$CH_3\underset{NO_2}{CH}\overset{NO_2}{CH}CH_2CH_2CH_3 \xrightarrow{-HNO_2} CH_3CH{=}\overset{NO_2}{C}CH_2CH_2CH_3 \longrightarrow \text{polymer}$$

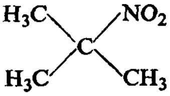
$$CH_3CH{=}\overset{NO_2}{C}CH_2CH_2CH_3 \xrightarrow{H_2O} CH_3CHO + CH_3CH_2CH_2CH_2NO_2$$

Nitrolefin- would polymerize or be hydrolysed to yield an aldehyde and lower nitroparaffin.

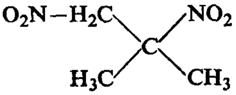
When lower reaction temperature (e.g. 220-230°) was used, the total yield of nitro compounds was lower: ca. 20%, but the proportion of primary nitrohexane was higher. Also the yield of the non-volatile fraction with a higher nitrogen content was higher (ca. 30%).

In 1949, Titov [34] obtained a larger proportion of secondary nitro compounds along with a smaller quantity of a primary nitro compound when nitrating n-pentane at 260-270°C and at a molar ratio N_2O_4:n-C_5H_{12} = 1:3.

In the nitration of a hydrocarbon having a >CH group, first of all this group was nitrated to form a tertiary nitro compound. Thus, for example, according to T. Urbanski and Wolnicki [66], isobutane gave tertiary nitroisobutane.



A quantity of the dinitro compound (primary-tertiary) was also obtained:



The same products of nitration of isobutane have been reported by Levy [66a].

According to Bachman, Hass and Addison [32] the addition of halogens (chlorine, bromine) to the reacting system hydrocarbon-nitrogen dioxide increases the yield of the nitro compounds.

Hass, Dorsky and Hodge [67] nitrated paraffins with nitrogen dioxide under pressure. They were able to nitrate methane to nitromethane.

Levy and Rose [68] reported that nitration of propane with nitrogen dioxide at 360°C under 10 atm gave a 75-80% yield of nitroparaffins. The mixture of products was composed of 20-25% nitromethane, 5-10% nitroethane, 45-55% 2-nitropropane, 20% 1-nitropropane and 1% 2,2-dinitropropane. Geiseler [69] nitrated paraffins under 4 atm at 190°C. Grundman and Haldenwanger [70] nitrated cyclohexane with nitrogen dioxide at 120-125°C under 4-5 atm and obtained both mono- and di-nitroproducts.

Titov [71] in 1948, carried out an extensive study on the nitration of aliphatic side-chain of aryl-aliphatic hydrocarbons with nitrogen dioxide. He found that, for example, the nitration of toluene may result in the formation of phenyldinitromethane along with phenylnitromethane. Low temperature facilitates the formation of the former (Table 13).

TABLE 13

RESULTS OF NITRATION OF 1000 ml OF TOLUENE WITH NITROGEN DIOXIDE AT DIFFERENT TEMPERATURES

Nitration temperature °C	Quantity of phenylnitromethane obtained g	Quantity of phenyldinitromethane obtained g
20	23.5	5.0
70	6.8	15.9
95	1.4	13.4

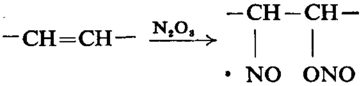
According to Titov the formation of phenyldinitromethane may be presented by the scheme:

$$C_6H_5CH_3 \xrightarrow{NO_2} C_6H_5CH_2. \xrightarrow{NO} C_6H_5CH_2NO \rightarrow C_6H_6CH = NOH \xrightarrow{N_2O_4} C_6H_5CH(NO_2)_2$$

Unsaturated hydrocarbons

When olefin hydrocarbons react with nitrogen dioxide or nitrous and nitric anhydride they are added to a double bond. For the reactions of N_2O_5 and N_2O_3 see also pp. 106 and 109.

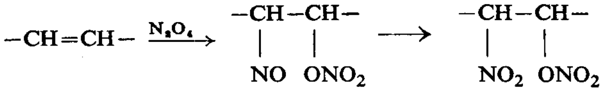
The addition of nitrous anhydride results in the formation of nitrosites (nitroso-nitrites) (I) :



$$-CH{=}CH- \xrightarrow{N_2O_3} \begin{array}{cc} -CH- & CH- \\ | & | \\ NO & ONO \end{array}$$

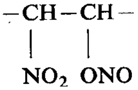
Nitrosite (I)

By the addition of nitrogen dioxide, nitrosates (II) (nitroso-nitrates) or dinitro compounds (III) or dinitrites (IV) are obtained. Nitrosates (II) can be oxidized to nitro-nitrates (IIa).



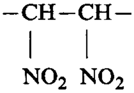
$$-CH=CH- \xrightarrow{N_2O_4} \underset{NO}{-CH}-\underset{ONO_2}{CH-} \longrightarrow \underset{NO_2}{-CH}-\underset{ONO_2}{CH-}$$

Nitrosate (II) Nitro-nitrate (IIa)



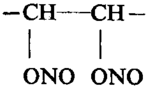
$$\underset{NO_2}{-CH}-\underset{ONO}{CH-}$$

Nitro-nitrite (IIb)



$$\underset{NO_2}{-CH}-\underset{NO_2}{CH-}$$

Dinitro compound (III)



$$\underset{ONO}{-CH}-\underset{ONO}{CH-}$$

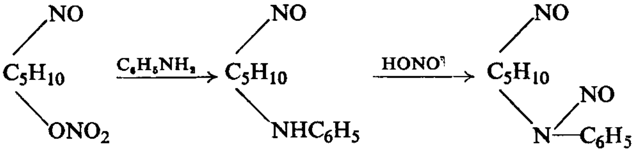
Dinitrite (IV)

Riebsomer [72] gave an extensive list of the reactions of NO_2 addition to unsaturated compounds.

Guthrie [73] obtained the first nitrosate in 1860 by treating amylene with nitrogen dioxide. Wallach [74] found it to be a well defined compound, while this is not the case with the amylene and N_2O_3 compound.

Although no amine was produced by the reduction of amylene nitrosate, and only ammonia was formed, Wallach inferred from the results of the experiments described below that the compound had the structure V.

By heating amylene nitrosate (V) with aniline in an alcoholic solution, amylenenitrosoanilide (VI) was formed, which under the influence of nitrous acid gave the N-nitroso compound (VII):

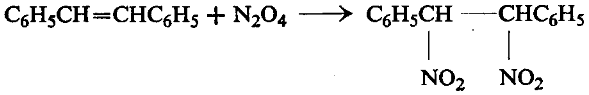


V VI VII

m. p. 140-141°C

The reaction was later widely used by Wallach for the identification of terpenes, which formed well defined, crystalline nitrosates and nitrosites and also by Jagelki [75] and Lipp [3].

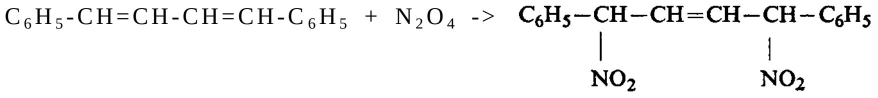
Extensive research work on the action of N_2O_3, N_2O_4 and N_2O_5 on olefins was carried out by Demyanov [76, 77, 78]. He found that both glycol esters and nitro compounds were obtained in these reactions. According to Wieland [13,55], the reaction of N_2O_4 with stilbene results in the formation of dinitrostilbene (VIII):



$$C_6H_5CH=CHC_6H_5 + N_2O_4 \longrightarrow \underset{NO_2}{C_6H_5CH}-\underset{NO_2}{CHC_6H_5}$$

VIII

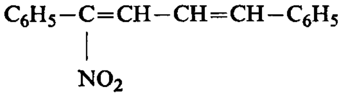
The addition of N_2O_4 to compounds with conjugated double bonds takes place in a way similar to the addition of halogens to these compounds. For example 1,4-diphenylbutadiene is converted to 1,4-diphenyl-1,4-dinitrobutylene-2 (IX) :



$$C_6H_5\text{-}CH{=}CH\text{-}CH{=}CH\text{-}C_6H_5 + N_2O_4 \rightarrow C_6H_5-\underset{NO_2}{\underset{|}{CH}}-CH{=}CH-\underset{NO_2}{\underset{|}{CH}}-C_6H_5$$

IX

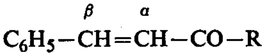
A further analogy with halogen derivatives discovered by Wieland lies in the fact that compound IX, when treated with an alcoholic solution of potassium hydroxide, gives off an HNO_2 molecule to form 1,4-diphenyl-1-nitrobutadiene (X):



$$C_6H_5-\underset{NO_2}{\underset{|}{C}}{=}CH-CH{=}CH-C_6H_5$$

X

Subsequently Wieland found that on treating unsaturated compounds containing a carbonyl group, of the general formula

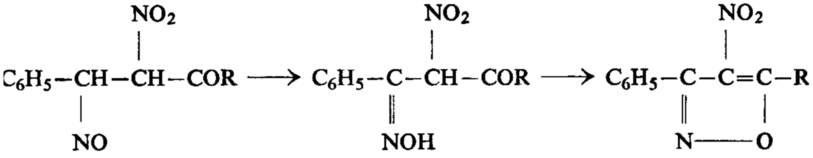


$$C_6H_5-\overset{\beta}{CH}{=}\overset{\alpha}{CH}-CO-R$$

XI

with N_2O_3 or N_2O_4, three types of compounds were obtained:

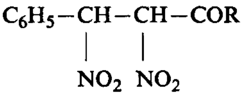
(1) On treating with N_2O_3 first the compound XII was formed which then isomerized to give the oxime (XIII), which in turn gave off water to form isoxazole (XIV):



$$C_6H_5-\underset{NO}{\underset{|}{CH}}-\overset{NO_2}{\overset{|}{CH}}-COR \longrightarrow C_6H_5-\underset{NOH}{\underset{\|}{C}}-\overset{NO_2}{\overset{|}{CH}}-COR \longrightarrow C_6H_5-\underset{\underset{N}{\|}}{C}-\overset{NO_2}{\overset{|}{C}}{=}\underset{\underset{O}{|}}{C}-R$$

XII XIII XIV

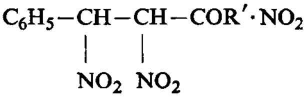
(2) N_2O_4 was added on, giving the dinitro compound (XV):



$$C_6H_5-\underset{NO_2}{\underset{|}{CH}}-\underset{NO_2}{\underset{|}{CH}}-COR$$

XV

(3) The R radical attached to the carbonyl group, when treated with N_2O_4, underwent nitration:

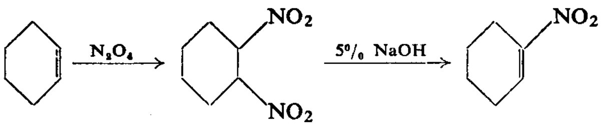


$$C_6H_5-\underset{NO_2}{\underset{|}{CH}}-\underset{NO_2}{\underset{|}{CH}}-COR'\cdot NO_2$$

XVI

where R’H is the radical R.

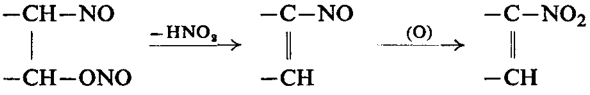
In such a way, by treating cyclohexene with N_2O_4, Wieland and Blümich [79] obtained a dinitro compound which, under the influence of an alkali hydroxide, was converted to nitrocyclohexene :



(22)

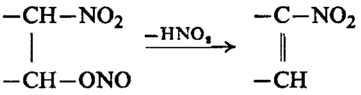
Numerous experiments on the action of nitrogen dioxides on olefins were carried out by Demyanov and Sidorenlco [76] between 1909 and 1934. They obtained products of the types IIa and III.

Schaarschmidt and Hoffmeier [40] found that on treating unsaturated hydrocarbon with N_2O_4 a mixture of products of the I, II, III, and IV types was obtained. Only the dinitro compounds of type III were stable. Others underwent decomposition in the following way:



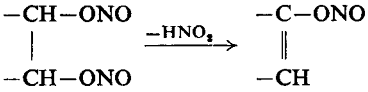
$$\begin{array}{l}\text{—CH—NO}\\ |\\ \text{—CH—ONO}\end{array} \xrightarrow{-HNO_2} \begin{array}{l}\text{—C—NO}\\ \|\\ \text{—CH}\end{array} \xrightarrow{(O)} \begin{array}{l}\text{—C—}NO_2\\ \|\\ \text{—CH}\end{array}$$

I Nitrosoolefin Nitroolefin



$$\begin{array}{l}\text{—CH—}NO_2\\ |\\ \text{—CH—ONO}\end{array} \xrightarrow{-HNO_2} \begin{array}{l}\text{—C—}NO_2\\ \|\\ \text{—CH}\end{array}$$

IIb Nitroolefin



$$\begin{array}{l}\text{—CH—ONO}\\ |\\ \text{—CH—ONO}\end{array} \xrightarrow{-HNO_2} \begin{array}{l}\text{—C—ONO}\\ \|\\ \text{—CH}\end{array}$$

IV Unstable nitrite

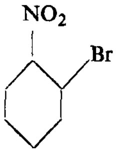
It was originally thought that the addition of dinitrogen tetroxide to the double bond of an olefin in a weakly basic solvent such as ether is a heterolytic (ionic $-NO_2^+NO_2^-$) addition.

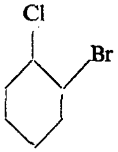
Results of recent study, however, have been interpreted in terms of a homolytic process. Schechter and Conrad [49] have observed that the production of methyl-3-nitroacrylate and methyl-2-hydroxy-3-nitropropionate in the reaction between N_2O_4 and methyl acrylate could not be explained on the basis of heterolytic addition, but was to be expected if a homolytic process were occurring. Brown [80] has shown that olefin nitration under circumstances in which the nitronium ion (NO_2^+) is the reactant has characteristics entirely different from those of the N_2O_4-olefin reaction. Brand and I. D. R. Stevens [81] also believed the reaction of addition of nitrogen dioxide to olefins to involve radicals. According to these authors the following experimental facts provide evidence for this:

(1) Cyclohexene reacted with dinitrogen tetroxide (N_2O_4) to yield 1,2-dinitrocyclohexane and 2-nitrocyclohexyl nitrite.

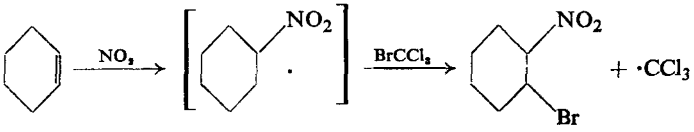
(2) However, in the presence of two moles of bromotrichloromethane the reaction followed a different course, and the normal products, 1,2-dinitrocyclo-

hexane and 2-nitrocyclohexyl nitrite, were not formed. Instead, the main products were : 2-bromonitrocyclohexane and 2-bromochlorocyclohexane.


(Yield 20.6%)

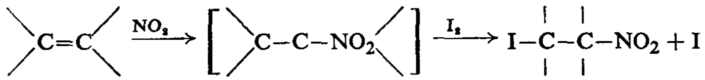

(Yield 31.5%)

These products derive from the interaction of the intermediate β– nitroalkyl radical and the bromotrichloromethane e.g. :


(23)

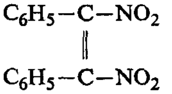
The main reaction was accompanied by a number of secondary reactions.

Recently T. E. Stevens and Emmons [82] examined the reaction between N_2O_4 and olefins in the presence of iodine in to order to trap the intermediate nitroalkyl radical, and they have been able to isolate β– nitroalkyl iodides in good yield:


(24)

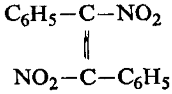
These experiments provide further proof of the radical nature of the N_2O_4-olefin addition reaction.

The nitration of acetylene hydrocarbons proceeds in a more complex way than that of olefins. The first member of the series-acetylene-undergoes various reactions, for example, with nitric acid (see p. 82 and p. 599) Tolane (diphenylacetylene) is nitrated with N_2O_4 to form dinitrostilbene. Two products are formed which are presumably α– and β– stereoisomers:



$$\begin{array}{c}C_6H_5-C-NO_2\\ \|\\ C_6H_5-C-NO_2\end{array}$$

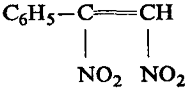
α m. p. 186-187°C



$$\begin{array}{c}C_6H_5-C-NO_2\\ \|\\ NO_2-C-C_6H_5\end{array}$$

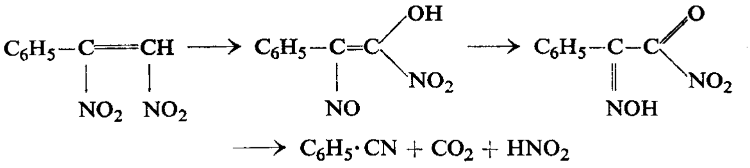
β m. p. 105-107°C

When nitrating phenylacetylene, Wieland and Blümich [79] obtained phenyldinitroethylene:

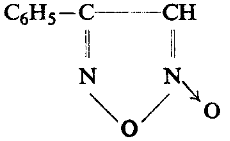


$$\begin{array}{ccc}C_6H_5-C & = & CH\\ | & & |\\ NO_2 & & NO_2\end{array}$$

an unstable product which decomposes giving off benzonitrile, CO_2 and HNO_2, probably according to the following scheme:



Phenylacetylene reacted with N_2O_3 to yield phenylfuroxane:



(25)

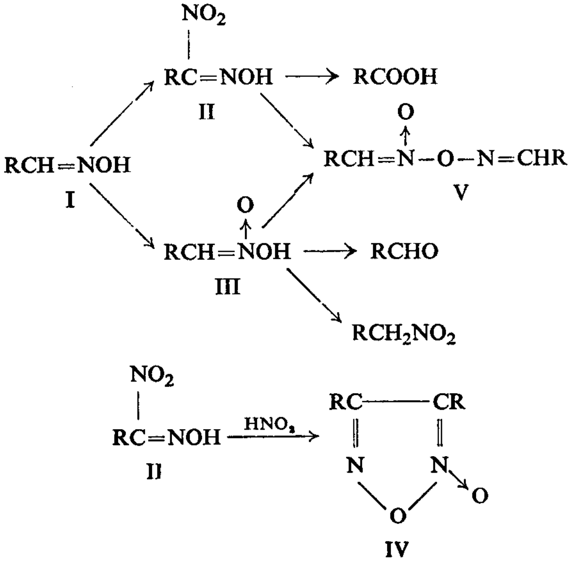
Petrov and Bulygina [6] found that under the conditions they used, transfer of the double bond into the β– position with reference to the nitro group occurred, similar to the transfer occurring in chlorination reactions, according to the mechanisms proposed by Lvov [83] and by Tishchenko [84]. For example, octene- Δ^1 gave 1-nitrooctene- Δ^2 under the action of dinitrogen tetroxide:

$$CH_2{=}CH(CH_2)_5CH_3 \xrightarrow{N_2O_4} NO_2CH_2CH = CH(CH_2)_4H_3 \qquad (26)$$

The action of dinitrogen tetroxide on aldoximes has several interesting features. This reaction has been studied by Scholl [85], Potio [35] (benzaldoxime), Mills [86] (isonitrosoacetone), and recently by Boyer and Alul [87].

The last authors investigated the reaction with acetaldoxime, propionaldoxime and benzaldoxime. They came to the conclusion that dinitrogen tetroxide both nitrates and oxidizes aldoximes. The nitration is more pronounced with increase of temperature whereas oxidation is most effective at 0°C and below.

Boyer and Alul suggest the following scheme for the reactions:

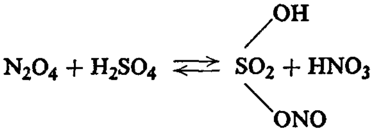


Nitrolic acids (II) are relatively stable when R is alkyl but can lose nitrous acid with furoxane (IV) formation (Wieland and Semper [14]). Aci-nitroparaffins (III) readily yield aldehydes when R is alkyl. At lower temperatures the product V ($R=C_6H_5$) predominates.

According to Ponzio [35], benzaldoxime can form phenyl-gem-dinitromethane $C_6H_5CH(NO_2)_2$, under the action of N_2O_4.

NITRATION WITH NITROGEN DIOXIDE IN THE PRESENCE OF SULPHURIC ACID

Pinck [88] studied the nitrating action of nitrogen dioxide in a sulphuric acid solution. According to this author, the nitrating action of the solution proceeds as follows, from each N_2O_4 molecule with the formation of one molecule of HNO_3 and one of nitrosylsulphuric acid:

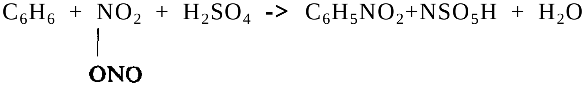


$$N_2O_4 + H_2SO_4 \rightleftarrows SO_2\left\langle\begin{matrix}OH\\ONO\end{matrix}\right. + HNO_3 \qquad (27)$$

When treating 1 mole of toluene with 1.05 mole of N_2O_4 in the presence of 1.6 moles of 95 % sulphuric acid at 50-55°C for 3½ hr, the yield of nitrotoluene obtained amounted to 87.5% of theory.

According to Battegay [58], nitration with nitrogen dioxide in the presence of sulphuric acid followed a course such that an addition product of H_2SO_4 and the aromatic hydrocarbon was formed initially. Battegay assumed the sulphuric acid activated the aromatic ring in a way similar to the role of aluminium or ferric chlorides in the Friedel-Crafts reaction, or as in a chlorination reaction. Indeed, Battegay found that benzene may be readily chlorinated in the presence of sulphuric acid instead of $FeCl_3$.

Benzene activated with sulphuric acid would add on to N_2O_4 which, according to Battegay, has the structure of "nitrosyl nitrate" $NO_2.ONO$. An addition product was thought to be formed which, in the presence of an excess of sulphuric acid, would decompose to yield a nitro compound and nitrosylsulphuric acid.



$$C_6H_6 + \underset{\displaystyle ONO}{\underset{|}{NO_2}} + H_2SO_4 \rightarrow C_6H_5NO_2 + NSO_5H + H_2O \qquad (28)$$

Titov and his co-workers [34] proposed the following mechanism of nitration of aromatic compounds with nitrogen dioxide in the presence of sulphuric acid:

$$RH + N_2O_4 \rightarrow RNO_2 + HNO_2 \qquad (a)$$

$$N_2O_4 + H_2SO_4 \leftrightarrow HNO_3 + NSO_5H \qquad (b)$$

$$2NSO_5H + H_2O \leftrightarrow N_2O_3 + 2H_2SO_4 \qquad (c)$$

$$2HNO_3 + N_2O_3 <-> 2N_2O_4 + H_2O \qquad (d)$$

$$H_2SO_4.qH_2O + H_2O = H_2SO_4.(q+1)H_2O \qquad (e)$$

Thus the overall equation would be:

$$RH + N_2O_4 + nH_2SO_4.mH_2O -> RNO_2 + NSO_5H + (n-l)H_2SO_4.(m+l)H_2O$$

The principal assumption was that nitration of aromatic compounds in the medium under consideration depends on the saturation of the free valences of the sulphuric acid with nitrous acid and water. To make use of the most N_2O_4 the ratio of free sulphuric acid to the amount of water (n-1) : (m+1), should by the end of the reaction be not less than a certain minimum value, characteristic for the compound being nitrated. For benzene the value is 4:1, for chlorobenzene 5:1, for toluene 1.8:1.

When using a solution of 1.1 mole N_2O_4 in 45% oleum for the nitration of 1 mole of benzene, Titov obtained dinitrobenzene with a yield 97-89% of theory. Similarly, by treating nitrotoluene with a solution of N_2O_4 in oleum, 2,4-dinitrotoluene was obtained with a yield 98% of theory. According to Titov, 2,4-dinitrotoluene could be converted into 2,4,6-trinitrotoluene with a yield 85% of theory.

According to more recent views, nitrogen dioxide in sulphuric acid solution gives the nitrosonium ion NO^+ and a nitric acid molecule. The latter, treated with an excess of sulphuric acid, gives a nitronium ion, which is the actual nitrating agent :

$$N_2O_4 + H_2SO_4 + NO^+ + HNO_3 + HSO_4^- \qquad (29)$$

$$HNO_3 + 2H_2SO_4 + NO_2^+ + 2HSO_4^- + H_3O^+ \qquad (30)$$

(Ingold, Gillespie, Graham, Hughes and Peeling [89]).

NITRATION WITH NITROGEN DIOXIDE IN THE PRESENCE OF FRIEDEL-CRAFTS CATALYST

Schaarschmidt [38a] has examined the nitration of aromatic hydrocarbons with nitrogen dioxide in the presence of aluminium or ferric chloride. Benzene with N_2O_4 and $AlCl_3$ forms a red complex at about 10°C, which decomposes on adding water with the formation of a small quantity of chlorobenzene. The composition of the complex, according to Schaarschmidt, was $2AlC1_3.3C_6H_6.3N_2O_4$. When heated to 30-35°C however it underwent a transformation, followed by the formation of nitrobenzene when diluted with water:

$$2AlCl_3.3C_6H_6.3.N_2O_4 + H_2O -> 2AlC1_3.H_2O + 3C_6H_6.N_2O_4 \qquad (31)$$

$$C_6H_6.N_2O_4 + H_2O -> C_6H_5.NO_2 + HNO_2 \qquad (31a)$$

Titov [34] assumed a different mechanism for this reaction, suggesting that heating a hydrocarbon with nitrogen dioxide and $AlCl_3$ led to the reaction:

$$3RH + 3N_2O_4 + 2AlC1_3 -> 3RNO_2 + 3NOCl + Al_2Cl_3(OH)_3 \qquad (32)$$

The nitro compound, nitrosyl chloride, and basic aluminium chloride formed a number of addition products, which are in equilibrium:

$$\begin{aligned} RH + N_2O_4 + 2AlCl_3 &\leftrightarrow RNO_2.AlCl_3 + AlCl_2OH.NOCl \leftrightarrow \\ &\leftrightarrow RNO_2.AlCl_2OH + AlCl_3.NOCl \end{aligned} \qquad (33a)$$

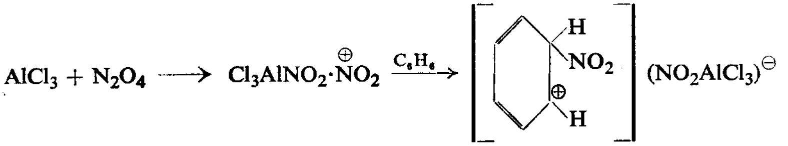
and then

$$RNO_2.AlCl_3 + N_2O_4 + RH \rightarrow AlCl_2(OH).(2RNO_2)(NOCl) \qquad (33b)$$

$$AlCl_2OH.NOCl + N_2O_4 + RH + AlCl(OH)_2(RNO_2)(2NOCl) \qquad (33c)$$

When heated, the complexes dissociated into their components.

Titov explained the activating action of aluminium chloride by the fact that aluminium chloride is coordinatively unsaturated and strongly polarizes the molecule of the compound being nitrated:

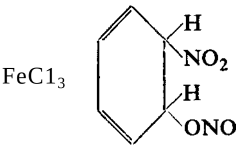


(34)

The hydrogen atom attached to the carbon atom linked to the nitro group is readily split off to form nitrobenzene.

Titov used the following technique for the nitration. A mixture of hydrocarbon and aluminium chloride was saturated with nitrogen dioxide. An exothermic reaction took place, $AlCl_3$ being dissolved. The intensity of the reaction diminished after all the aluminium chloride had been dissolved. The saturation of the mixture with NO_2 was stopped at 95% of the theoretical amount. Then the unreacted nitrogen dioxide was expelled by passing CO_2. The liquid nitro compound phase was separated from the solid aluminium salt. The yield of the nitro derivatives of toluene and chlorobenzene was 88% and 96% of theoretical for toluene and chlorobenzene respectively.

Bogdanov [90] investigated the nitration of aromatic compounds with nitrogen dioxide in the presence of ferric chloride. He assumed that in the first stage of the reaction a complex was formed:



Chlorine introduced into the mixture activated the nitration reaction by promoting the decomposition of the complex into nitrobenzene and ferric chloride, the latter again taking part in the reaction.

Among more recent work Topchiev's experiments [60] should be mentioned, in which boron fluoride was used as a catalyst for the nitration with nitrogen dioxide. At a temperature of 55-50°C and with an N_2O_4 to benzene molar ratio 0.5:1 he obtained 18% of the theoretical yield.

G. B. Bachman and his co-workers [91] investigated the action of the boron trifluoride and nitrogen dioxide complex, formed by combining the two compounds at 0°C:

$$BF_3 + N_2O_4 \rightarrow \underset{\text{Crystalline complex salt}}{[F_3B \leftarrow NO_2]^- NO_2^+} \tag{35}$$

The complex salt acted on benzene to give nitrobenzene (40% yield) and a small quantity (1.5%) of *m*- dinitrobenzene at 0°C. At room temperature only *m*- dinitrobenzene in 7% yield was formed.

The action of this reagent on naphthalene is of interest. A mixture of dinitronaphthalene isomers is formed in 65% yield, the ratio of the 1,5- to l,8-isomer being 2:1, the reverse of the ratio obtained by nitration with the ordinary nitrating mixture.

NITRATION WITH NITROGEN DIOXIDE IN THE PRESENCE OF ACTIVATED SILICA

McKee and Wilhelm [92] found that the highest yield of nitration of benzene with nitrogen dioxide in the vapour phase was obtained at 310°C. In the presence of activated silica the yield was higher than that obtained without a catalyst and could amount to 83.6%. Nitrophenol was also formed in a yield rising with temperature, so that at 330°C it was the principal reaction product. The authors supposed that the catalytic action of activated silica was probably a specific one and did not consist only in binding the water formed during the nitration process.

PHOTONITRATION WITH NITROGEN DIOXIDE

Gorislavets [93] claimed that the nitration of benzene or nitrobenzene with nitrogen dioxide readily occurred on irradiation with rays of certain definite wavelengths, which activate nitrogen dioxide.

Thus, benzene was nitrated quantitatively at the wavelengths 4000 - 7000 Å at a temperature of 55-60°C. The highest yield of dinitrobenzene was obtained at wavelengths 1800 - 2900 Å. The experiments of other workers did not confirm his results (Hastings and Matsen [94]).

On the other hand Lippert and Vogel [95] assert that on irradiation with high intensity ultra-violet light nitro compounds undergo dissociation into free radicals:

$$ArNO_2 \rightarrow Ar + .NO_2 \tag{36}$$

On the basis of this statement it may be concluded that differences in the results of various authors may be due to the difference in intensity of applied irradiation.

NITROGEN PENTOXIDE (NITRIC ANHYDRIDE)

As is well known, nitrogen pentoxide is a solid, crystalline, colourless product, melting at 30°C. Nitrogen pentoxide was first used as a nitrating agent for the O-nitration of cellulose (Hoitsema [96]; Berl and Klaye [97], and others (see Vol. II)).

Titov [34] suggested in 1941 that nitrogen pentoxide undergoes a heterolytic dissociation:

$$N_2O_5 \rightarrow NO_2^+ + NO_3^- \tag{37}$$

It is the presence of the nitronium ion that accounts for the nitrating properties of nitrogen pentoxide.

Ogg [98] studied the heat of dissolution of nitric anhydride is water, and on the basis of the results obtained came to the conclusion that the compound underwent the following reactions (a), (b), (c) and (d):

$$N_2O_5 \rightarrow NO_3 + NO_2 \tag{a}$$

$$NO_3 + NO_2 + N_2O_5 \tag{b}$$

$$NO_3 + NO_2 \rightarrow NO_2 + O_2 + NO \tag{c}$$

$$NO + N_2O_5 \rightarrow 3NO_2 \tag{d}$$

The (a) reaction corresponds to the reaction (37). Reaction (c) proceeds slowly as compared with reaction (b), while, on the contrary, reaction (d) is a fast one.

In general, the reaction of decomposition of N_2O_5, which is seemingly of the first order (according to Smith and Daniels [99], Johnston and his co-workers [100-102]), is in fact the resultant of reactions (a) and (b) and of the second order reactions (c) and (d). Indeed, Johnston [100] found the decomposition of nitrogen pentoxide in the presence of nitrogen dioxide to be a second order reaction.

In 1951, Titov and Shchitov [103] when examining the action of nitric anhydride on normal paraffins and cycloparaffins, found that in the presence of an inert solvent the reaction already started at 0°C, with the evolution of heat. Nitric acid esters were formed in the reaction which, according to the authors, proceeded through the following stages:

$$\begin{aligned} &N_2O_5 \leftrightarrow .ONO_2 + .NO_2 \\ &RH + .ONO_2 \rightarrow R. + HONO_2 \\ &R. + .ONO_2 \rightarrow RONO_2 \end{aligned} \tag{38}$$

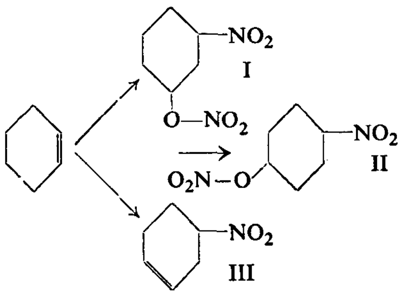
For example, from n-hexane, secondary n-hexyl alcohol nitrate was obtained:

$$\underset{\text{n-Hexane}}{C_6H_{14}} \xrightarrow{+NO_2} \underset{\text{2-Hexyl}}{C_6H_{13}\cdot} \xrightarrow[-NO_2]{+N_2O_5} \underset{\text{2-Hexyl nitrate}}{C_6H_{13}ONO_2} \tag{39}$$

NO_2 formed in reaction (39) also reacted in accordance with (8) to give a nitro compound along with an ester.

In reactions of N_2O_5 with the olefins the products obtained had structures that confirmed Titov's view on the heterolytic decomposition of N_2O_5 into NO_2^+ and NO_3^-. For example, when treating cyclohexene with nitrogen pentoxide, T. E.

Stevens and Emmons [82] obtained three compounds: the nitro-nitrates (I) and (II) as well as a nitro-olefin (III)



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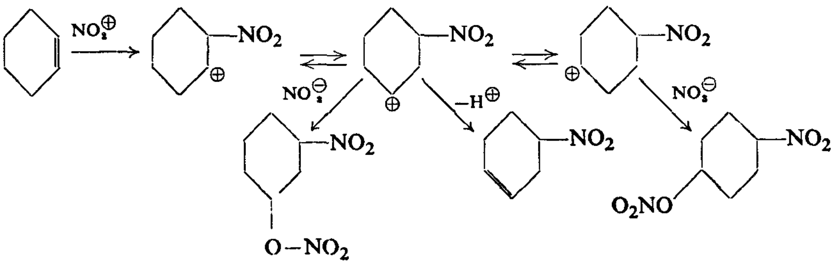
They suggested the following reaction mechanism:



(41)

G. B. Bachman and Hokama [104] have recently found that nitrogen pentoxide forms a complex with boron trifluoride: $BF_3.N_2O_5$. The complex is a colourless, stable liquid in the presence of polychlorinated paraffins and a white solid in nitroparaffins. It decomposes at ca. 75°C with evolution of brown fumes.

G. B. Bachman and Dever [105] suggest that the complex has the structure

$$(F_3B<\text{-}ONO_2)^{-}NO_2^{+}$$

The complex seems to be a somewhat more powerful nitrating agent than an anhydrous mixture of HNO_3-H_2SO_4.

Nitrobenzene reacts with two moles of the complex in carbon tetrachloride to give an 86% yield of *m*- dinitrobenzene after 18 hr at 75°C.

Benzoic acid reacts with three moles of the complex in 36 hr at 70°C to form 3,5-dinitrobenzoic acid (70% yield) and *m*- nitrobenzoic acid (9.3% yield).

The complex forms an addition molecular compound with *m*- dinitrobenzene (m.p. 89.5°C).

NITRYL CHLORIDE (NITRONIUM CHLORIDE, NO_2Cl)

It was found by Steinkopf and Kühnel [106] that the so-called nitryl chloride is an agent that both nitrates and chlorinates aromatic hydrocarbons. However, the reaction could be selective. Thus, only *o*- nitrophenol was formed when nitryl chloride interacted with phenol below room temperature, but at room temperature 2,4-dichloro-6-nitrophenol was obtained. Naphthalene was chlorinated and nitrated simultaneously to give α– nitro- and α– chloro-naphthalene.

A very interesting result was obtained with benzene. At room temperature nitryl chloride dissolved in benzene without reacting. When warmed the nitryl chloride evaporated off unchanged. When benzene and nitryl chloride were heated under pressure, 1-chloro-2-nitrocyclohexadiene was formed and decomposed, producing nitrobenzene.

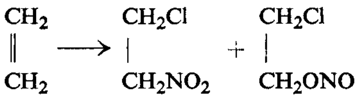
On the other hand Price and Sears [107] studied the reactions of nitryl chloride with various aromatic compounds in the presence of aluminium chloride, and found that phenol, anisole and naphthalene tended to undergo oxidative degradation. In the case of naphthalene they obtained a 31% yield of α– nitronaphthalene, whereas with anisole and phenol they were able to isolate only traces of nitro compounds without any evidence of chlorination.

Goddard and co-workers [108-111] found that nitryl chloride in various solvents at room temperature and below (-10°C) chlorinates, rather than nitrates, toluene, ***m***- and *p*- xylene, and mesitylene, though not benzene.

Thus, *p*- xylene yielded 2,5-dichloro-p-xylene. The principal reaction with anisole was also chlorination and with phenol nitration when nitration temperature was low (-80°C) both *o*- and *p*- nitrophenols were formed. At room temperature chlorination also occurred yielding 2,4-dichloro-6-nitrophenol and 3,6-dichloro-2-nitrophenol.

Steinkopf and Kühnel [106] also examined the action of nitryl chloride on ethylene and reported that only 1,2-dichloroethane was formed. Petri [112] however reported the formation of 1-chloro-2-nitroethane (with 45% yield) and 2-chloroethyl nitrate (35% yield). Ville and DuPont [113] confirmed the formation of 1-chloro-2-nitroethane (50% yield) and Goddard [111] confirmed the results of Petri. Price and Sears [107] obtained 2-chloro-1-nitropropane from propane.

Thus it should be accepted that the main reaction of ethylene (and probably olefins in general) with NO_2Cl is:



$$\begin{array}{c} CH_2 \\ \| \\ CH_2 \end{array} \longrightarrow \begin{array}{c} CH_2Cl \\ | \\ CH_2NO_2 \end{array} + \begin{array}{c} CH_2Cl \\ | \\ CH_2ONO \end{array}$$

(42)

According to Goddard, styrene reacted with nitryl chloride to yield 1,2-dichloro-1-phenylethane in 70-80% yield. Another product 1-chloro-2-nitro-l-phenylethane was thought to be present, but could not be isolated. On distillation it decomposed, evolving HCl, and *o*- nitrostyrene was obtained.

Finally T. Urbanski and Siemaszko [114] used nitryl chloride in the gas phase to O-nitrate cellulose. They obtained a stable product containing 12.2% N.

On the basis of the formation of chloroalkyl nitrites (e.g. 2-chloroethyl nitrite from ethylene) Goddard drew the conclusion that nitryl chloride could be subjected to heterolysis :

$$ClNO_2 \rightarrow Cl^+ + NO_2^- \qquad (43)$$

This dissociation would also be confirmed by the chlorinating action of the substance.

NITRYL FLUORIDE (NITRONIUM FLOURIDE, NO_2F)

Nitryl fluoride is a gas which liquifies at -73°C and solidifies at ca. -160°C.

Nitryl fluoride was prepared for the first time, by Ruff, Manzel and Neumann [115] in 1932, by acting with fluorine on nitrogen dioxide. (The earlier report of Moissan and Lebeau [116] in 1905 is uncertain.) Aynsley, C. Hetherington and Robinson [117] improved the method in 1954 by acting on dry sodium nitrite with fluorine.

Nitryl fluoride reacts with sulphuric acid according to the following equation (Hetherington, Hub and Robinson [118]) :

$$NO_2F + H_2SO_4 \rightarrow NO_2^+ + HF + HSO_4^- \qquad (44)$$

After that the reaction becomes reversible:

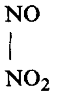
$$HF + 2H_2SO_4 \leftrightarrow HSO_3F + HSO_4^- + H_3O^+ \qquad (45)$$

On the basis of eqn. (45) it would be expected that nitryl fluoride in sulphuric acid is a nitrating agent (besides also possessing fluorinating and sulphofluorinating effects).

NITROGEN TRIOXIDE (NITROUS ANHYDRIDE)

Although solid N_2O_3 can exist as a pure compound (m.p. ca. -102°), nevertheless in the liquid phase it very soon begins to dissociate, and exists only at low temperature under an atmosphere containing free nitrogen oxide. At temperatures above -100°C dissociation begins and the gaseous phase is enriched with nitrogen oxide, and the liquid phase with the dioxide. Thus, the “blue-green” liquid commonly described as N_2O_3 is a solution of greater or smaller quantities of NO_2 in N_2O_3.

d’Or and Tarte [119], on the basis of the infra-red spectrum of the compound, have given its constitutional formula as:



$$\begin{array}{c} NO \\ | \\ NO_2 \end{array}$$

(the N-N bond produces an absorption band similar to that given by N_2O_4).

It is assumed that the mechanism of dissociation of nitrogen trioxide involves its separation into disproportionate amounts of the nitrosonium and nitrite ions:

$$N_2O_3 \rightarrow NO^+ + NO_2^- \qquad (46)$$

Hence the formation of nitroso compounds (C-nitroso- and O-nitroso, i.e. nitrous acid esters) is possible.

Nitrogen trioxide combines with boron trifluoride to form a complex salt, the structure of which, as assumed by G. B. Bachman and Hokama [104], should be either:

$$(F_3B \leftarrow NO_2)^- NO^+ \quad \text{or} \quad (F_3B^+NO)^- NO_2^+$$

In consequence of its dual form the compound can act both as a nitrosating (diazotizing) and as a nitrating agent.

Bachman and Hokama found that benzene was nitrated by the complex in 5-6% yield, whereas nitrotoluene formed gum. If, however, toluene is nitrated in nitroethane, then 56% of *o*- nitrotoluene, 1% of *p*- nitrotoluene and 3% of 2,4-dinitrotoluene are obtained. *o*- Nitrotoluene can be nitrated to 2,4-dinitrotoluene by the complex in 40% yield.

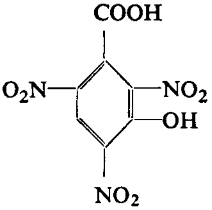
The above mentioned authors have diazotized aniline with the complex and obtained fluorobenzene.

Recently Tedder [120, 121] has shown that by acting directly with the complex on aromatic hydrocarbons, diazonium salts can be obtained.

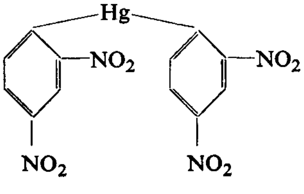
NITRIC ACID IN THE PRESENCE OF MERCURIC NITRATE

The catalytic action of mercuric nitrate in the nitration of anthraquinone with nitric acid was observed in 1906 by Holdermann [122]. Soon after that, Wolffenstein and Boters [123] observed the specific influence that mercuric nitrate exercised on the formation of the products of nitration of benzene. They showed that at a certain concentration of nitric acid, mostly nitrophenols were formed ("oxynitration" reaction).

In his later studies Wolffenstein found that the hydroxyl group could be introduced in this way into the aromatic ring, not only in the case of benzene but also with its derivatives as well. For example, benzoic acid yielded trinitro-m-hydroxybenzoic acid in the presence of mercuric nitrate:

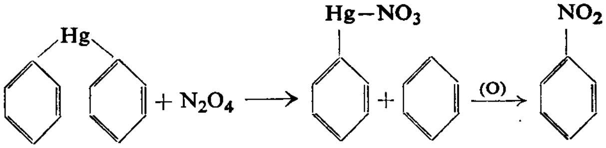


Broders [124] isolated from the nitration products an organomercuric compound to which he ascribed the following formula:



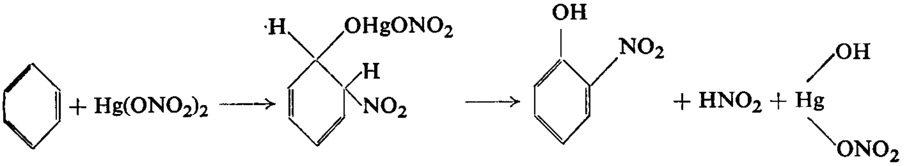
On this basis Desvergnes [125] suggested a mechanism for nitration in the presence of mercuric nitrate that assumes the formation of diphenylmercury as an intermediate product.

Nitrobenzene is also formed besides nitrophenols and this has been explained by Desvergnes according to the following series of reaction:



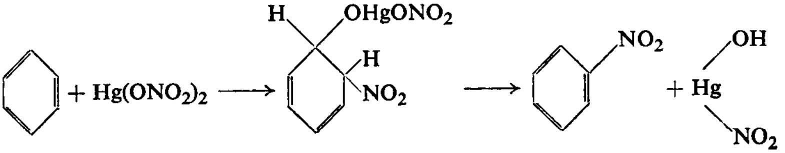
Zakharov [126] criticized Desvergnes's view, which he considered to be inexact in a number of points.

On the basis of his own experiments, Zakharov suggested a different mechanism of reaction. He believed that the catalyst initially weakens the stability of the aromatic ring by the rupture of a double bond on the attachment of mercuric nitrate, e.g.:



(48)

Nitrobenzene would be formed as result of the following reaction:



(49)

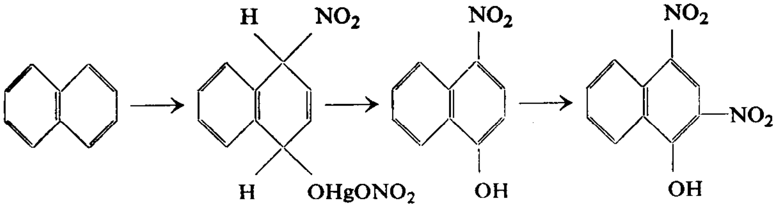
Zakharov found oxynitration to proceed best at 60% concentration of nitric acid.

Davis [127,128] and later Blechta and Patek [129] found that as a result of nitrating toluene in the presence of mercuric nitrate, besides nitrotoluenes, trinitro-*m*- cresol and *p*- nitrobenzoic acid could also be obtained. The authors explained the mechanism of the reaction by assuming the formation of toluene and the mercury salt complex to be the first stage. On decomposition of the complex by the action of nitric acid, the activated hydrocarbon thus formed was nitrated.

According to Kholevo and Eitington [130] the nitratiton of *m*- xylene leads to formation of 4-nitro-3-methylbenzoic acid. Here the mercuric nitrate also enhances the oxidation of the methyl group.

Davis and his co-workers [127,128] found chlorobenzene also undergoes oxynitration by action of 65% nitric acid, with formation of trinitro-m-chlorophenol along with chloronitrobenzenes, while naphthalene when nitrated with more dilute acid, for example, at a concentration of 65%, yielded 2,4-dinitro-a-naphthol besides 2-nitro-a-naphthol.

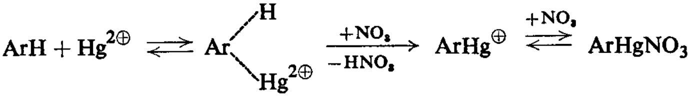
To explain the reaction Davis proposed the following mechanism consistent in the main with Zakharov's view referred to above:



(50)

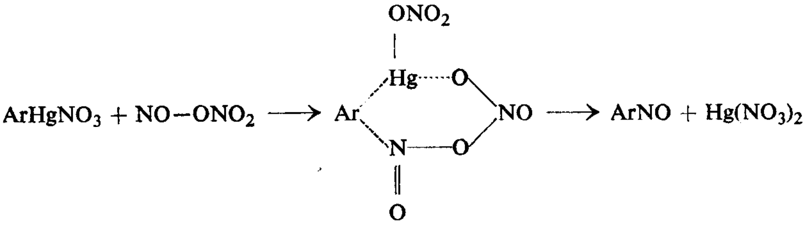
However, the explanation of the reaction, proposed by Titov and Laptev appears to be the most probable and full. Laptev [131] and later Titov and Laptev [71] have suggested that nitration in the presence of mercuric salts proceeds in the following stages:

(1) Formation of a mercury-aromatic compound:



$$\mathrm{ArH + Hg^{2\oplus} \rightleftharpoons Ar\begin{smallmatrix}H\\ Hg^{2\oplus}\end{smallmatrix} \xrightarrow[-HNO_2]{+NO_2} ArHg^{\oplus} \overset{+NO_2}{\rightleftharpoons} ArHgNO_3} \qquad (51)$$

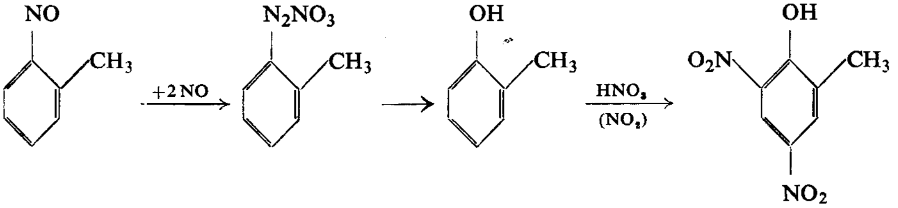
(2) Formation of a nitroso compound by the reaction of the mercury-aromatic compound with N_2O_4:



(52)

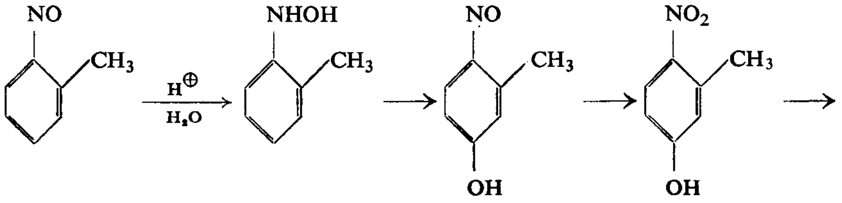
(3) Conversion of the nitroso compound into the nitro compound under the influence of nitrogen oxides and a hydrogen ion.

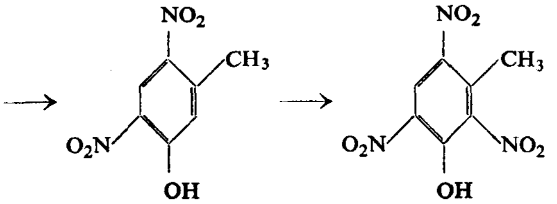
The conversion may consist simply in oxidation or be the result of a more complex reaction. For example, nitrosotoluene can be converted into diazonium nitrate under the influence of nitrous acid. Bamberger [132] found in 1918 that nitrosobenzene could be converted into benzenediazonium nitrate under the influence of nitrous acid. According to Bamberger [133] and Nesmeyanov [134], mercury-aromatic compounds also give nitrates of corresponding diazonium compounds under the influence of N_2O_3, presumably also through nitroso compounds.



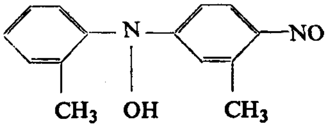
(53)

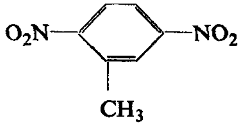
Titov and Laptev also suggest the possibility of conversions with the aid of the hydrogen ion, causing the reduction of nitroso compounds to hydroxylamine derivatives followed by an oxidation:





Moreover, diphenylhydroxylamine derivatives and *p*- dinitrotoluene may be formed, e.g. :

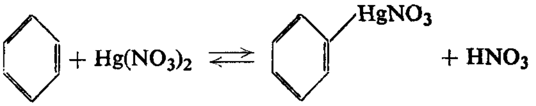




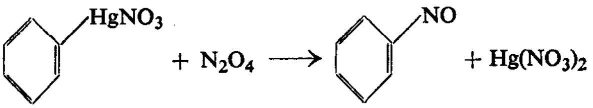
It seems to be certain that the oxynitration reaction in the presence of mercury salts proceeds through the formation of phenylmercuric nitrate. The isolation of phenylmercuric nitrate from a reaction mixture in dilute nitric acid by several authors (Carmack and his co-workers [135], Titov and Laptev [71], and also Broders [124]) favours this view. If an intermediate nitroso compound is formed in the reaction its formation should be ascribed to the reaction between phenylmercuric nitrate and nitrous acid. This view, based on earlier experiments of Baeyer [136], Bamberger [137], Smith and Taylor [137a], has since been confirmed by Westheimer, Segel and Schramm [138], who considered the nitroso compound formed from an organo-mercuric compound to be the principal intermediate product in the Wolffenstein and Böters reaction.

Nitrogen dioxide plays an important role in the reaction. It is this compound that is responsible for the conversion of mercury aryl nitrates into nitroso derivatives.

Westheimer and his co-workers formulated the reaction mechanism in the following way :



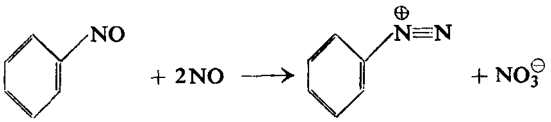
(55a)



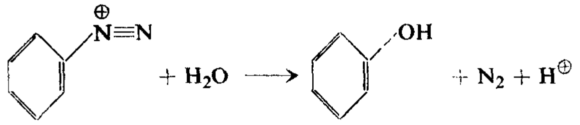
(55b)

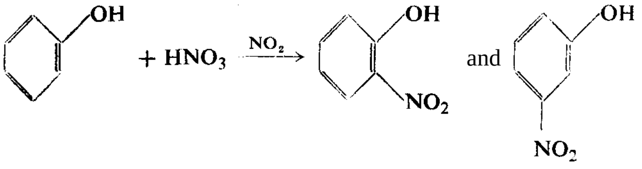
The nitrosobenzene formed in the reaction (55b) can then react in either of two ways :

(1)

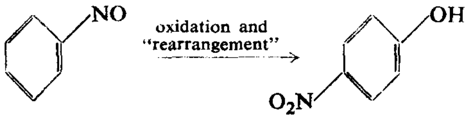


(55c)


(55d)


(55e)

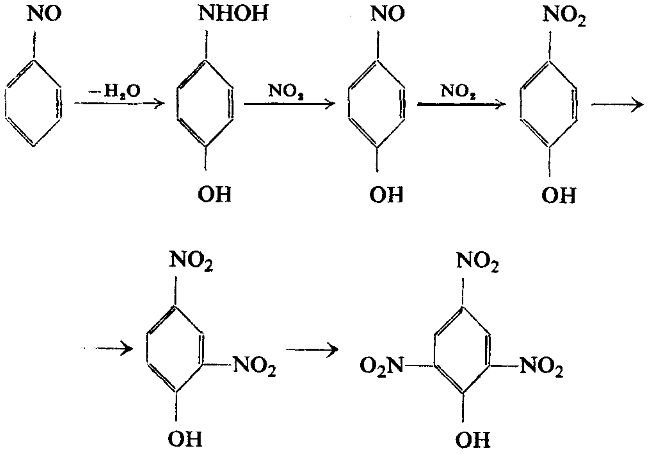
or (2)


(55f)

The mononitrophenol formed either by the reaction (55e) or by reaction (55f) is, then further nitrated to dinitro- and trinitro-phenols if the concentration of nitric acid is sufficiently high.

Westheimer's formulation of the mechanism of the reaction appears to be the most accurate of all the attempts to elucidate the mechanism of "oxynitration".

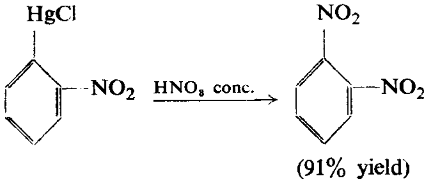
Laptev [131] suggested a mechanism based on reactions (55/1) and (55/2), followed by formation of *p*- hydroxyphenylhydroxylamine :


(56)

If nitric acid does not contain nitrogen oxides, a reversible decomposition of the organo-mercuric compound can take place, as has been shown by Baryshnikova and Titov [139]:

$$\text{Ar-HgNO}_3 + \text{HNO}_3 \rightarrow \text{Ar-H} + \text{Hg(NO}_3)_2$$

At a sufficient concentration of nitric acid, mercury is replaced by the nitro group. This was shown by Ogata and Tsuchida [40] by means of the following reaction:



(57)

It is rather important to note that if an aromatic nitro compound is the substance being nitrated, addition of mercuric nitrate to the nitric acid has no effect on the reaction. For example, nitrobenzene is nitrated to dinitrobezene in the same yield both in the presence of a mercury salt and in its absence. This can be explained by the fact that nitro compounds such as nitrobenzene do not yield addition product with mercuric salts.

Wright and his co-workers [141] found mercury plus a small amount of aluminium (ca. 2%) and manganese (ca. 5%) to be a more efficient catalyst than mercury alone. The experiments have shown that mercury increases the reaction rate while manganese, though it has no influence on the principal reaction, assists in the complete oxidation of oxalic acid which would otherwise contaminate the reaction product.

It is of interest to point out the observation of the above authors that addition of copper and especially vanadium inhibits the reaction.

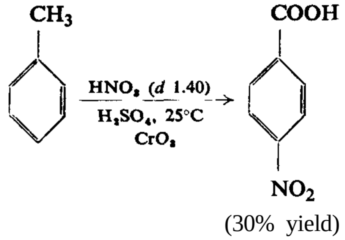
McKie [142] found the yield of the nitration product to be higher when mercuric nitrate was present in nitric acid. Thus for example, phenanthrene, when nitrated with anhydrous nitric acid in the presence of $Hg(NO_3)_2$, gave nitrophenanthrene in a yield higher by 13% than when nitric acid alone had been used. Likewise the yields of nitro derivatives of phenol and α– naphthol could be increased by addition of mercuric nitrate to dilute nitric acid.

Numerous industrial studies have been carried out to investigate the possibility of using the oxynitration method for the commercial production of picric acid. However, they have failed to provide a reliable method for industrial application. Particulars on some experiments on the industrial scale are dealt with in the chapter on nitro derivatives of phenol.

NITRATING MIXTURES WITH STRONG OXIDIZING AGENTS

T. Urbanski, Semenczuk *et al.* [143] developed a method of “nitroxidation” that consists in nitrating an aromatic hydrocarbon which contain an aliphatic side chain, using nitrating mixtures containing strongly oxidizing agents, such as CrO_3.

Toluene can be nitrated to yield *p*- nitrobenzoic acid and *p*- nitrotoluene to yield 2,4-dinitrobenzoic acid :



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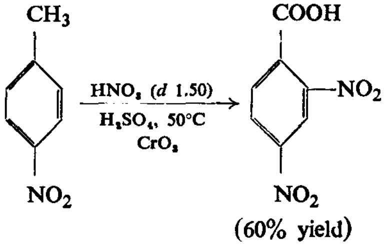


(59)

NITROUS ACID AS A NITRATION CATALYST AND AS A NITRATING AGENT

The name “nitrous acid” is usually applied to substances which give HNO_2 when dissolved in water. Thus not only is N_2O_3 a nitrous acid anhydride, but so also is nitrogen dioxide, which, as is known, may be regarded as a mixed nitrous-nitric anhydride.

Ingold and his co-workers [144] present the dissociation of nitrogen dioxide and nitrous anhydride in the following way:

$$2N_2O_4 + H_2O \leftrightarrow N_2O_3 + 2HNO_3 \tag{60}$$

$$NO + NO_2 \leftrightarrow N_2O_3 \leftrightarrow NO^+ + NO_2^- \tag{61}$$

The nitrous ion NO_2^- attracts a proton, thus facilitating the nitrosating action of the nitrosonium ion NO^+.

In his work on the nitration kinetics, which has already been referred to, Martinsen [145] found that in the nitration of phenol with nitric acid, nitrous acid, if present, acted as a catalyst on the nitration process. The presence of nitrous acid was necessary for initiating the reaction, further quantities being formed in the reaction of oxidation of phenol with nitric acid, which accompanied the nitration reaction. Thus the reaction of nitrating phenol is an autocatalytic one.

Amall [146] inferred from his investigations on the nitration of phenol in an alcoholic or acetic acid solution that nitrous acid was formed only initially as a result of side reactions and then the following reactions took place:

$$HNO_3 + HNO_2 \rightarrow N_2O_4 + H_2O \tag{62}$$

$$C_6H_5OH + N_2O_4 \rightarrow NO_2.C_6H_4.OH + HNO_2 \tag{63}$$

On the basis of Arnall’s experiments, Zawidzki [147] had deduced the following equation for the rate of phenol nitration:

$$\frac{dx}{dt} = k(a-x)(b-x)(c-x)$$

where x is the concentration of nitrophenol just being formed; a, b, c are the initial concentrations of phenol, nitric acid and nitrous acid respectively: (a-x), (b-x), (c-x) are the concentrations of these compounds after the lapse of time t. The reaction rate constant equals k = ca. 0.043.

Klemenc and Schüller [148] have derived the following formula for the rate of nitration (v) with nitric acid:

$$V = k[HNO_3]^{5/2}\,[HNO2]^{\frac{1}{2}}c^2$$

where c is the concentration of the compound being nitrated.

It can be seen from this equation that nitrous acid as an agent increasing the reaction rate is of great importance.

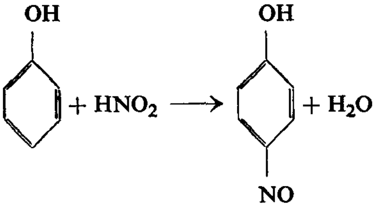
Kartashev [149] has investigated the reaction of phenol with nitric acid in detail. The author assumes the mechanism of the nitration of phenol with nitric acid to be as follows:

(1) In the first stage nitric acid oxidizes phenol and forms nitrous acid.

(2) Nitrous acid reacts with phenol to form nitrosophenol.

(3) Nitrosophenol is oxidized by nitric acid to nitrophenol forming again new quantities of nitrous acid.

$$HNO_3 \rightarrow HNO_2 + O \qquad (64)$$



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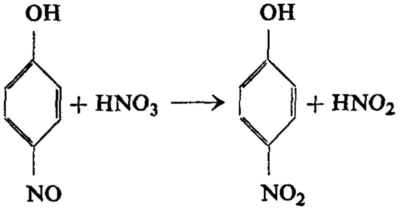
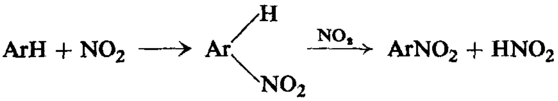


(66)

It has been shown that the addition of nitrous acid lowers the initiation temperature of the reaction; the addition of *p*- nitrosophenol affects the reaction in a similar way. The addition of urea to nitric acid results in lowering the reaction rate. A similar nitration scheme was given by Veibel [150].

Cohen and Wibaut [151] in their work, already mentioned (p. 44), on the nitration of aromatic hydrocarbons with a mixture of nitric acid and acetic anhydride, confirmed the catalytic action of nitrous acid in this case too. As the reaction proceeded the concentration of nitrous acid increased owing to the oxidizing action of nitric acid on the hydrocarbon.

Titov [34] proved, after having investigated a large group of aromatic compounds, including phenols, naphthalene, etc. that pure nitric acid (d 1.40) free from nitrous acid had no nitrating properties at all. The true nitrating agent, the author believed, was NO_2, as mentioned before. Titov's scheme is as follows:



$$ArH + NO_2 \longrightarrow Ar\begin{matrix}H\\NO_2\end{matrix} \xrightarrow{NO_2} ArNO_2 + HNO_2 \qquad (67)$$

lngold and his co-workers [152] when investigating the nitration of phenols and their ethers, came to the conclusion that it was the nitrosonium ion, NO^+, formed as a result of the hypothetical reactions (a) and (b):

$$HNO_2 + HNO_3 \leftrightarrow H_2NO_2^+ + NO_3^- \qquad (a)$$

$$H_2NO_2^+ \leftrightarrow NO^+ + H_2O \qquad (b)$$

$$NO^+ + NO_3^- \leftrightarrow N_2O_4 \qquad (c)$$

that had initiated nitration reactions, eqn. (c) deriving from eqns (a), and (b).

The nitrosonium ion may react according to the equation:

$$ArH + NO^+ \rightarrow ArHNO^+ \rightarrow ArNO + H^+ \qquad (68)$$

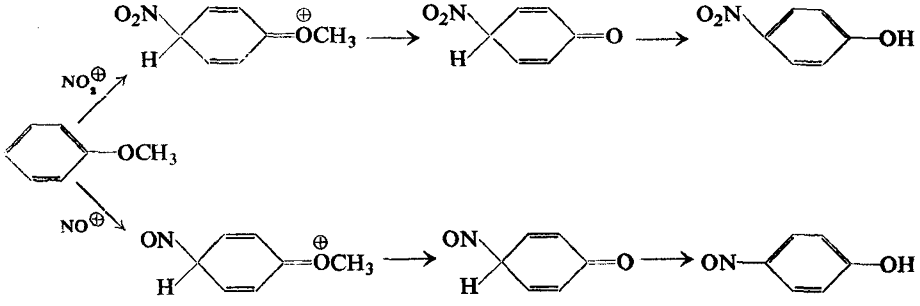
the nitroso compound formed being rapidly oxidized to a nitro compound:

$$ArNO + HNO_3 \rightarrow Ar\text{-}NO_2 + HNO_2 \qquad (69)$$

Schramm and Westheimer [153] have observed that when a phenyl ether such as anisole is nitrated, the presence of nitrous acid is also necessary. The authors believed nitrosoanisole was formed as an intermediate product as in the nitration of phenol. Their assumption was based on the fact that *p*- nitrosoanisole yields nitration products identical to those given by anisole, viz. nitroanisoles and 2,4-dinitrophenol. Thus, beside the nitration, a partial break-down of the ether bond takes place.

A partial dearylation of diarylether during nitration had already been observed by Reilly, Drumm and Barrett [154]. The dealkylation, observed by Schramm and Westheimer, has been confirmed by Ingold and his co-workers [152]. For example *p*- chloroanisole, when nitrated with a 6N solution of nitric acid in the presence of acetic acid at 20°C gave 4-chloro-2-anisole in 66% yield and 4-chloro-2,6-dinitrophenol in 33% yield of theory.

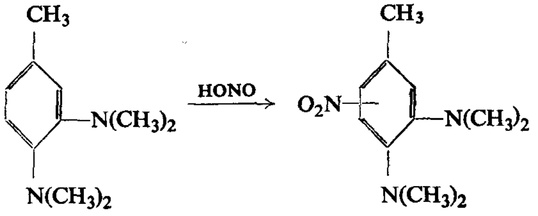
Simultaneously the methyl group, after being split off from *p*- chloroanisole, formed methyl acetate. Cook and Bunnett [155] have tried to explain the phenomenon of splitting off the methyl group as the result of the formation of a transient oxonium ion, which, as is known, is able to give off an alkyl radical:



On the other hand Ingold and co-workers [144,155a] have proved that the presence of nitrous acid in the nitrating acid decreases the rate of nitration of aromatic compounds in general with the exception of phenols. The same holds true for phenyl ethers (e.g. anisole) which are more difficult to nitrate with higher concentrations of nitric acid in acetic acid (e.g. 8N) in the presence of nitrous acid, whereas with a less concentrated nitric acid (e.g. 5N), nitrous acid accelerates the reaction.

Nitrous acid itself can act as a nitrating agent. This was noticed for the first time by Niementowski [156] and Koch [157].

Niementowski reacted sodium nitrite with a solution of 3,4-bis(dimethylamine)-toluene in acetic acid and obtained a nitro derivative:



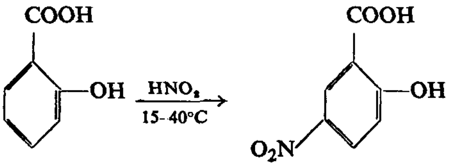
(70)

m. p. 63°C

Similarly Koch prepared chloronitrodimethylaniline by acting with a stoichiometric quantity of sodium nitrite on an acid solution of *p*- chlorodimethylaniline. Pinnov and Schuster [158] confirmed his results.

A number of other authors have also nitrated aromatic amines, acting with sodium nitrite on the amine dissolved in hydrochloric or acetic acid. Thus, triphenylamine and its methyl derivative in acetic acid were nitrated by Häussermann and Bauer [159], and Rupe, Braun and Zembruski [160] and Tsuruta and Oda [161] nitrated derivatives of dimethylaniline in hydrochloric acid to yield mononitro products.

Deninger [162] discovered that salicylic acid can be nitrated with nitrous acid to yield mononitrosalicylic acids :



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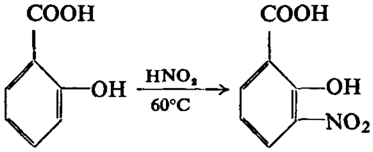
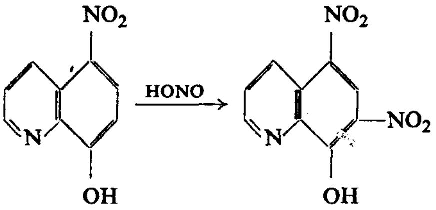


(72)

T. Urbanski and Kutkiewicz [70] found that 5-nitro-8-hydroxyquinoline, when boiled with a solution of sodium nitrite in 10% hydrochloric or sulphuric acid, yielded 5,7-dinitro-8-hydroxyquinoline:



(73)

The sodium nitrite is used in an excess. The yield of dinitro-8-hydroxyquinoline obtained amounts to about 30% (cf. also the reaction 7, p. 85). The mechanism of this reaction cannot consist in the formation of a nitroso compound which would be oxidized to a nitro compound, as no nitrosation of a nitrophenol is known.

NITROUS ACID IN THE PRESENCE OF HYDROGEN PEROXIDE

Hydrogen peroxide reacts with nitric and nitrous acids to form the corresponding pernitric acids, of which pernitrous acid is a better defined compound. Baeyer and Williger [163] reported the possibility of obtaining it by reacting ethylhydroperoxide with alkyl nitrate. Raschig [164] has studied the action of hydrogen peroxide on nitrous acid and found such a mixture to be a more powerful oxidizing agent than each of the components taken separately.

Raschig was not correct in ascribing the structure of pernitric acid, HNO_3, to the product of reaction of H_2O_2 with HNO_2. Schmidlin and Massini [165] have proved it to be a pernitrous acid HO-ONO. Extensive studies on pernitrous acid have been carried out by Trifonov [166], who found that hydrogen peroxide when reacted with nitrous acid formed the peroxide, N_2O_6, which gave nitrous acid under the influence of water, the solution appearing yellow for a while.

Kortüm and Finckh [I67] found the absorption spectrum of the yellow solution was similar to that of the nitrate ion, showing however some difference.

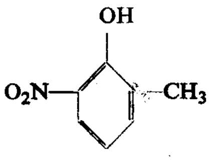
The kinetics of the reaction of nitrous acid with hydrogen peroxide have been studied by Shills, Rybakov and Pal [168], Shilov and Stepanova [169] and Halfpenny and P. L. Robinson [170].

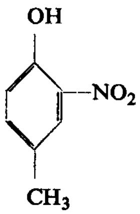
The experiments so far performed have sometimes been contradictory, but they have led to the conclusion that pernitrous acid does exist.

Nitration with pernitrous acid. The first investigations into the nitration of benzene with per-nitrous acid were performed by Trifonov [166]. In 1922 he found *o*- nitrophenol to be the reaction product and suggested the application of the reaction for detecting benzene and other aromatic hydrocarbons. His results were confirmed by the experiments of Halfpenny and P. L. Robinson [170].

It has been shown that aromatic hydrocarbons can be nitrated by pernitrous acid even at very low acid concentrations (e.g. 2%) at room temperature. The hydroxylation of the hydrocarbon takes place simultaneously in many cases. A characteristic feature of the reaction is that the nitro group mostly takes the *meta* position with respect to the substituent already present. If a nitro and a hydroxyl group are introduced simultaneously the hydroxyl group nearly always takes the *ortho* or *para* position with respect to the substituent already present. Diphenyl derivatives are also formed.

Toluene also yields nitro derivatives of *o*- and *p*- cresol besides nitrotoluenes and benzaldehyde :



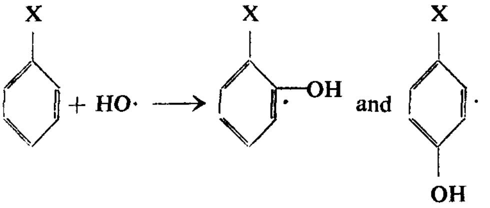


Nitrobenzene gives *m*- dinitrobenzene along with small quantities of the *ortho*- and *para*- isomers, a mixture of *o*-, *m*- and *p*- nitrophenols and a small quantity of 3,3'-dinitrodiphenyl.

Chlorobenzene is converted mainly into *m*- chloronitrobenzene and *o*- chlorophenol and 2-nitro-4-chlorophenol are also formed.

The yield of nitro compounds is, however, not high and does not generally exceed 10%. The method is therefore not of practical importance as yet, although it is interesting from the theoretical point of view. A high dilution of nitrous acid during nitration provides evidence that the nitronium ion cannot be the nitrating agent in the reaction. Halfpenny and Robinson assume the nitration does not take place through nitrosation and oxidation as in the case of nitrophenols (p. 117), and they advance the hypothesis that the nitrating action of pernitrous acid consists in the formation of a free aromatic radical, which reacts with nitrogen dioxide, split off from the pernitrous acid:

$$\mathrm{HOONO} \rightarrow \mathrm{HO}^{*} + {}^{*}\mathrm{NO_2} \tag{74}$$



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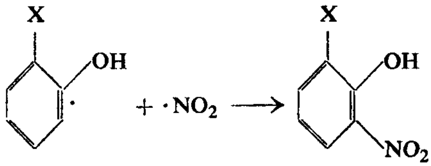


(76)

Nitrous esters can react with alkyl peroxides to yield alkyl nitrates [163,221] (see also Vol. II).

ORGANIC COMPOUNDS AS NITRATING AGENTS

NITRIC ACID ESTERS

Nitric acid esters can be used as nitrating agents in the presence of sulphuric acid and in some cases in a strongly alkaline medium.

Nitric esters in mixtures with sulphuric acid. Raudnitz [171] was the first to draw attention to the nitrating properties of solutions of ethyl nitrate in sulphuric acid. Later in 1941, Titov [34] expressed the view that such a solution contains the nitronium ion, and L. P. Kuhn (p. 15) proved this by cryometric measurements. A solution of ethyl nitrate in sulphuric acid has been used for nitrating aromatic compounds.

The application of other nitric acid esters is also possible. Thus, Bucherer [172] suggested the use of a solution of nitrocellulose in sulphuric acid to nitrate benzene to nitrobenzene, while Plaiek and Ropuszyliski [173] suggested solutions of nitric esters of polyalcohols, such as nitroglycerine, nitromannite, pentaerythritol tetranitrate, for nitration of aromatic hydrocarbons. Ropuszyliski [174] recently investigated the action of a solution of nitroglycerine in sulphuric acid more fully and inferred that decomposition of nitroglycerine by sulphuric acid to form a nitronium ion was probably taking place by stages:

$$C_3H_5(ONO_2)_3 + H_2SO_4 \leftrightarrow C_3H_5(ONO_2)_3H^+ + HSO_4^- \qquad (77)$$

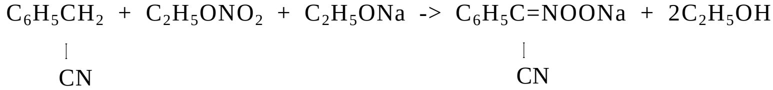
$$C_3H_5(ONO_2)_3H^+ \leftrightarrow C_3H_5(OH)(ONO_2)_2 + NO_2^+ \qquad (77a)$$

With an excess of sulphuric acid, glycerine dinitrate was decomposed to give further nitronium ions, etc. Finally a double ester nitric and sulphuric of glycerol was formed :

$$C_3H_5(OH)_2(ONO_2) + H_2SO_4 \rightarrow C_3H_5(OH)(ONO_2)(OSO_3H) + H_2O \qquad (77b)$$

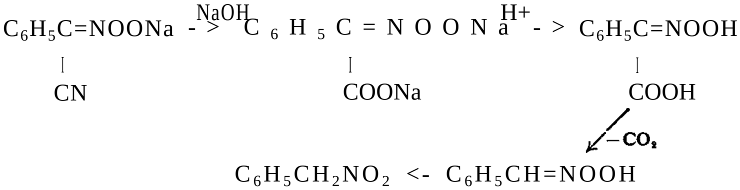
Nitric esters in alkaline medium. In some instances compounds containing an active methylene group can be nitrated with nitric esters in the presence of sodium alcoholates. This is a generally known method for obtaining phenylnitromethane from benzyl cyanide (Wislicenus and Endres [175] ; Meisenheimer [175a]).

The reaction proceeds as follows:



$$\underset{\text{CN}}{\underset{|}{C_6H_5CH_2}} + C_2H_5ONO_2 + C_2H_5ONa \rightarrow \underset{\text{CN}}{\underset{|}{C_6H_5C}}{=}NOONa + 2C_2H_5OH$$

(78)

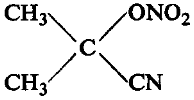


$$\underset{\text{CN}}{\underset{|}{C_6H_5C}}{=}NOONa \xrightarrow{NaOH} \underset{\text{COONa}}{\underset{|}{C_6H_5C}}{=}NOONa \xrightarrow{H^+} \underset{\text{COOH}}{\underset{|}{C_6H_5C}}{=}NOOH$$

$$C_6H_5CH_2NO_2 \leftarrow C_6H_5CH{=}NOOH \quad (-CO_2)$$

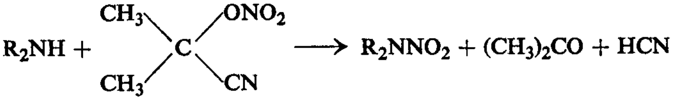
(78a)

The use of acetone cyanohydrin nitrate has recently been proposed for reactions of this type:



(Anbar, Dostrovsky, Samuel and Yoffe [176]; Emmons [177]; Emmons and Freeman [178]).

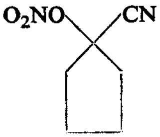
The advantage of this compound over simple alcohol esters is that the O-N bond is weakened by the highly electronegative nitrile group. Besides, the compound does not contain α– atoms of hydrogen and in this way the oxidation to an aldehyde or ketone by the NO_2 groups can be avoided. According to Emmons, McCallum and Freeman [179], this reagent has proved to be particularly useful in the nitration of amines:



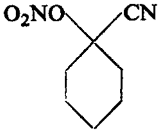
(79)

The yield amounts to 80% for the nitration of secondary amines, and 60% for primary ones.

Nitrates of cyclopentanone or cyclohexanone cyanohydrin (I and II) may also be nitrating agents.



I



II

ACYL NITRATES (MIXED ANHYDRIDES)

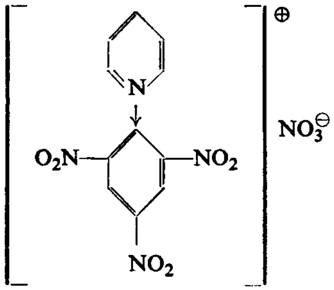
Acyl nitrates are rather powerful nitrating agents. The simplest of them, acetyl nitrate, CH_3COONO_2 (b. p. 22°C at 70 mm Hg), is formed by reacting acetic anhydride with N_2O_5. It is presumably present in nitrating mixtures consisting of nitric acid and acetic anhydride (Pictet and Khotinsky [180]). The aromatic hydrocarbons are nitrated to mononitro derivatives in a yield close to theoretical. Toluene was nitrated to a mixture of 88% of *o*- and 12% of *p*- nitrotoluene and phenol to a mixture of 51% *o*- and 48% *p*- nitrophenol. Mononitro compounds are not nitrated further to dinitro derivatives by acetyl nitrate.

Benzoyl nitrate $C_6H_5COONO_2$ (prepared by reacting silver nitrate with benzoyl chloride) can in certain cases be a useful nitrating agent (Francis [181]). For example, thiophene is nitrated with this compound in theoretical yield, while if conventional methods are used, only a low yield is obtained and this only with great difficulty.

NITRATES OF SOME ORGANIC BASES

Battegay and Brandt [181a] succeeded in nitrating anthracene to 9-nitroanthracene with 70% yield by heating anthracene with pyridine nitrate and excess of pyridine to 125°C. Naphthalene was nitrated to a-nitronaphthalene (40% yield) at 130°C in presence of zinc chloride.

Okoli [181b] has prepared picrylpyridinium nitrate I by acting on picrylpyridinium chloride with nitric acid or metal nitrates:



I (m.p. 103-105°C)

Okon and Hermanowicz [181c] have found that the nitrate I can serve as a nitrating agent.

Thus the authors prepared α– nitronaphthalene from naphthalene with the yield of 80% by warming I with naphthalene. In a similar way toluene was nitrated at 80°C to 2,4-dinitrotoluene (yield 65%). By warming chloroform with I at 40-50°C chloropicrine resulted with the yield of *ca.* 30%.

ALIPHATIC NITRO COMPOUNDS

Some nitro compounds (C-nitro compounds and nitramines-N-nitro compounds) can serve as nitrating agents.

Tetranitromethane and hexanitroethane

In the presence of alkalis, tetranitromethane shows nitrating properties. This is explained by the fact that alkalis decompose it by splitting off the nitro group and giving rise to nitroform (more exactly to its salt), according to the reaction (Hantzsch and Rinckenberger [182]) :

$$C(NO_2)_4 + 2KOH \rightarrow KNO_3 + KC(NO_2)_3 + H_2O \qquad (80a)$$

Apart from this, other, more complex side reactions take place, involving oxidation-reduction processes and a complete decomposition of the substance with the formation of nitrite and CO_2 (E. Schmidt [183]) :

$$C(NO_2)_4 + 6KOH \rightarrow 4KNO_2 + K_2CO_3 + 3\ H_2O \qquad (80b)$$

The main reaction may be expressed by the equation:

$$C(NO_2)_4 + KOH \rightarrow KC(NO_2)_3 + HNO_3 \qquad (80c)$$

in which the transient formation of nitric acid is acknowledged.

Nitration with tetranitromethane is carried out mostly in the presence of pyridine which with nitroform forms a crystalline addition product.

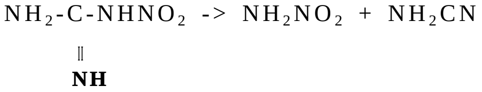
Hexanitroethane may be used as a nitrating agent in a similar way (for example, Alsop and Kenner [184]).

Nitroguanidine

Davis and Abrams [184a] have observed that aromatic compounds easy to nitrate such as phenol, acetanilide, etc. can be nitrated by a freshly prepared solution of nitroguanidine in sulphuric acid.

There is no evidence that a solution of nitroguanidine in sulphuric acid contains free nitric acid, although the solution turns diphenylamine blue and reacts with mercury, thus behaving identically like nitric acid. It is estimated that nitric acid can be formed only in the presence of compounds that are readily nitrated.

According to this view, nitroguanidine decomposes in the presence of sulphuric acid to give nitramine (eqn. 81), which is hydrolysed in the presence of substances convertible to nitro compounds to form ammonia and nitric acid (eqn. 81):

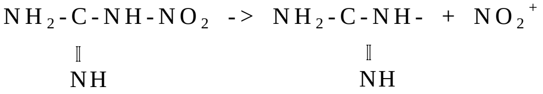


$$NH_2\text{-}\underset{\underset{NH}{\|}}{C}\text{-}NHNO_2 \rightarrow NH_2NO_2 + NH_2CN \qquad (81)$$

$$NH_2NO_2 + H_2O \rightarrow NH_3 + HNO_3 \qquad (82)$$

The presence of cyanamide, NH_2CN, in the solution after nitration, as stated by Davis and Abrams, may serve as evidence confirming the above view.

More convincing, however, is the hypothesis that in nitroguanidine, under the influence of sulphuric acid, a loosening of the nitrogen atoms bond takes place, and a nitro group in the form of a nitronium ion breaks off:



$$NH_2\text{-}\underset{\underset{NH}{\|}}{C}\text{-}NH\text{-}NO_2 \rightarrow NH_2\text{-}\underset{\underset{NH}{\|}}{C}\text{-}NH\text{-} + NO_2^+ \qquad (83)$$

Some of the primary nitramines have similar properties and can act as nitrating agents. However, no systematic studies on the subject have been reported in the literature as yet.

NITRATION UNDER INFLUENCE OF GAMMA RADIATION

It has recently been found by Mint and his co-workers [185] that nitration of benzene occurs when benzene in an aqueous solution of calcium nitrate is irradiated with gamma rays. The yield is up to 45% of nitrobenzene and a certain amount of picric acid is also formed. Mint suggested the formation of the nitronium ion. through the following sequence of reactions:

$$NO_3^- + H \rightarrow NO_2^- + OH \rightarrow NO_2 + OH^- \qquad (a)$$

$$NO_2 + OH \rightarrow NO_2^+ + OH^- \qquad (b)$$

Nitration would proceed as (c) in accordance with the radical mechanism or as (d) assuming an ionic mechanism:

$$*C_6H_5 + NO_2 \rightarrow C_6H_5NO_2 \qquad (c)$$

$$C_6H_6 + NO_2^+ \rightarrow C_6H_5O_2 + H^+ \qquad (d)$$

The radical, $*C_6H_5$, would be formed through the reaction between benzene and OH or HO_2 radicals.

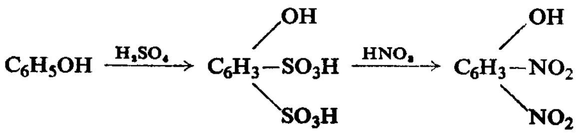
Falecki, Mint, Slebodziliski and T. Urbanski, [185a] have also found that paraffin hydrocarbons dissolved in dinitrogen tetroxide are nitrated at 28°C when they are subjected to irradiation with gamma rays. The yield for n-hexane was up to 15% of non-gaseous products of both nitration and oxidation. The characteristic feature of the reaction differentiating it from nitration at elevated temperature described above (p. 94) is the fact that no pyrolysis of the hydrocarbon occurs, and therefore long chain paraffins are not so readily split into shorter fragments as it occurs at high temperature. The authors also found that n-hexane reacts with dinitrogen tetroxide at 28°C without irradiation. However, the yield of non-gaseous products is lower ***(ca.*** 8%) and the products containing nitrogen are mainly nitrous esters. This would suggest that N_2O_4 probably forms ions NO_2^+ or $*NO_2$ radicals under the action of irradiation. Without irradiation a considerable amount of nitrite ions ONO^- are present and these are responsible for the formation of nitrous esters.

INDIRECT METHODS OF INTRODUCING A NITRO GROUP

It has already been mentioned (p. 5) that indirect methods of introducing a nitro group are used in many cases.

SUBSTITUTION OF SULPHONIC GROUPS

Sulphonation of compounds followed by substituting the sulpho group by a nitro group is the method of great practical importance. This method is widely used for the nitration of phenols. The reaction occurs as follows:



$$C_6H_5OH \xrightarrow{H_2SO_4} C_6H_3{-}\overset{OH}{\underset{SO_3H}{SO_3H}} \xrightarrow{HNO_3} C_6H_3{-}\overset{OH}{\underset{NO_2}{NO_2}} \qquad (84)$$

Owing to this course of the reaction the oxidation of phenols and the formation of side-products can be largely avoided. This is discussed in more detail in the chapter on the nitration of phenols (p. 502).

Another method, of great importance in laboratory practice, is the substitution of a halogen by a nitro group.

SUBSTITUTION OF HALOGEN

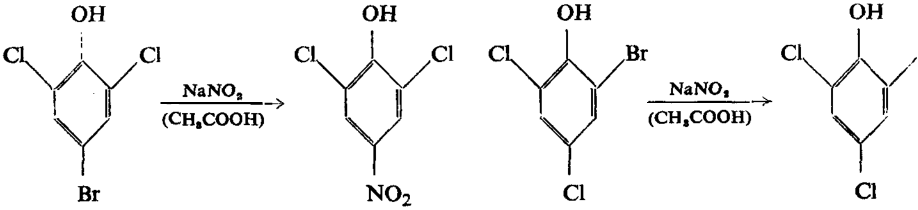
In laboratory methods for the preparation of aliphatic nitro compounds, the V. Meyer reaction [186] consisting in reacting alkyl iodides or bromides with silver nitrite, is widely used. As is well known, the reaction can proceed in two directions, resulting in the formation of a certain quantity of a less stable nitrous ester besides a nitro compound. Instead of silver nitrite mercuric nitrite may be used (Ray[187]).

Kornblum and his co-workers [188, 188a] have recently improved the method used for the preparation of nitroparaffins with longer aliphatic chain (over C_8). They reacted an alkyl chloride with sodium nitrite in the solvent (dimethylformamide) for several hours at low temperature, obtaining a homogeneous solution:

$$RCH_2Cl + NaNO_2 \rightarrow RCH_2NO_2 + NaCl \tag{85}$$

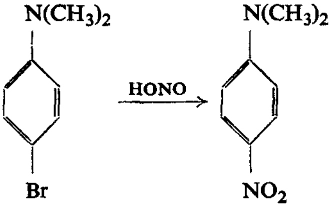
The addition of urea to the reacting system prevents side reactions, e.g. the formation of nitrous esters. The yield amounts to about 60%.

In aromatic compounds such a reaction is possible only in the case of polybromo- or polyiodo-derivatives of phenol. Sodium nitrite and acetic acid may be used for replacing one of the Br or I atoms by the nitro group (Zincke [189], Raiford [190-193]):



(86)

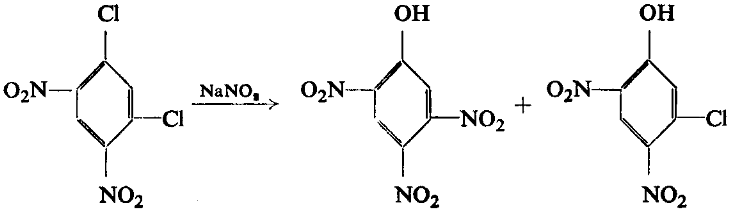
Not only salts of nitrous acids but also nitrous acid itself can replace halogen by the nitro group. This has been discovered by Wuster and Scheibe [194] when they reacted sodium nitrite with bromodimethylaniniline in hydrochloric acid:



(87)

In addition, a certain quantity of bromonitrosodimethylaniline was formed.

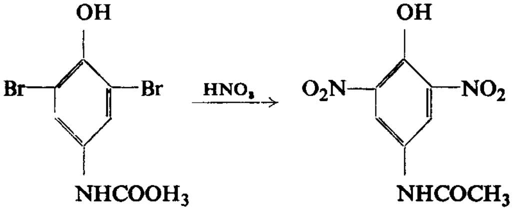
An interesting case of introducing the nitro group, accompanied by hydrolysis, was reported by Leandri [195] :



(88)

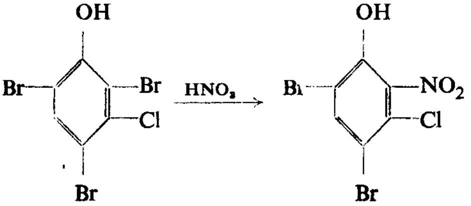
When halogenated phenols or phenolic ethers are nitrated with nitric acid a halogen *o*- or *p*- to hydroxyl or alkoxyl group can also be replaced. The ease of replacement appears to be in the order Cl< Br<I.

A typical and the oldest example was given by P. W. Robertson [195a]:



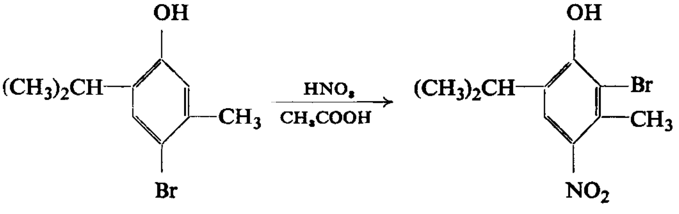
(89)

Hodgson and Smith [196] give an example which indicates the mobility of various halogen atoms:



(90)

Sometimes the free halogen liberated in this displacements itself enters the aromatic ring, thus giving rise to an apparent substitution. Thus P. W. Robertson [196a] and P. W. Robertson and Briscoe [196b] found that 6-bromothymol on nitration in dilute acetic acid gives 2-bromo-6-nitrothymol:

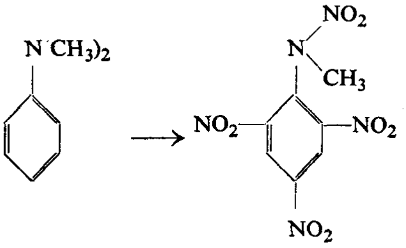


(91)

Aliphatic nitro compounds may be obtained in the well known Kolbe reaction [197] by acting with sodium nitrate on α– halogen fatty acids. During the substitution the carboxyl group splits off.

OTHER NITRATION REACTIONS BY SUBSTITUTION

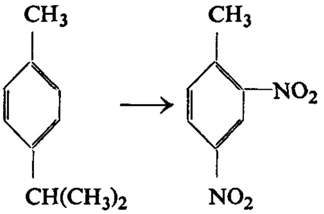
An alkyl group is sometimes replaced by a nitro group. This happens particularly when nitrating amines to nitramines. As a classical example, the formation of trinitrophenylmethylnitramine (tetryl) from dimethylaniline can be mentioned: (Vol. III)



Tetryl

(92)

Some branched alkyl groups, especially the isopropyl group, can readily be replaced by a nitro group, even when they are attached to an aromatic ring. For example, under certain nitration conditions thymol ethers can yield the corresponding trinitro-m-cresol ethers (Giua [198]). Similarly, the nitration of *p*- cymene may lead to dinitrotoluene (Alfthan [199]):



(93)

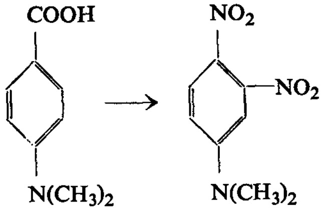
The nitration reaction that consists in replacing a hydroxyl group by a nitro group is not often used. It is usually applied to tertiary alcohols. For example, tert-butyl alcohol (trimethylcarbinol) reacted with nitric acid to yield tert-nitrobutane in 10% yield in relation to the alcohol weight (Haitinger [4]):

$$(CH_3)_3COH \xrightarrow{HNO_3} (CH_3)_3CNO_2 \qquad (94)$$

In the aliphatic series the substitution of a carboxyl group by a nitro group can only be accomplished with a small yield. gem-Dinitropropane, for example, is obtained from isobutyric acid (Bredt [200]):

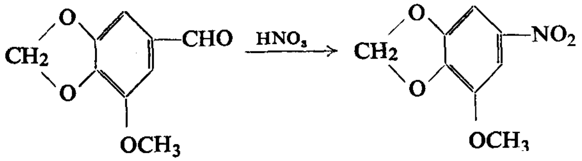
$$(CH_3)_2CHCOOH \xrightarrow{HNO_3} (CH_3)_2C(NO_2)_2 \qquad (95)$$

In the aromatic series such a reaction is more often observed. For example, *p*- dimethylaminobenzoic acid can be nitrated to 2,4-dinitrodimethylaniline (Reverdin [201]) :



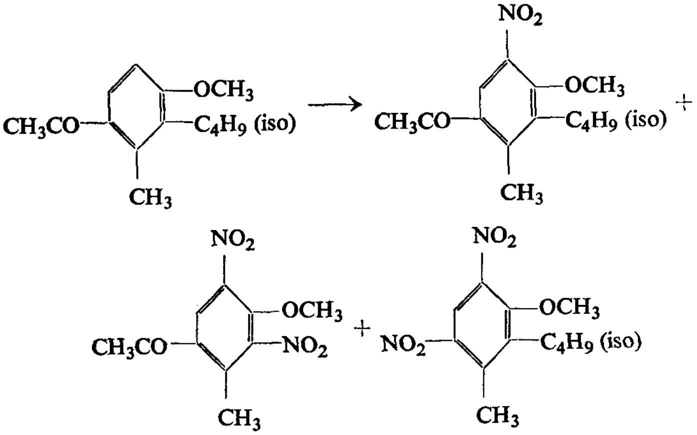
(96)

An aldehyde group can be replaced by a nitro group as shown by Salway [202] and Harding [202a]:



(97)

A ketone group can also be replaced by a nitro group along with an alkyl group (Barbier [203]) :

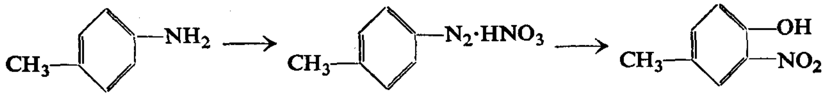


(98)

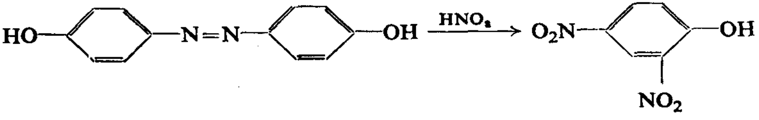
A new type of substitution of the chloromercuric group described by Ogata and Tsuchida [140] has been already mentioned (p. 118).

The substitution of a primary amino group by a nitro group generally occurs by diazotization and the Sandmeyer reaction. (“Körner and Contardi reaction“) [222].

In certain cases, diazonium salt nitrates, when boiled in aqueous solution, are converted to nitrophenols. For example p-toluidine, when diazotized in nitric acid solution, forms nitro-p-cresol after the solution had been brought to the boil (Nölting and E. Wild [203a]):

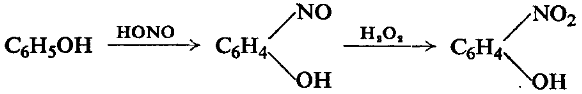


An azo group can be replaced by nitro group on nitration (P. W. Robertson [204])



INTRODUCING THE NITRO GROUP BY OXIDATION

In addition to the nitration of phenols by substitution of sulpho groups (p. 130) the method of nitrosation of phenols, followed by oxidation of the nitroso to the nitro group has some practical application:



$$C_6H_5OH \xrightarrow{HONO} C_6H_4\begin{matrix}NO\\OH\end{matrix} \xrightarrow{H_2O_2} C_6H_4\begin{matrix}NO_2\\OH\end{matrix} \qquad (101)$$

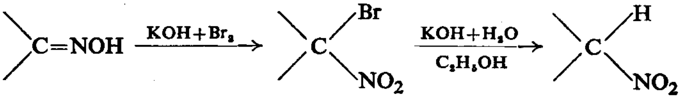
The method is used for those readily nitrated phenols (e.g. resorcinol), when less nitro groups are to be introduced than is possible in the direct nitration (Kostanecki and Feinstein [205]).

Oxidation of diazo compounds may result in the formation of nitramines, for example, phenylmtramine :

$$C_6H_5N{=}NOK \xrightarrow{K_3Fe(CN)_6} C_6H_5NK{\cdot}NO_2 \xrightarrow{HCl} \underset{\text{Phenylnitramine}}{C_6H_5NHNO_2} \qquad (102)$$

This is one of the reactions which were used to prove that nitramines are compounds with the nitro group attached to the nitrogen atom.

A nitro group may also be introduced by the oxidation of oximes. For this, salts of hypobromous acid are generally used. This method is sometimes applied for the preparation of aliphatic nitro compounds. The reaction proceeds in the following way (Forster [206], Cherkasova and Mehrikov [207], Iffland *et al.* [208]):



(103)

Iffland and Criner [209] have improved the method. They obtained nitrocyclohexanone from cyclohexanone in about 50% yield, using N-bromosuccinimide as an oxidizing and brominating agent.

Introducing a nitro group by oxidation of a primary amino group. The method of oxidizing a primary amino group to a nitro group is sometimes used commercially. A nitroso compound is an intermediate product of the reaction and it can generally be isolated :

$$-NH_2 \rightarrow -NO \rightarrow -NO_2$$

The oxidation is carried out by means of the so-called Caro's acid (H_2SO_5), which is prepared by reacting sulphuric acid with persulphuric acid salts, or by reacting concentrated hydrogen peroxide with sulphuric acid.

In this way nitrosobenzene may be obtained from aniline, as has been shown by Bambergcr and Tschirner [220]. Nitrosobenzene may then be oxidized to nitrobenzene.

Page and Heasman [210] obtained 3,6- (or 2,5-) dinitrotoluene by reacting Caro’s acid with 5-nitro-o-toluidine. Brady and Williams [211] used the same method for the preparation of 2,3,4- and 2,4,5-trinitrotoluencs from 3,4- or 4.5-dinitro-o-toluidine. Holleman [211a] also used this method for the last stage of the preparation of tetranitrotoluene (p. 339).

In this way nitro derivatives of anthraquinone are prepared on an industrial scale from corresponding derivatives of aminoanthraquinonc (Kopetsehni [212]; Mosby and Berry [213]). This is rather advantageous since pure individuals are obtained instead of the mixtures of isomers which would be formed if anthraquinone were nitrated.

Aminopyridines are especially convenient as a starting material for the preparation of nitropyridines by oxidizing the amino group. Kirpal and Böhm [214] have obtained 2-nitro- and 4-nitro-pyridines by this method.

Among other oxidizing agents which can be used for the conversion of the amino group to the nitroso and nitro group the following compounds should be mentioned: peracetic acid (D'Ans and Kneip [215], Greenspan [216], Mosby and Berry [213]), an aqueous solution of sodium peroxide (O. Fischer, Trost [217]), and an acid solution of ammonium persulphate with addition of silver nitrate as a catalyst (Witt and Kopetschni [218]).

Emmons [177] has recently suggested the oxidation of anilines to nitrobenzenes by trifluoroperacetic acid ($CF_3.COOOH$). He obtained high yields, for example:

TABLE 14

Substrate	Product
Aniline	89% of nitrobenzene
o- Nitroaniline	92% of *o*- dinitrobenzene
p- Nitroaniline	94% of *p*- dinitrobenzene
p- Phenylenediamine	86% of *p*- dinitrobenzene
p- Toluidine	78% of *p*- nitrotoluene
2,4-Dinitroaniline	87% of 1,2,4-trinitrobcnzene

2,4,6-Tribromo- and -trichloro-aniline give nearly theoretical yields of 2,4,6-tribromo- and -trichloro- 1- nitrobenzene (100% and 98% respectively).

The method of conversion of an amino into a nitro group has not found application in the nitration of aliphatic amines, since only insignificant yields of nitroso and nitro compounds could have been obtained together with considerable quantities of oxidation products. For example, ethylamine, reacted with Caro's acid, yields, according to Bamberger [219], the following products: acetic acid, as the principal product and along will1 it small quantities of nitroethane, acetohydroxamic acid, acetoxime and acetonitrile. If an amino group is attached to a tertiary alkyl carbon, higher yields of nitroso compounds can be obtained. Thus, tert-butylamine gives oxime in good yield, and then nitroso-tert-butane is obtained (Bamberger and Tschirner [220]).

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CHAPTER IV

NITRATION WITH NITRATING MIXTURES

NITRATING MIXTURES

COMPOSITION OF NITRATING MIXTURES

THE composition of a nitrating mixture should be chosen very carefully with regard to the compound being nitrated and the number of nitro groups to be introduced. It is clear that the more nitro groups to be introduced, the higher the acid concentration should be.

The nitration of aromatic compounds is carried out with only a slight excess of nitric acid. This is smaller when lower nitrated compounds are prepared (0.2-5% of HNO_3 in excess of the calculated weight) and larger when higher nitrated compounds are to be obtained (3-100% or more in excess of the calculated weight of HNO_3).

The ratio of the quantities of components of the nitrating acid, HNO_3, H_2SO_4 and H_2O, is also important. The fact that water is formed during the nitration process, thus diluting the nitrating mixture, must be taken into consideration. Since among the components of the mixture, sulphuric acid is the principal one which binds water, the amount of H_2SO_4 must be chosen in such a proportion that it can take up all the water formed during the nitration. Otherwise nitration might be incomplete.

The concentration ratio, or the so-called *spent acid strength* or *dehydrating value of sulphuric acid* (D. V. S.) is of importance:

$$\text{D.V.S.} = \frac{[H_2SO_4]}{[H_2O]_i + [H_2O]_f}$$

where: $[H_2O]_i$ is the initial concentration of water in the nitrating mixture before nitrating and $[H_2O]_f$ is the concentration of water formed during nitration.

For example, if benzene is being nitrated according to the equation:

$$\begin{array}{lccccccccc} & C_6H_6 & + & HNO_3 & \rightarrow & C_6H_5NO_2 & + & H_2O & & (1) \\ \text{mol. weight} & 78 & & 63 & & 123 & & 18 & & \end{array}$$

with a mixture:

HNO_3	32%
H_2SO_4	60%
H_2O	8%

then for each 100 kg of mixed acids, i.e. for 32 kg of HNO_3, x kg of water is formed.

$$x = \frac{18 \text{ x } 32}{63} = 9.14 \text{ kg} = [H_2O]_f$$

hence

$$\text{D.V.S.} = \frac{60}{8 + 9.14} = 3.50$$

This is the "theoretical" value of D.V.S. In practical work allowance should be made for the presence of the excess of HNO_3 used. The above calculations may be made with theoretical reference to either hydrocarbon or nitric acid. When 95% of the theoretical hydrocarbon is used, the hydrocarbon factor is calculated. :

$$\frac{C_6H_6}{HNO_3} = \frac{78}{63} = 1.24$$

Hydrocarbon factor = 1.24 x 95% = 1.18

Water of nitration per 100 kg of hydrocarbon is $= \frac{18\text{x}100}{78} = 23.08$

HNO_3 used in the mixed acid is:

1.18*32 = 37.76 kg HNO_3 per 100 kg of mixed acid.

Hence the water of nitration per 100 kg of mixed acid $= \frac{37.76 \text{ x } 23.08}{100} = 8.71$

$$\text{D.V.S.} = \frac{60}{8 + 8.71} = 3.59$$

Instead of 95% of hydrocarbon, 105% of nitric acid can be used:

$$\frac{HNO_3}{C_6H_6} = \frac{63}{78} = 0.808$$

Nitric acid factor = 0.808 x 105% = 0.848.
HNO_3 used in mixed acid is:

$$\frac{32}{0.848} = 37.74 \text{ kg } HNO_3 \text{ per 100 kg of mixed acid.}$$

This gives approximately the same figure for the water of nitration per 100 kg of mixed acid:

$$\frac{37.74 \text{ x } 23.08}{100} \; 8.71 \text{ and D.V.S.} = 3.59$$

(according to Groggins [1]).

The D.V.S. should be as high as possible. For example if benzene is nitrated with two acid mixtures A and B, both containing the same quantity of water but having different D.V.S. values, nitration with the A mixture, for which D.V.S.

= 2.96, is incomplete, while with the B mixture, where D.V.S. = 3.5, results in complete nitration. The mixtures have the following composition:

A HNO_3 38.0%, H_2SO_4 54.0%, H_2O 8.0%
B HNO_3 32.0%, H_2SO_4 60.0%, H_2O 8.0%

The nitrating acid and its weight should also be carefully chosen so as to obtain a spent acid with a composition corresponding, where possible, to the lowest solubility of the nitration product in it.

In the U.S.S.R., the D.V.S. is often named the *coefficient of dehydration and* a slightly different way of calculating the nitric composition of sulphuric acid mixtures is in use there. This is *F* or “f.n.a.“, the *factor of nitrating activity* suggested by Kholevo. According to Gorst [2], it is the concentration of sulphuric acid in the mixture when the nitric acid is converted into the equivalent quantity of water.

Here is the method of calculating *F* according to the same author.

Let the symbols S, ***N, S’*** denote the following:

S - % concentration of H_2SO_4 in the mixture
N - % concentration of HNO_3 in the mixture used for nitration
S’ - % concentration of H_2SO_4 in the spent acid, when all the nitric acid ***N*** is used and from 1 mol. of HNO_3 1 mol. of H_2O is formed.

One kg of HNO_3 yields z = 0.286 kg of H_2O.

The weight of the nitrating mixture is therefore reduced by 1-0.286 = 0.714 kg for every kg of HNO_3. The reduction of the weight of 100 kg is 0.714 N.

The concentration of H_2SO_4 in the spent acid ***S’*** will be:

$$S' = \frac{100\ S}{100-0.714\ N}$$

or

$$S' = \frac{140\ S}{140-N}$$

The expression for is:

$$\Phi = \frac{140\ S}{140-N}$$

or

$$\Phi = \frac{S}{1-\frac{N}{140}}$$

It is not advisable to use a high value of the factor of nitrating activity *F* for economic reasons. Nor should low *F*, be applied as this leads to incomplete utilization of the nitric acid in the nitrating mixture.

Orlova [3] gives a number of examples of the values of *F* and of the quantity of HNO_3 used during the nitration (Table 15).

When F (the quantity of sulphuric acid in the spent acid) is given, it is easy to calculate the quantity of sulphuric acid to be used.

If G_N is the quantity (in kg) of nitric acid of concentration N (% HNO_3) and G_s is the quantity (in kg) of sulphuric acid of concentration S (% HNO_3), the quantity of the spent acid can be expressed as:

$$G_S + G_N \frac{100-0.714\,N}{100}$$

TABLE 15

Nitration	F	Quantity of HNO_3 in % of theory
Benzene to NB	70	103-105
NB to DNB	88	110-115
Toluene to MNT	70	103-105
MNT to DNT	82	110-115
DNT to TNT:		
in the three stage process	93	180-200
in the two stage process	87	170-l 80
Xylene to DNX	72	110-115
DNX to TNX	90	150-160
Naphthalene to MNN	61	103-105
MNN to DNN	72	130-140

Notation: NB - nitrobenzene., DNB - dinitrobenzene, MNT - mononitrotolueoe. DNT - dinitrotoluene, TNT - trinitrotoluene, DNX - dinitroxylene, TNX - trinitroxylene, MNN - monottitronaphthalene, DNN - dinitronaphthaleoe.

The quantity of sulphuric acid in the spent acid in per cent F can be calculated as a ratio between the quantity of H_2SO_4 used for nitration $G_S \frac{S}{100}$ and the quantity of spent acid:

$$\Phi = \frac{G_S \times S \times 100}{100\,G_S + G_N(100-0.714\,N)}\,\%$$

hence

$$G_S = \frac{G_N}{140} \cdot \frac{140-N}{S-\Phi}$$

(according to Orlova [3]).

UTILIZATION OF SPENT ACID

The spent acid from a nitration process is usually re-used in the process, viz. after being suitably fortsed it is passed from a higher nitration stage to a lower one. For example, spent acid from the manufacture of trinitrotoluene is used for the nitration of mononitro- to dinitro-toluene while the spent acid from the latter is used for the nitration of toluene to mononitrotoluene. The portion of the spent acid re-used is sometimes called re-cycle acid.

There are two ways of utilizing the spent acid in the nitration process:

(1) An earlier method, which consists in blending the spent acid with concentrated nitric acid and oleum in such proportion as to obtain a mixture of the exact composition required for the manufacture of the nitro compound to be produced. A drawback of this method is that the compound being nitrated is mixed with concentrated acid. Therefore the nitration may sometimes proceed too vigorously. Taking this into consideration, the reaction must be very carefully controlled, avoiding any rise of temperature, especially in the initial period of nitration.

The rise of temperature is brought about not only by the heat generated by the reaction, but also by the heat of dilution of the nitrating acid by the water formed during the nitration.

The more concentrated the acid, the higher the heat of dilution (Table 16). Therefore, the temperature jump caused by the formation of a given amount of water is higher in the initial period of nitration than at a later stage after dilution has taken place.

Heat capacity also affects the rise of temperature during nitration. Since the heat capacity of a concentrated acid is much lower than that of a dilute acid (Table 17), the same amount of heat generated brings about a higher rise of temperature at the beginning of the nitration than at the end. So this is yet another factor which makes for difficulties when carrying out nitration with concentrated acid.

The considerable effect of accumulated heat and a big rise of temperature may be avoided by applying a more modern method such as that described below.

(2) The substance to be nitrated is mixed with the spent acid and then nitric acid is introduced slowly, the concentration of the acid being increased gradually so that nitration proceeds slowly.

As soon as the substance being nitrated is mixed with the spent acid, it uses up the HNO_3 present in it. Further addition of nitric and sulphuric acids does not result in such a considerable rise of temperature as that occurring in the first method. Two reasons account for this:

(a) The water formed during the nitration process, when evolved in the already dilute acid, does not produce such a large quantity of heat as in the first method (heat of dilution of sulphuric and nitric acids and their mixtures are given in Table 16 (Rhodes and Nelson's data [4]). See also [16].

(b) As mentioned above the heat capacity of dilute acid is higher than that of concentrated acid. For this reason, during the initial period of the reaction when the acid is more dilute the rise of temperature is lower than when, on adding concentrated nitric and sulphuric acids or oleum, an increase in concentration takes place.

It follows from the above that nitration by the second method is safer. It may

TABLE 16

HEAT OF DILUTION OF NITRATING ACID

Ratio $\frac{H_2SO_4}{HNO_3}$		Ratio $\frac{H_2O}{acid}$		Total heat of dilution by adding 500 moles of H_2O	
mole	weight	mole	weight %	kcal/mole	kcal/kg
100 0	100 0	0.0	0.0	18.26	84.4
		0.5	8.42	14.53	61.5
		1.0	15.5	11.57	45.1
		1.5	21.6	9.47	34.3
		2.0	26.9	8.28	28.0
		3.0	35.5	6.56	19.7
85.3 14.7	90 10	0.016	0.3	15.10	73.6
		0.435	7.78	12.83	57.7
		0.943	15.47	10.19	42.1
		1.56	23.22	8.06	30.2
		3.41	39.8	5.08	14.9
68.5 30.5	78 22	0.015	0.3	13.23	68.5
		0.277	5.4	11.70	57.5
		0.631	11.5	10.15	46.1
		1.282	20.9	7.65	31.5
		2.14	30.6	5.78	20.9
		3.485	41.8	4.10	12.3
54.7 45.3	65.3 34.7	0.014	0.3	11.67	64.3
		0.418	8.4	9.66	48.9
		0.818	15.2	8.34	39.1
		1.47	24.4	6.14	25.7
		2.91	38.9	3.95	15.4
39.2 60.8	50 50	0.013	0.3	10.13	59.9
		0.27	5.97	8.90	49.4
		1.008	19.15	6.16	29.5
		1.93	31.2	4.35	17.6
		3.03	41.6	3.03	10.3
0 100	0 100	0.0	0.0	7.43	53.4
		1.0	22.2	4.16	23.2
		2.0	36.4	2.65	12.1
		3.0	46.2	1.72	6.7

be carried out at higher temperatures without any risk of exceeding the safety limit and due to the higher temperature, nitration can proceed more rapidly.

Gelfman [5] has revised the generally accepted data for calculation of the heat generated during mixing the acids and during their dilution with water [16]. He found the absolute value of the heat generated in the reaction between sulphuric and nitric acids to be lower in the presence of water than when the acids are in an anhydrous state. He also found it decreased on diluting the acids with water. This relationship presented graphically is close to a linear one (Fig. 19). On the diagram

TABLE 17

PHYSICAL PROPERTIES OF SULPHURIC ACID

Specific gravity	H_2SO_4 %	Specific heat cal/g
1.84	98.5	0.33
1.82	90.0	0.36
1.77	83.4	0.38
1.71	77.5	0.41
1.61	69.0	0.45
1.53	62.5	0.49
1.45	55.0	0.55

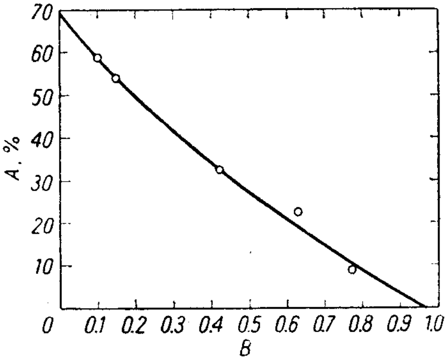


FIG. 19. Heat evolved on mixing nitric acid with sulphuric acid in relation to the water content *A* in these acids. Quantity of heat Q = *A B* (Gelfman [5]).

A is the percentage of water in the mixture and ***B*** the coefficient of the thermal effect of mixing the acid, It ranges from 1 (maximum value) for anhydrous acids, and is zero for water. The thermal effect of mixing hydrated acids will be expressed by the product ***B*Q*,** where Q is a value taken from another of Gelfman's diagrams (Fig. 20).

In this diagram the heat of interaction between the anhydrous acids, H_2SO_4, and HNO_3, calculated on 100 g of mixture, has been presented, where Q is the heat of mixing (in calories) and x is the H_2SO_4 content in the mixtures (wt. %). The heat maximum corresponds to x = ca. 67% of H_2SO_4.

Gelfman points out that the heat of interaction between sulphuric and nitric acids is the heat of reaction for:

$$HNO_3 + H_2SO_4 <-> NO_2+ + HSO_4^- + H_2O \qquad (2)$$

The interaction heat must not be identified with the heat of mixing. On adding water to The mixture, the equilibrium is shifted to the left. Therefore the heat of interaction between sulphuric and nitric acids in the presence of water is lower than that between anhydrous acids.

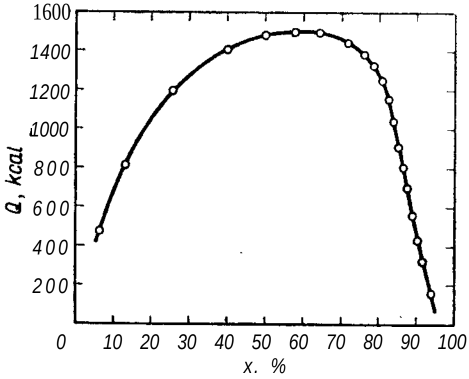


FIG. 20. Dependence of the heat of mixing Q of anhydrous HNO_3 and H_2SO_4 on the content of H_2SO_4 (x %) in the mixture (Gelfman [5]).

During nitration partial separation of the acids takes place. This is the inverse of the mixing process. The absolute value of the thermal effect of separation equals, of course, that of mixing, but its value is negative. For this reason the thermal effects of nitration calculated so far have been too high.

For example, the conversion of phenol into picric acid is accompanied by the generation of 917.4 kcal per kg of the phenol, whereas the thermal effect, calculated by earlier methods, was 1106 kcal/kg.

Similarly the heat of O-nitration of 1000 kg of glycerol with a nitrating mixture comprising 5000 kg of HNO_3 (50%) and H_2SO_4 (50%) is 251,669 kcal, though according to earlier calculations it was 347,000 kcal.

ENTHALPY OF NITRATING MIXTURES

Figure 21 is a diagram by McKinley and Brown [6] showing the relative enthalpies of nitric and sulphuric acids and their mixlures. Another diagram (Fig. 22) shows the relationship between the specific heat of mixtures of acids and their composition.

From diagrams it is possible to calculate the relative enthalpies of nitrating mixtures and of the heats generated during the mixing of acids. The following examples illustrate how to use the diagrams:

Example 1. To find the relative enthalpy of a mixture of acids:

HNO_3	30%
H_2SO_4	20%
H_2O	50%

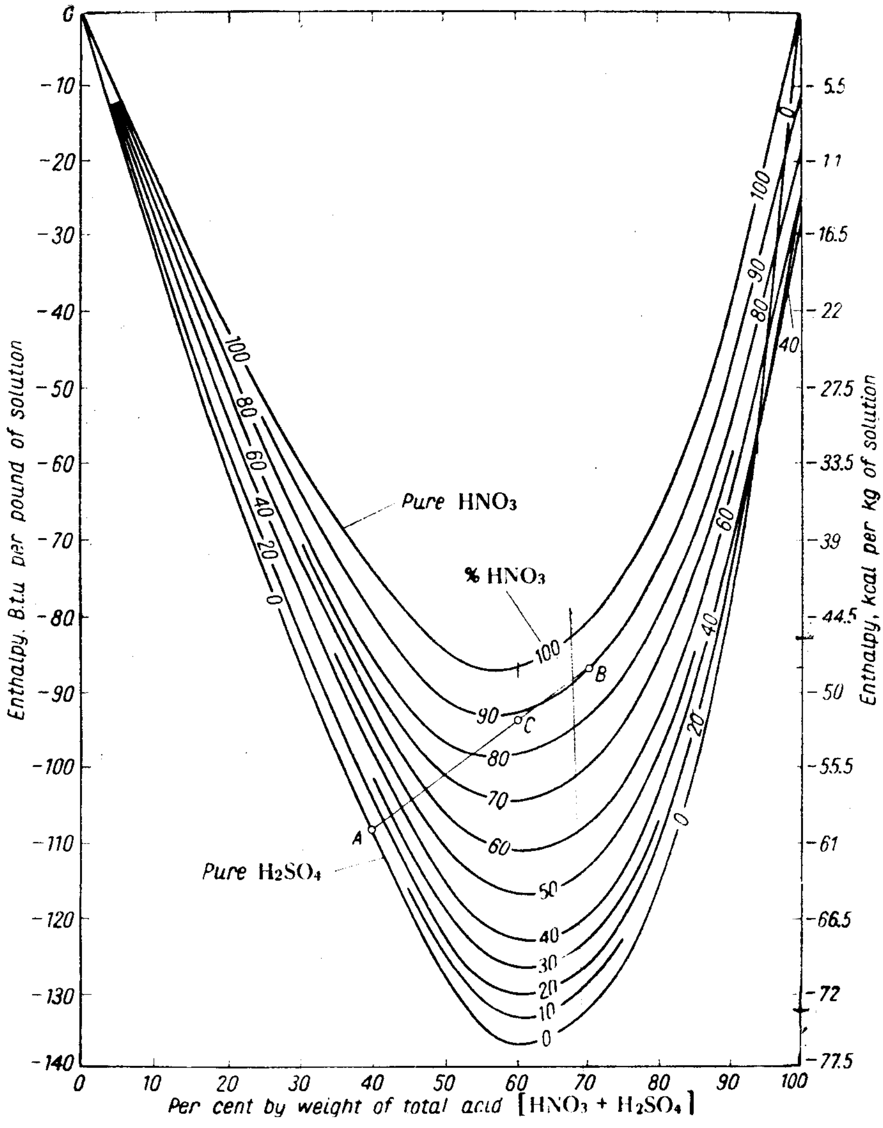


FIG. 21. Enthalpy of nitric acid, sulphuric acid, and water mixtures (McKinley and Brown [6]).

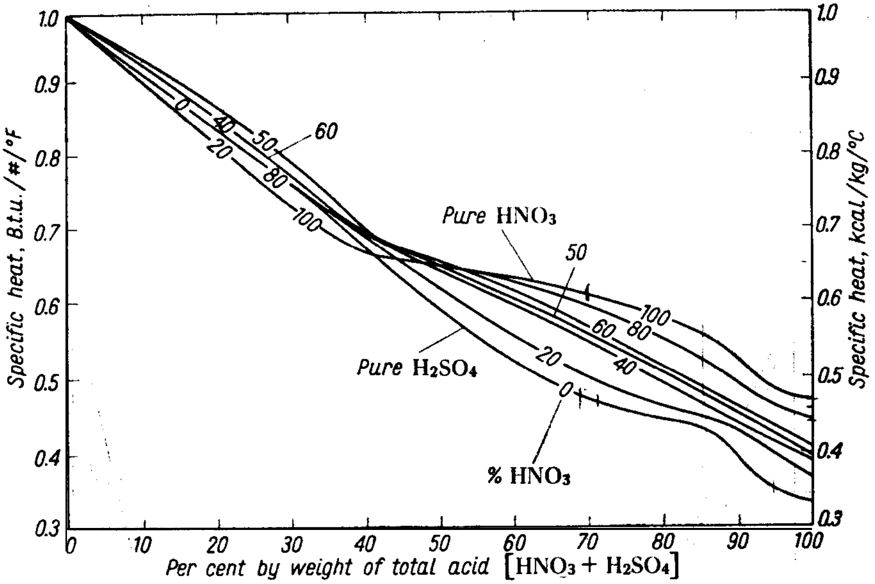


FIG. 22. Specific heat of nitric acid, sulphuric acid, and water mixtures (McKinley and Brown [6]).

at a temperature of 32°C. The total acid content in the mixture is 50%, and the HNO_3 content in the anhydrous mixture is 30/50 x 100 = 60%.

The value 50 corresponding to the total acid in the mixture is found on the x-axis (Fig. 21) and then the point of intersection of the coordinate with the curve, that represents the 60% content of HNO_3 in the mixture of acids, is sought. The ordinate of this point gives the enthalpy value at 0°C equal -58.8 kcal/kg. In the diagram shown in Fig. 22, the specific heat of the mixture is found in an analogous way. It equals 0.66 kcal/kg°C.

Hence the relative enthalpy of the acid at 32°C is:

$$H_{32} = -58.8 + 6.66\ (32-O) = -\ 37.7\ \text{kcal/kg}$$

Example 2. A mixture of acids having a temperature of 35°C and the composition:

HNO_3	21%
H_2SO_4	62%
H_2O	17%

is to be prepared.

To obtain 100 kg of the mixture, it is necessary to mix:

30.0 kg of 70% nitric acid
65.3 kg of 95% sulphuric acid
4.7 kg of water

The temperature of all the compounds should be 24°C

The relative enthalpy of the mixture of acids is calculated in the same way as in example 1, taking into account that the total acid content (HNO_3+H_2SO_4) is 83% and the HNO_3 content in the anhydrous mixture amounts to 25.3%. The relative enthalpies of the mixture are determined from the tables as in example 1.

TABLE 18

	Specific heat Cal/g	Enthalpy at 0°C kcal/kg	Enthalpy at 24°C kcal/kg	Enthalpy at 35°C kcal/kg
Mixture of acids	0.47	-54.8	-	-. 38.3
Nitric acid	0.61	-44.9	-30.5	-
Sulphuric acid	0.36	-24.4	-15.9	-
Water	1.0	0	+24	-

Thus, for the 100 kg mixture the enthalpies of the components at 24°C are:

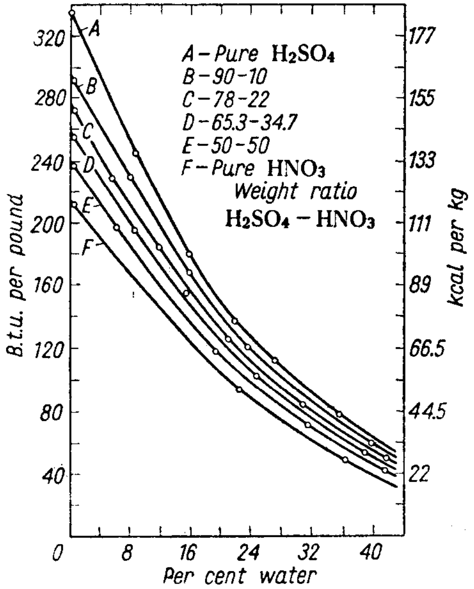
nitric acid -30.5 x 30 = - 915.0 kcal
sulphuric acid -15.9x65.3 = -1038.3 kcal
water +24 x 4.7 = + 112.8 kcal

The total enthalpy of the components at 24°C is -1840.5 kcal. The enthalpy of 100 kg of the mixture of acids at 35°C is

-38.3x100 = -3830 kcal

Hence the heat which must be removed during the preparation of 100 kg of the mixture so as to maintain 35°C is

3830-1840.5 = 1989.5 kcal or 19.9 kcal/kg



Fro. 23. Heats of dilution of nitric acid, sulphuric acid, and their mixtures (Rhodes and Nelson [4]).

HEATS OF DILUTION

Heats of dilution at 18°C of mixed acid containing various known percentages of sulphuric acid, nitric acid, and water were given in Table 16 (p. 144). The data are presented graphically in Fig. 23. Thus for a mixed acid containing

60% HNO_3 or the weight ratio H_2SO_4/HNO_3 = 40/60 the intercept on the ordinate representing 20% water indicates a heat of dilution of ca. 115 B.t.u. per lb, in agreement with the foregoing calculations. It can be seen from the curves that as the nitration progresses the heats of dilution decrease and as the water content of the nitrating acid increases. There is greater danger of violent or explosive reaction at the early stages of nitration, owing to the lower specific heats of the more concentrated acids, than later on in the reaction. (See also [17]).

The curves also indicate why it is comparatively safe to carry out rapid nitration at relatively high temperatures with spent acid or with nitric acid alone.

MIXING THE ACIDS

The operation of mixing is carried out in iron vessels equipped with cooling jackets and stirrer.

A schematic diagram of a mixing plant is given in Fig. 24. It consists of a large vessel (1) for storing the acids, a measuring tank for the acids (2), a mixer (3), a pressure-egg (4) and a vessel for the storage of the prepared nitrating mixture (5):

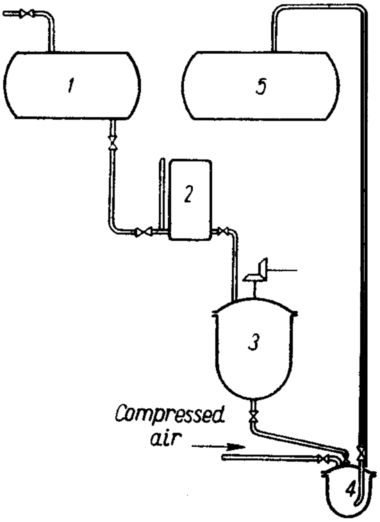


FIG. 24. Diagram of a plant for mixing acids.

Vessels and pipes for concentrated nitric acid are made of pure aluminium. Those for sulphuric acid, oleum and the mixture of acids are made of iron. Steam pipes must be laid close to oleum pipes and the whole should be coated with thermal insulation. In this way the oleum pipes are heated, thus preventing the oleum from freezing in winter.

Calculation of acid mixtures. A mixture of the composition:

HNO_3	A%
H_2SO_4	B%

is to be prepared from:

(1) n% nitric acid
(2) s% sulphuric acid
(3) spent acid with n'% H_2SO_4 content and s'% HNO_3 content.

To obtain 100 kg of the mixture we take

x kg of nitric acid
y kg sulphuric acid
z kg of spent acid

The following three equations with three unknowns must then be worked out:

$$x+y+z = 100$$
$$zn' + xn = A$$
$$zs' + ys = B$$

By solving the system of equations we obtain the formulae for the calcnlation of x, y, r.

$$x = \frac{A(s-s') + n'(B-100s)}{s(n-n')-ns'}$$

$$y = \frac{B(n--n) + s'(A-100n)}{s(n-n')-ns'}$$

$$z = \frac{n(100s - B) - As}{s(n-n')-m'}$$

If oleum is used it is assumed that

$$s = p+1.225\, g$$

where p and g are the percentages of H_2SO_4 and SO_3 in the oleum respectively (122.5 parts of H_2SO_4 are obtained from 100 parts of SO_3).

TEMPERATURE OF NITRATION

The nitration temperature has considerably less effect on the position of the nitro group in an aromatic nucleus than for example the sulphonation temperature. Nevertheless, keeping the desired temperature constant is of greatest importance from the viewpoint of safety and of the purity of the product. The use of too high a temperature causes the reaction to proceed violently. At high temperature by-products, especially oxidation products, are readily formed. The oxidation reactions are accompanied by the evolution of nitrogen dioxide. This is why the temperature must be kept as low as possible, especially at the initial stage of reaction when the substance is not yet or only at the initial stage of the nitration.

The safety limit of temperature depends on the chemical structure of the compound being nitrated. For example, in the nitration of dinitrotoluene to trinitrotoluene or of phenol to picric acid, temperatures near 120°C and over are considered dangerous. In the nitration of dimethylaniline to tetryl, a temperature higher than 80°C must be considered dangerous. Esterification with nitric acid should be carried out at a temperature close to room temperature or lower.

MIXING OF REAGENTS DURING NITRATION

There are three methods of mixing organic substances to be nitrated with nitrating mixtures:

(1) adding the substance to the acid,
(2) adding the acid to the substance,
(3) simultaneous introduction of both acid and organic substance into the nitrator.

The first method is the one most frequently applied. It has, however, certain drawbacks. The first portions of the nitrated substance are introduced into an excess of nitrating mixture and may be converted to a higher degree of nitration than required and may also undergo oxidation processes; hence the uniformity of the product may not be satisfactory. Also some substances sensitive to concentrated acid may be decomposed by contact with an excess of acid necessitating application of the second method. In the second method the substance to be nitrated is contacted with an inadequate quantity of nitrating acid. This might be advantageous for the reason mentioned above. However, when aromatic hydrocarbons with alkyl side groups (e.g. toluene) are nitrated, reaction of the hydrocarbon with an inadequate amount of nitrating mixture may lead to the formation of dark coloured complex compounds and even tarry matter (see p. 77). In this instance the first method is more advantageous. The best method, which consists in simultaneous introduction of both reactants into the nitrator, has the advantage that it is applicable in continuous nitration processes.

As already mentioned earlier, nitration proceeds mainly in the acid phase. Strictly speaking the acid phase consists of an acid saturated with an organic substance. On the other hand, the organic phase is in turn saturated with an acid. The reaction rate in an acid phase is much higher than that in an organic phase (see p. 40). By vigorous stirring the contents of the nitrator are kept emulsified and the phases are kept mutually saturated due to diffusion over a very large interfacial area.

Insufficient mixing may easily result in a low nitration rate owing to the small interfacial area. It can also lead to a non-uniform nitration process. Owing to inadequate construction of the stirrer, too low a speed of rotation, or an interruption in stirring, so-called dead spaces may easily be formed in which non nitrated or not fully nitrated substances accumulate. If a rather large quantity of the mixture is stirred suddenly, rapid extension of the interfacial area takes place, followed by the generation of large amounts of heat and a rise in temperature. This may cause a spontaneous decomposition of the reaction mass in the nitrator, and then an explosion.

Such an accident, well known in the history of the chemical industry, happened at the Rummelsburg factory in 1914 during the nitration of benzene. The transmission belt slipped off and caused the stirrer to stop. In spite of this benzene continued to flow into the nitrator. When the fault was noticed, the stirrer was set in motion by putting the belt in the right place, with the result that an explosion followed (see also p. 446).

Stirring should be particularly vigorous at the beginning of nitration when the reaction is most violent and the largest amount of heat is evolved. There is a further reason which makes very fast stirring necessary at the beginning, namely the fact that the two liquid phases-that of a light substance being nitrated and that of the heavy nitrating acid-differ considerably in specific weight. As the reaction goes on, and the organic phase is nitrated, its specific weight increases while that of the acid decreases because of its dilution. Toward the end of nitration, the difference between specific weights having been much reduced, mixing of the two phases is greatly facilitated.

A few workers have investigated recently the problem of the influence of stirring on the rate of nitration and the yield of the reaction. McKinly and White [7] reported that the rate of nitration of toluene to nitrotoluene increased by 3% only when the stirring speed was increased from 1327 to 2004 r.p.m.

However, much larger increases (4 to 5 times higher) were obtained in the same reaction by Barduhn and Kobe [8] when they changed the stirring rate from 1000 to 2175 r.p.m.

The results of their experiments are given in Fig. 25.

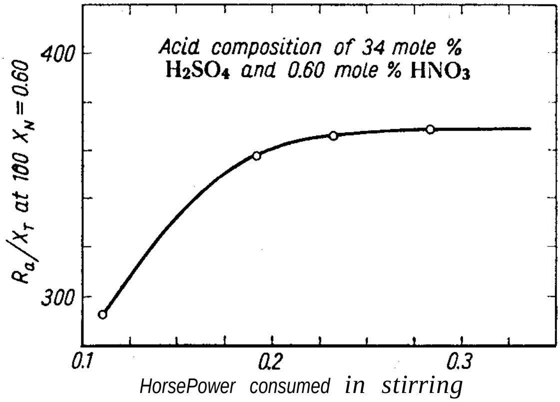


FIG. 25. Rate of nitration (R_a) as a function of stirring rate: X_T and X_N are the concentrations of toluene and nitric acid respectively. (Barduhn and Kobe [8]).

SOLUBILITY OF NITRO COMPOUNDS

The solubility of a substance being nitrated in the acid used is an important factor in the nitration process. The more easily the substance dissolves in the acid, the higher the reaction rate, and hence the higher degree of nitration to be obtained during a given time.

Since aromatic compounds are more ready soluble in sulphuric acid and in mixtures in which its concentration is high, completion of full nitration is accelerated by using such mixtures. The solubility of dinitrobenzene in sulphuric acid of various concentrations and at various temperatures is shown in Fig. 26.

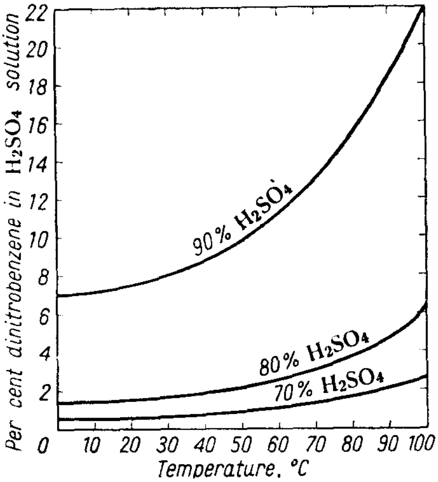


FIG. 26. Solubility of *m*- dinitrobenzene in sulphuric acid (Groggins *et al.* [1]).

Sometimes it is difficult to fulfill all the conditions a nitration mixture should satisfy, such as a low solubility of the nitro compound at an adequate strength of the acid. Sometimes water may be added, after the nitration has been completed, to reduce the solubility of the nitro compound so as to obtain quantitative separation of the product. This can be justified economically although the acid becomes diluted, thus necessitating the use of more oleum for fortifying the spent acid.

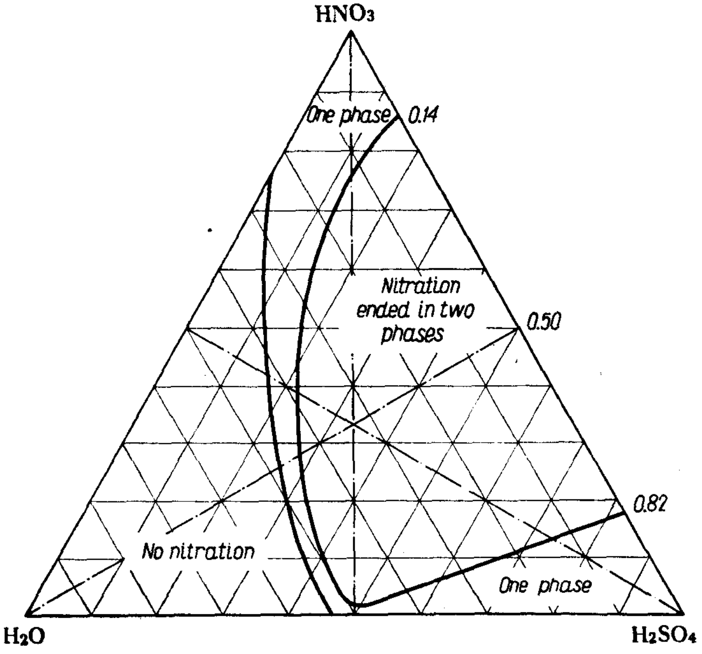


FIG 27. Influence of the concentration of nitrating mixtures on the nitration of nitrobenzene to dinitrobenzene and phase conditions after cooling to 35°C (Hetherington and Masson [9]).

Figure 27 shows the influence of the concentration of a nitrating mixture on the nitration of nitrobenzene and the phase conditions at the completion of the nitration of nitrobenzene to dinitrobenzene, after cooling the mixture down to 35°C. The relationship between the rate of nitration of benzene to dinitrobenzene and the molar concentration of sulphuric acid arc shown in Fig. 28 (Hetherington and Masson's data [9]).

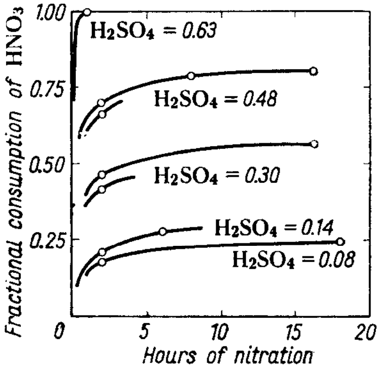


Fig. 28. Rate of nitration of benzene to dinitrobenzene as a function of the molar concentration of sulphuric acid. (Various curves correspond to various molar concentrations of H_2SO_4, when $[HNO_3] = 1$.) (Hetherington and Masson [9]).

The influence of sulphuric acid in O-nitration processes, as for example in the esterification of cellulose with a mixture of sulphuric and nitric acids, appears to be somewhat different. This will be dealt with in the chapter on esters (Vol. II).

DESIGN OF NITRATORS

The nitrators used in the manufacture of aromatic nitro compounds consist of iron vessels (Fig. 29), equipped with a stirrer (I) and a jacket (2) for cooling or heating the contents, as well as with a lid (3), connected with a ventilation pipe (4). Gaseous products from the nitration process (NO, NO_2, HNO_3, SO_3, SO_2, CO, CO_2) are conducted away through it. The ventilation duct is equipped with a sight glass (5), which permits the observation of waste gases - mainly their colour.

In addition to the ventilation duct the lid is equipped with two feed pipes, one for acids, (6), and one for the substance to be nitrated, (7), a thermometer sleeve (8), a delivery pipe for compressed air (9) and a pipe (10), reaching down to the bottom, for discharging the nitrator contents by means of compressed air. It is essential to furnish the lid with a manhole (II). During nitration, the manhole opening is closed by a thin sheet of aluminium, which at the same time plays the role of a safety valve in case the pressure should rise inside the vessel.

The nitrator capacity may vary and may be as large as 15 m^3. Its dimensions depend on the compound to be nitrated and on the method of nitration; for example, nitrators for continuous nitration are as a rule smaller for a given output. More dangerous reactions are also carried out in nitrators of smaller size.

Cast iron was the material most often used for the construction of nitrators, and forged sheet iron less so. Now stainless sheet steel is generally used. Stainless steel sheet must be welded by modern methods (under a hydrogen atmosphere), since otherwise the seam would be a site relatively easily corroded. Formerly before reliable methods of welding had been developed, metal sheets were riveted to fabricate nitrators. In certain cases sheet lead was widely used, e.g. for the nitration of glycerol. For certain substances easy to nitrate (phenols) earthenware vessels may be used or iron nitrators with an inner lining of an acid resistant ceramic material.

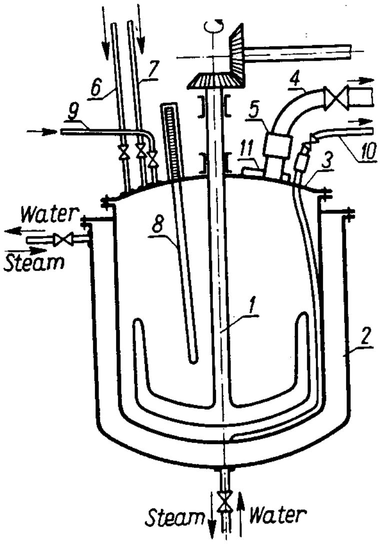


FIG. **29. Diagram of the construction of nitrator.**

HEAT EXCHANGE DEVICES

If a nitrator is equipped only with a cooling or heating jacket, the ratio of the heat exchange area to the nitrator capacity depends on the latter. When the capacity is cubed the surface area is squared. Thus, when the dimensions of a nitrator are increased, the heat exchange area may no longer be adequate. Then, a stainless steel coil or a lead coil must be mounted inside the nitrator.

STIRRERS

The influence of stirring on the nitration rate and the safety of the operation has already been emphasized. It is evident that special attention must be paid to the stirring equipment provided in a nitrator. Various types of stirrers are used.

Horseshoe stirrers, the shape of which fits well into the inside of a nitrator, are the simplest type (Fig. 29).

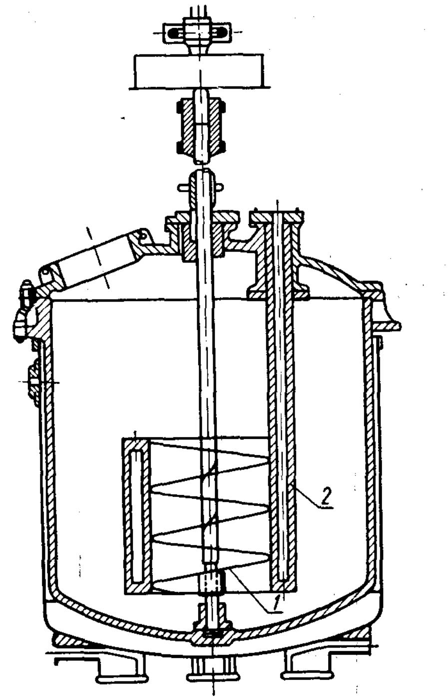


Fig. 30. Diagram of a nitrator with a spiral screw stirrer.

Another type of simple stirrer is one with a set of blades or bars mounted vertically on a vertical axis. A more complex form of this type of stirrer consists of two

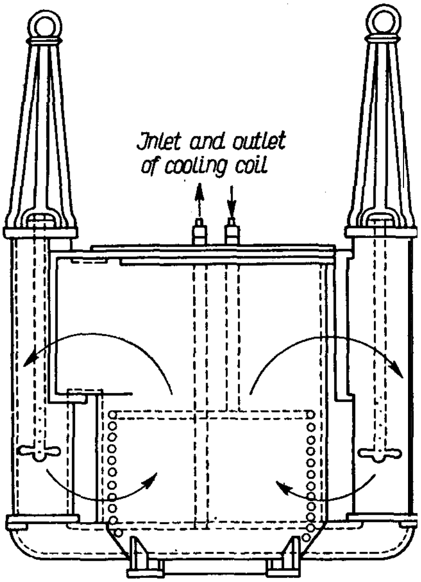


FIG. 31. Diagram of a nitrator with two external chambers.

sets of blades or bars, mounted on two axes, which rotate either in the opposite or in the same direction, sometimes at different speeds. This type of stirrer is used for the nitration of cellulose and is often mounted in small nitrators in which additional internal cooling (or heating) would be difficult to apply.

The types of stirrers mentioned are particularly useful when the contents of the nitrator are highly viscous or semi-liquid, for example a mixture of acid and a crystalline product.

For liquids of low viscosity a spiral screw stirrer may be used (Fig. 30). Circulation can be facilitated by surrounding the stirrer (I) with a sheet metal cylinder (2), provided with double walls through which cooling water or steam circulates for additional cooling or heating,

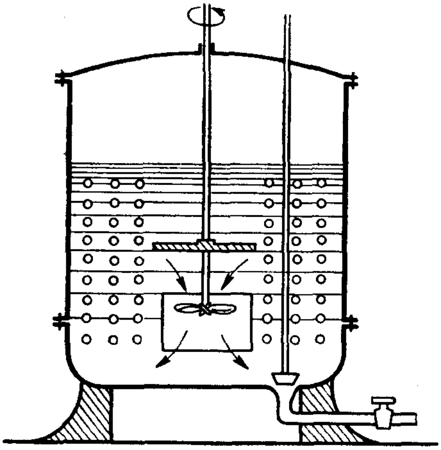


FIG. 32. Diagram of a nitrator with a propeller stirrer.

One rather unusual design comprises a mixing system with two external chambers (Fig. 31). The nitrator is connected with both sides of each chamber, in each of which a propeller stirrer is rotated at 200-400 r.p.m. The speed of rotation and cross-sections of the chambers are so selected as to enable the whole of the nitrator contents to make one round within one minute.

Propeller stirrers with the propeller located inside a sheet metal cylinder (Fig. 32) or in the space delineated by a heating coil are frequently used. The propeller draws the liquid from the top of the cylinder, forcing it downwards. In the space between the cylinder and the nitrator walls the liquid flows in the opposite direction. If a well designed propeller is used and a suitable rotation speed applied, circulation of the liquid is sufficient to secure adequate mixing. The system is also used for continuous nitrators, not only for nitration of aromatic compounds, but also for nitration of alcohols, for example glycerol.

Mixing by means of a draw-lift turbine is the most modern and efficient method (Fig. 33). The turbine is rotated at high speed (several hundred r.p.m.) and powered by an electric motor with a worm reduction gear. The turbine draws the liquid from the top and bottom and throws it out at a tangent. The stream of liquid hits the cooling coil. Then the liquid flows partly upward and partly downward between the coil, some of it being reflected by the coil.

The shape of the nitrator bottom should also be carefully selected for a given stirring system. The efficiency of mixing with a propeller or turbine is higher when the nitrator has a conical or spherical bottom.

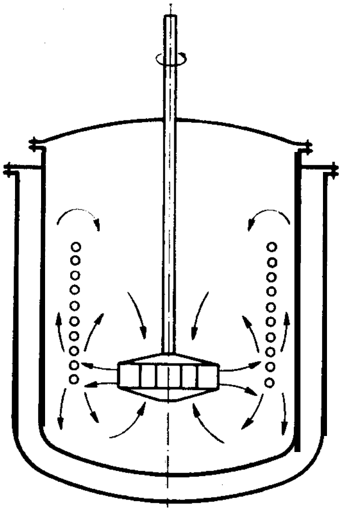


FIG. 33. Diagram of a nitrator with a draw-lift turbine and a cooling coil (circulation of the liquid content is marked with arrows).

The construction of nitrators for the continuous production of nitro compounds is somewhat different. Figure 90 (p. 374) shows a schematic diagram of one type of continuous nitrator. Nitrators for preparing nitric esters (e.g. nitroglycerine, nitrocellulose) are of yet another design. New types of nitrators based on the principle of passing two streams of reacting liquids (organic substance and nitrating acid) through an injector, are now being introduced (Vol. II). They may bring about a radical change in many existing designs of nitration plant.

PRODUCT SEPARATION AND DISCHARGE OF THE NITRATOR

When the reaction has been completed the nitrator contents must remain at rest for some time to allow the product to separate from the spent acid. This may be done in the nitrator itself or the mixture may be transferred into a special settler-separator. The latter is more advantageous if the next nitration is to be carried out in the nitrator immediately after the first reaction.

The nitrator is discharged either through an outlet located in the bottom (Fig. 34) or by forcing the contents out by means of compressed air (Fig. 35). In the latter case the nitrator lid should fit tightly and the fume outlet should also close tightly with a valve. If the nitrator itself has been used as a separator, the spent acid layer is transferred to a special tank while that of the product goes to another tank (for example direct for washing if it is an end product, or to another nitrator if it is to be nitrated further). To make practicable the transport of the two layers to different locations the discharge pipe should be equipped with a sight glass, through which the partition boundary of the phases can be seen.

An advantage of discharge by means of compressed air is that the whole plant can be located in a low building. If the nitrator is emptied through an outlet in its base a high building is necessary. This is of particular importance when underground plant is to be constructed, for the cost rises considerably as the depth increases. A drawback associated with the use of compressed air for discharging the nitrator contents is the risk of damage and the operatives being burned consequent on breakage of the sight glass.

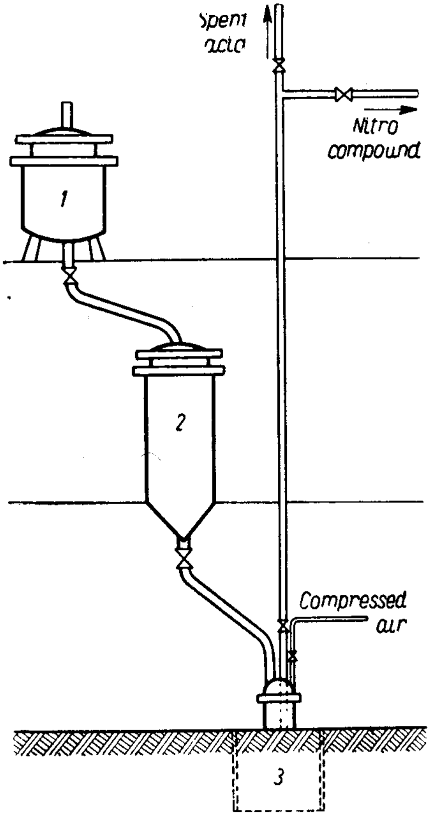


FIG. 34. Flow diagram, nitration, the discharge of the nitrator through the bottom: 1 - nitrator; 2 - separator; 3 - pressure-egg.

Discharging the nitrator through an outlet has the further drawback that it makes the reactor more difficult to construct.

In the case of substances that solidify (for example, TNT) all pipes and valves should be provided with heating jackets. If the nitration product solidifies at a high temperature and cannot be kept molten it is necessary to create the necessary conditions to ensure the formation of a fine-crystalline or granular product. It is only then that bottom discharge will be feasible. The nitrator contents are then transported immediately to a centrifuge, or in the case of explosives sensitive to impact (sensitivity of the order of that of tetryl or higher), the solid product is filtered off under reduced pressure.

The separated solid or liquid product is then washed with water in order to remove acids, and subsequently purified according to its properties and the nature of the impurities present. Finally the pure product is obtained in the required physical form.

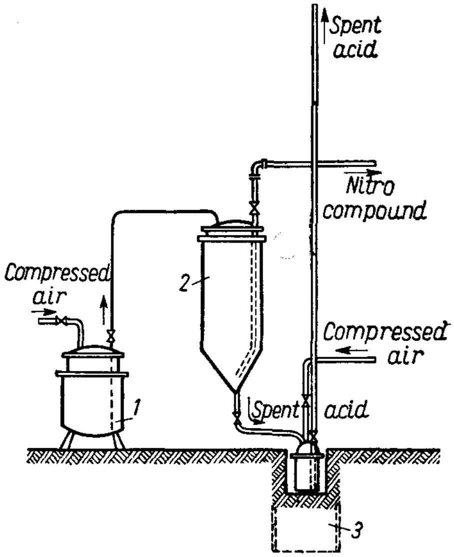


FIG. 35. Flow diagram, nitration discharge of the nitrator by means of the compressed air: 1 - nitrator; 2 - separator; 3 - pressure-egg.

WASTE WATER

The technology of nitration processes is unavoidably associated with the problem of waste water disposal. The water, which comes from washing the nitration product, contains acid components from the nitrating mixture, and nitro compounds.

Both the acids and the nitro compounds in solution, or suspended, or in both states are highly noxious for the flora and fauna of rivers and lakes.

Thus, nitro compounds in a concentration as low as a few milligrams per litre are lethal to fish. Wastes from the manufacture of hexyl (hexanitrodiphenylamine) are particularly toxic, killing fish at a concentration as low as 0.1 mg of hexyl per litre. For this reason, the removal of these compounds from the waste water prior to its discharge is of primary importance.

As a rule acids are removed from waste water by discharging it into pits filled with limestone, where they are neutralized.

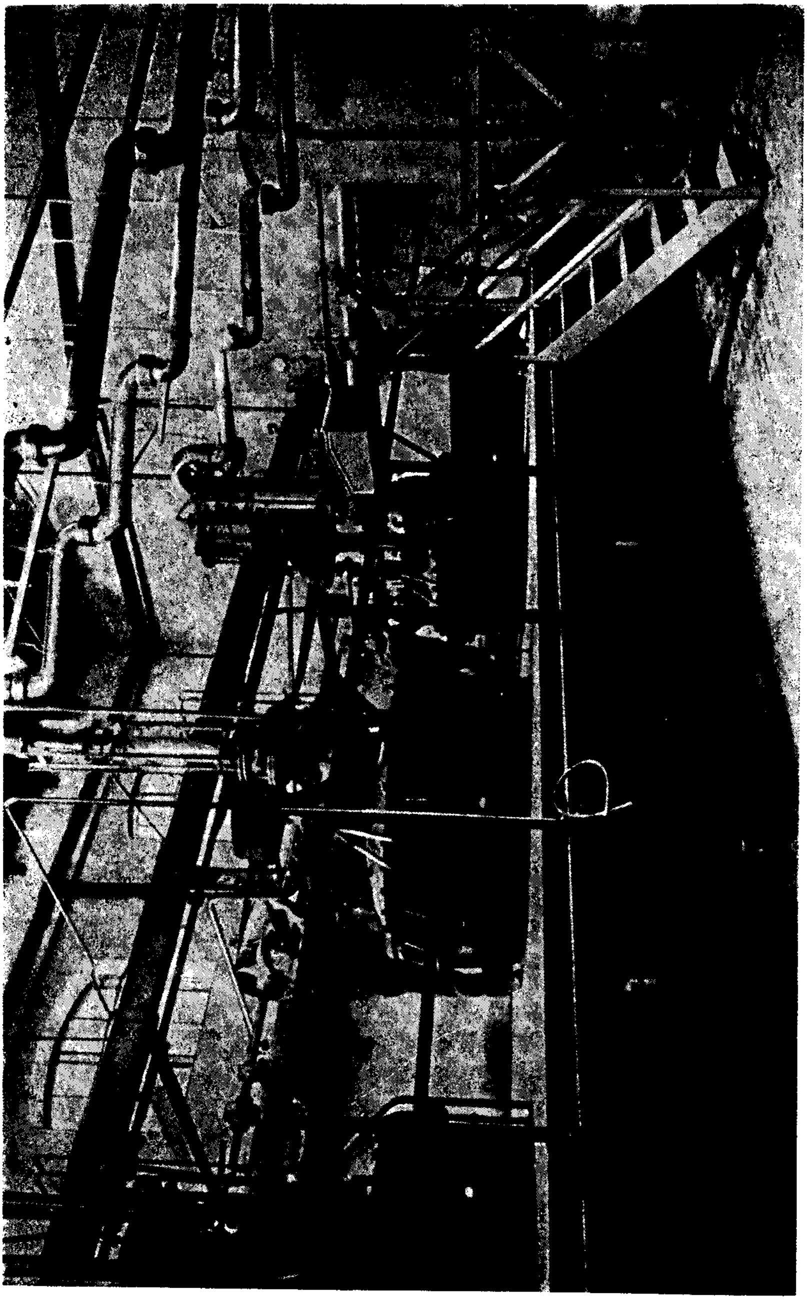


FIG. 36. General view of a nitration room (Bofors Nobelkrut).

Clearly, nitro compounds suspended in water are easily removed by passage through settling tanks or filters. Nitro compounds dissolved in water are most difficult to remove. Various methods are possible, which make use of various physical and chemical properties of the nitro compounds. For example, physical methods which have been suggested and applied include adsorption of the nitro compounds on absorptive agents (e.g. carbon) and extraction with solvents of low volatility (e.g. phthalic esters). Among chemical methods, the destruction of nitro compounds by oxidation with hypochlorous acid is possible. Since nitro compounds are often resistant to oxidation, a more complex process is sometimes more efficient, consisting first of the reduction of the nitro compound, then its oxidation. Chemical methods are generally expensive and are rarely used. In particular, oxidation by hypochlorous acid consumes considerable quantities of chlorine - up to 3 g for 1l of solution.

Biological methods of destroying nitro compounds are of considerable interest. Up to now they have not been practiced on a large scale, but they are promising because of their economy. The first investigations into the possibility of destroying nitro compounds by biological methods were carried out in 1941 by Erikson [10], who found that nitro compounds such as nitrobenzene, picric acid, and trinitroresorcinol can be used as a nutrient by some *Actinomyceres.* The observation was later confirmed by Moore [11] and by Rogovskaya [12], who suggested destroying nitro compounds by fermentation.

Simpson and Evans [I 31 reported that nitrophenols such as o- and p-nitrophenols, 2,4-dinitrophenol or such a nitro compound as chloramphenicol could be destroyed by some ***Pseudomonas*** species to form nitrous acid salts.

According to Petersen [14], the well known herbicide, dinitro-o-cresol, is rapidly deactivated in soil by Gram-positive micro-organisms belonging to the *Corynebacterium* family. This served as a starting point for Jensen and Gundersen [15] in their research work in which they found that *p*- nitrophenol, 2,4-dinitrophenol and picric acid are destroyed by the same micro-organisms with the formation of nitrites. The same authors have investigated the rate of decomposition of dinitro-o-cresol. Moreover, they have observed the interesting fact that *o*- and *m*- nitrophenols, 2,5- and 2,6-dinitrophenols and 3,5-dinitrobenzoic acid do not undergo such a decomposition. It seems that only those nitrophenols that have the nitro group in the *para* position are prone to decomposition.

Since nitro compounds have certain specific properties, which influence the choice of methods for heating wastes, some special methods are described later in the technological section dealing with methods of the manufacture of individual nitro compounds. Diminishing water pollution by washes from the manufacture of TNT is a most complex problem. This will be discussed in detail on p. 390.

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CHAPTER V

GENERAL INFORMATION ON NITRO COMPOUNDS

NITRO compounds are substances in which the nitro group is directly attached to a carbon atom:

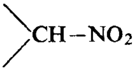
$$-C-NO_2$$

The evidence for the fact that the nitro group is actually linked with carbon is that reduction of nitro compounds leads to the formation of primary amines

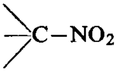
$$-C-NO_2 \rightarrow -C-NH_2 \tag{1}$$

Depending on whether or not and how many hydrogen atoms are linked with a carbon atom, they are known as primary, secondary and tertiary nitro compounds :

$-CH_2-NO_2$ Primary



secondary

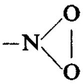


tertiary

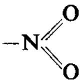
All aromatic nitro compounds are tertiary derivatives. Aliphatic or aryl-aliphatic nitro compounds can be primary, secondary and tertiary.

CONSTITUTION OF THE NITRO GROUP

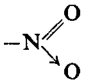
The constitution of the nitro group has been the subject of numerous discussions. Three types of formulae can be found in the literature:



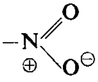
I



II



IIIa



IIIb

The first of these was abandoned long ago, since the existence of an unstable three-membered ring in such a stable group as the nitro group can hardly be postulated. Besides, the formula does not explain the tautomerism, that exists in primary nitro compounds, analogous to the tautomerism of the CH_2CO system:

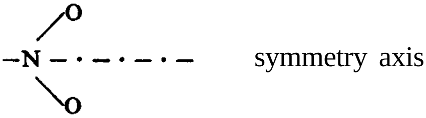
$$-CH_2NO_2 \rightarrow -CH{=}NO(OH) \qquad (2a)$$

$$-CH_2CO- \rightarrow -CH{=}C(OH)- \qquad (2b)$$

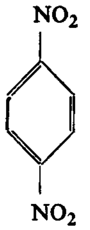
Formula II presents a pentacovalent nitrogen atom surrounded by 10 electrons. All five valences are the ordinary, nonpolar ones. Compounds of pentacovalent nitrogen such as the type $N(CH_3)_5$ are not known. On the other hand formulae III present nitrogen as a tetracovalent atom, surrounded by an electron octet. Here, one of the nitrogen atoms is bonded with an oxygen atom by a coordinate (semi-polar) link.

Confirmation of formulae III is provided by data on the molecular refractivity of nitro compounds. The refractivity for the bonds present in formulae III (6.708) is consistent with the experimental data (6.761).

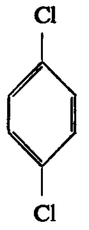
At present formulae III are generally accepted. Nevertheless, they offer some difficulties. Thus, measurements of dipole moments of nitro compounds have shown the nitro group symmetry along the central nitrogen bond:



For example, the dipole moment of p-dinitrobenzene is close to zero, like that of *p*- dichlorobenzene

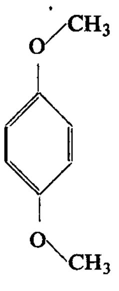


$\mu = 0.6$ D

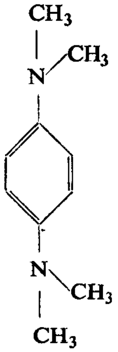


$\mu = 0.3$ D

contrary to, for example, hydroquinone or tetramethyl-p-phenylenediamine esters, which have a relatively high dipole moment, since the substituents introduce asymmetry into molecules:



$\mu = 1.7$ D



$\mu = 1.23$ D

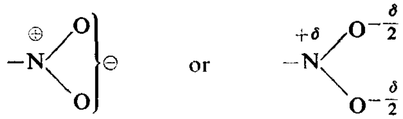
The dipole moment of the nitro group alone, present in an aliphatic nitro compound is :

in the gaseous phase	3.50-3.70 D
in solutions	3.20-3.40 D

In the case of nitrobenzene the dipole moment is:

in the gaseous phase	4.20 D
in solution	4.00 D

For this reason formulae IV are the most probable. They present the negative charge as uniformly distributed between the two oxygen atoms:



IV

The treatment of the nitro group from the molecular orbital point of view is based on the formulae IV. Delocalization of bonds increases its stability - the two oxygen atoms are equivalent. Figure 37 represents: (a) the lowest energy level, (b) the highest energy level and (c) the ground state energy level.

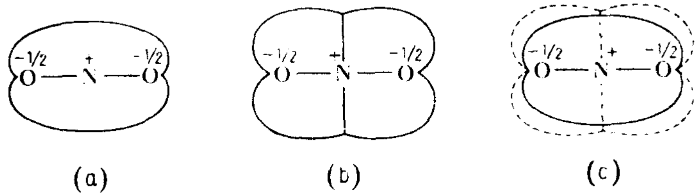
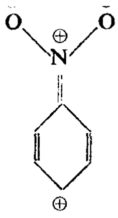


FIG. 37. Molecular orbitals of the nitro group: (a) with the lowest energy level, (b) with the highest energy level, (c) with the ground state energy level [88].

The symmetrical structure of the nitro group is also supported by X-ray analysis of nitro compounds. This is described on the pp. 179- 181.

Likewise, the constitution of, for example, nitrobenzene can be represented as follows:



The formula contains a quinonoid ring to which the slightly yellow colour of nitro compounds can be ascribed. The problem of the quinoid structure of aromatic nitro compounds is discussed on pp. 176, 220.

VISIBLE AND ULTRA-VIOLET ABSORPTION SPECTRA

The nitro group is a chromophor. It produces an absorption band in the ultra-violet region of the spectrum. The position and the intensity of the band depend on several factors which will be discussed later.

In the case of simplest nitro compounds the absorption band produced by this group corresponds to the following values. For aliphatic nitro compounds, for example nitromethane, nitroethane, 1- and 2-nitropropanes, they are: 260-270 mμ at extinctions ε = 40-120. (According to Ungnade and Smiley [l] the values for higher nitroparaffins are 274-278 mμ, ε = 24-41.) For aromatic nitro compounds, such as nitrobenzene the bands are: 250-260 mμ at extinctions ε = 9000-10,000. When a primary or secondary nitro group takes an aci-form, the maximum disappears, as shown by earlier research work of Hantzsch and Voigt [2].

The absorption maximum of a nitro group can be shifted and its intensity may change under the influence of a larger number of nitro groups on the aromatic nucleus.

Changes occurring on the conversion of nitrobenzene to trinitrobenzene have been the subject of investigations of a number of authors (Radulescu and Elexa [3], Kortüm [4], Fielding and Le Févre [5]). All of them obtained similar results. Fielding and Le Févre give the following data for compounds in an alcoholic solution (Table 19).

TABLE 19

Substance	λ_{max} mμ	ε_{max}
Nitrobenzene	260	8130
m- Dinitrobenzene	235	17,400
sym-Trinitrobenzene	225	25,700
Trinitromesitylene	below 220	over 15,800

The data for trinitromesitylene illustrate the steric influence due to the accumulation of substituents around the benzene ring.

Steric influence on the absorption spectra of aromatic nitro compounds has been studied in detail by Brown and Reagan [6]. They investigated the influence of alkyl groups on the absorption spectra curves. As may be seen from the curves, substitution with an alkyl group in the orrho position results in a decrease of the intensity of the nitro group band (compare the absorption spectrum of nitrobenzene with those of *o*- nitrotoluene, *o*- nitrocumene, *o*- nitro-tert-butylbenzene). The larger the alkyl group the stronger its influence. Thus, the band of the nitro group present in *o*- nitro-tert-butylbenzene disappears entirely. The presence of three methyl groups in a molecule gives a similar effect, as may be seen from the nitromesitylene spectrum (Fig. 38).

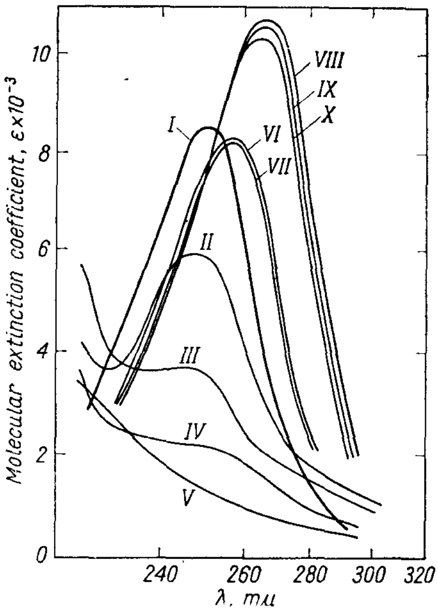


FIG. 38. Absorption spectra of nitrobenzene and its alkyl derivatives: Z-nitrobenzene, II-o-nitrotoluene, III-o-nitrocumene, IV-nitromesitylene, V-o-nitro-tert-butylbenzene, VI-m-nitro-tert-butylbenzene, VII-m-nitrotoluene, VIII-p-nitro-tert-butylbenzene, IX-p-nitrocumene, X-p-nitrotoluene (Brown and Reagan [6]).

A systematic study of the ultra-violet absorption spectra of polynitro compounds were recently carried out by Conduit [7]. By comparing the spectra of isomeric dinitrobenzenes, Conduit came to the conclusion that steric hindrance is responsiblefor the considerable deviation of the spectrum of *o*- dinitrobenzene from those of the two other isomers (Table 20).

He observed a similar effect in isomeric dinitrotoluenes. The most probable

TABLE 20

ULTRA-VIOLET ABSORPTION SPECTRA OF POLYNITRO COMPOUNDS

	λ_{max} mμ	ε_{max}
o- Dinitrobenzene	210	47,600
m- Dinitrobenzene	242	41,300
p- Dinitrobenzene	265	37,140
2,4-Dinitrotoluene	252	39,700
2,6-Dinitrotoluene	241	41,500
1,3,5-Trinitrobenzene	235	42,530
2,4,6-Trinitrotoluene	232	43,100

reason for this is the simultaneous twisting of both o-nitro groups out of plane. Consequently the conjugation of the two nitro groups with the ring is reduced almost to zero.

Methyl groups in nitrotoluenes enhance the conjugation of the nitro groups, except when they are situated in the *ortho* position.

The comparison of the absorption spectrum of *p*- nitrodimethylaniline with those of its derivatives which substituted with the methyl group in the *ortho* position to the nitro group, according to data reported by Remington [8], (see Fig. 39) is also of interest. The presence of one methyl group does not have a marked effect upon the absorption spectrum of the nitro group (approx. 260 mμ), but the presence of a second group causes a considerable fall in the intensity of the band. Another band produced by these compounds, near 420 mμ, is less affected by nitro groups.

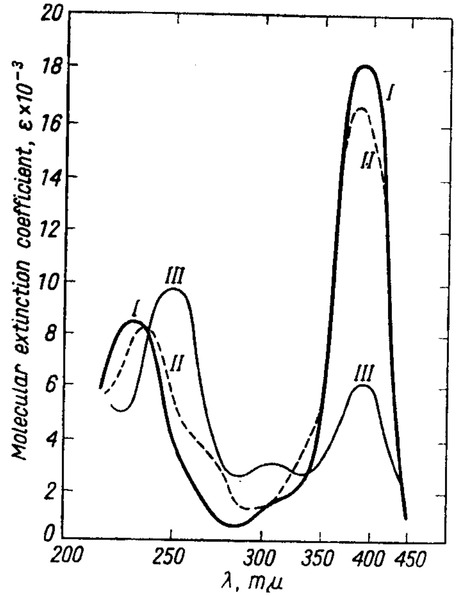
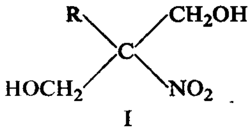


Fig. 39. Absorption spectra of N,N-dimethyl-p-nitroaniline (I) and its methyl derivatives: 3-methyl- (II), 3,5-dimethyl-p-nitrodimethylaniliie (III) (Remington [S]).

The influence of aliphatic rings condensed with *p*- nitroaniline or *p*- nitrodimethylaniline has also been studied (Arnold and Richter [9], Arnold and Craig [10]). They decrease the intensity of the nitro group band, and also that of a band near 370-390 mμ.

According to T. Urbanski [l l] the band of cu. 270 mμ the nitro group in aliphatic compounds can be considerably weakened or it can even disappear under the influence of hydrogen bonds which link the nitro group with two hydroxyl or one amino group as is shown in schemes Ia and IIa.



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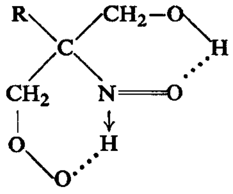
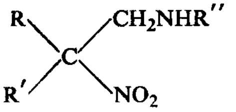


la (with hydrogen bonds)



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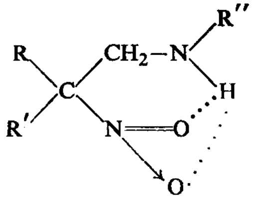


IIa (with hydrogen bonds)

Consequently the absorption curves of compounds I and II do not contain maxima but only shoulders (Fig. 40). They are shifted towards longer wavelength (bathochromic effect) as compared with the original nitroparaftlns.

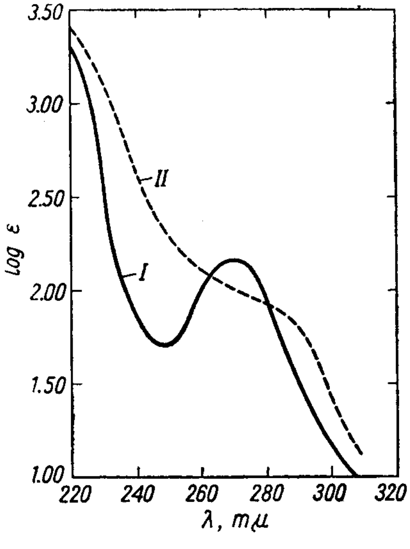


FIG. 40. Absorption spectra of nitroparaffins (I), and nitrodiols and aliphitic aminonitro compounds (II) (T. Urbanski [ll]).

Thus 1-nitropropane shows a maximum at 270 mμ, and the diol (I) obtained from the same compound by adding 2 mol. of formaldehyde shows a bend at 280mμ. A shift of 8-20 mμ was also observed on the corresponding conversion of other nitroparaffins to nitrodiols.

It is important to note that two hydroxyl groups reduce the intensity of the absorption maximum of one nitro group and transform it into a shoulder. One primary amino group and one secondary amino group can produce the same effect as two nitro groups and one nitro group respectively.

In other words one N-hydrogen atom which is able to form a six-membered ring with one nitro group is sufficient to produce an effect similar to that caused by two hydroxylic hydrogen atoms.

The difference between the ability of a hydroxyl and an amino group to reduce the intensity of the maximum produced by a nitro group may be due to the stronger electron repelling power of amino groups. The much stronger influence of the amino group may serve (according to T. Urbanski) as one of the arguments that the hydrogen bond has mainly an electrostatic character.

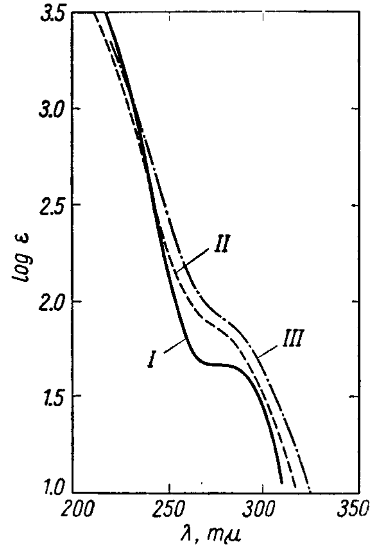


FIG. 41. Absorption spectra of p-halogen derivatives of β– nitroalcohols, e.g. $[(CH_3)_2CHCH_2CH(OH)]_2CXNO_2$: I-X = H, II-X = Cl, III-X = Br (Eckstein, Sobótka and T. Urbanski [12, 13]).

Eckstein, Sobótka and T. Urbanski [12,13] have also found that in β– halogen derivatives of β– nitroalcohols, the shape of the absorption curve depends on the halogen attached to the carbon combined with the nitro group. The increase of the van der Waals radius of the halogen produces a decrease in the intensity of the band characterizing the nitro group. The same rule was observed by the authors when comparing some nitro- and halogenonitro-diols (Fig. 41). This is probably due to the steric effect of shielding the nitro group by a halogen atom.

The influence of a solvent on the absorption spectra of nitro compounds has been examined by several authors. When studying the spectrum of nitromethane, Bayliss and Brackenridge [14] stated that under the influence of a polar solvent the nitro group band underwent a hypsochromic shift (Table 21).

It is interesting to note that ranging from non-polar solvents to sulphuric acid through polar solvents affects aromatic nitro compounds in the opposite direction, i.e. it results in a bathochromic shift. This can be seen from Hammond and Modie's data [15] for nitrobenzene (Table 22).

TABLE 21

ABSORBTION SPECTRA OF NITROMETHANE

Solvent	Absorption maximum mμ
Heptane	277.6
Ethanol	274
Water	268.8
Sulphuric acid	252.5

From the results of investigations into the absorption spectra of nitromethane in non-polar solvents (cyclohexane and carbon tetrachloride) de Maine and his co-workers [16] drew an important conclusion. They found that dilute solutions of nitromethane do not obey Beer's law, unlike more concentrated solutions in carbon tetrachloride. From this the authors deduced that in more concentrated solutions nitromethane was present as a dimer, while in dilute solutions it is a monomer. Thus there is a state of equilibrium between the two forms:

TABLE 22

ABSORPTION SPECTRA OF NITROBENZENE IN VARIOUS SOLVENTS

Solvent	Absorption maximum mμ
Hexane	252
Water	267
69.6% H_2SO_4	276
98.4% H_2SO_4	288.5

$$2CH_3NO_2 \rightarrow (CH_3NO_2)_2 \qquad (3)$$

Brand and his co-workers [17] carried out extensive studies on the absorption spectra of aromatic compounds in sulphuric acid solutions, i.e. in a strongly protonizing solvent. They found that under the influence of the sulphuric acid the maximum of the nitro group shifted. These shifts were most pronounced in the case of mononitro compounds, and the least in the case of trinitro compounds. They were smaller when sulphuric acid was used as a solvent, and larger when oleum was used. The absorption curves for 2,4-dinitrotoluene are shown in Fig.

42, and those for 2,4,6-trinitrotoluene in Fig. 43. The observation is in agreement with Hantzsch's old view (p. 218), that assumed nitrotoluene to possess a basic character, which appears when it is dissolved in sulphuric acid. Later studies have shown that as the number of the nitro groups increases, the basic properties weaken.

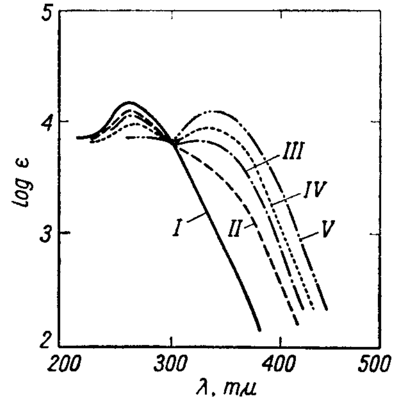


FIG. 42. Absorption spectra of 2.4-dinitrotoluene in sulphuric acid of various concentrations: I - 99.0, II - 102.74, III - 105.46, IV - 107.30, V - 114.5% H_2SO_4 (Brand [17]).

(On the addition of a proton to nitro compounds see also the chapter on the reactivity of aromatic nitro compounds, p. 218.)

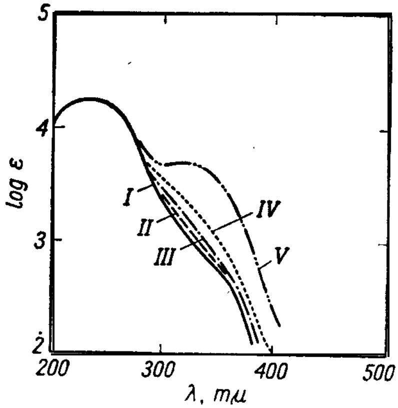
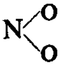
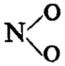
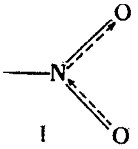


FIG. 43. Absorption spectra of 2,4,6-trinitrotoluene in sulphuric acid of various concentrations: I - 99.0, II - 102.1, III - 105.5, IV- 108.3, V- 114.5% H_2SO_4 (Brand [17]).

Mention should also be made of recent work of Tanaka [18], who has applied wave mechanics to calculate the σ– electron orbitals (two orbitals) and π– electron orbitals (one orbital with two electrons and two with one electron) of the nitro group. From these figures the author inferred that the absorption of the nitro group near 280 mμ arises from the transition of free electrons surrounding oxygen atoms to the π orbital.

INFRA-RED ABSORPTION SPECTRA

In the infra-red region the nitro group produces two bands of high intensity: one near 6.4μ (1563 cm^{-1}), which characterizes asymmetric vibrations of the  bonds of the nitro group (I), and another near 7.4μ (1351cm^{-1}), which characterizes symmetric vibrations of the  bonds of the nitro group (II).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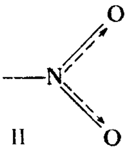

II

In addition to this, vibrations of the nitro group ranging from 4.0-4.17μ (2500-2398 cm^{-1}) exist (Kornblum, Ungnade and Smiley [19]), but they are of little significance for identification according to the authors.

On the basis of their investigations of nearly 35 nitro compounds, Kornblum, Ungnade and Smiley have distinguished the vibrations of primary, secondary and tertiary nitro groups in aliphatic nitro compounds (Table 23).

TABLE 23

Nitro compounds	Vibrations			
	asymmetric		symmetric	
	μ	cm^{-1}	μ	cm^{-1}
primary	6.45±0.01	1550±2	7.25±0.02	1379±3
secondary	6.45±0.01	1550±2	7.37	1357
tertiary	6.51±0.01	1536±2	7.41±0.02	1348±3

It can be seen from these data that the position of the nitro group band depends on whether the group is primary, secondary or tertiary.

The results of the above investigations are at the same time a summary of the earlier data obtained by several authors: Barnes et ***al. [20],*** Smith et *al.* ***[21],*** Haszeldine ***[22]*** and Brown [23].

Bellamy [24] gives the figures:

1565-1545 cm^{-1} and 1383-1360 cm^{-1}

for both primary and secondary nitroaliphatic compounds. In tertiary nitro compounds the frequencies are lower:

1545-1530 cm^{-1} and 1358-1342 cm^{-1}

Conjugation of the nitro group by attachment to an ethylenic double bond leads to a fall in both frequencies, according to Shechter and Shepherd [25] and Brown [23], to

1524-1515 cm^{-1} and 1353-1346 cm^{-1}

α– Halogen substitution has also a marked effect upon nitro group frequencies. According to Brown and Haszeldine the frequencies increase under tie influence of the α– chlorine atom.

They are: 1575±5 cm^{-1} and 1348±6 cm^{-1}, while under the influence of two α– chlorine atoms they are displaced:

1587±10 cm^{-1} and 1332±5 cm^{-1}

According to T. Urbanski [26] the bands of the nitro group in aliphatic nitro compounds under the influence of the hydrogen bond can be shifted to lower frequencies :

for asymmetric vibrations by	12-24 cm^{-1}
for symmetric vibrations by	30-42 cm^{-1}

Aromatic nitro compounds have been the subject of investigation by numerous authors: France1 [27], Lothrop et al. [28], Randle and Whiffen [29], and Brown [23].

Kross and Fassel [30], on the basis of investigation of over thirty aromatic compounds, gave the following vibration frequencies of the nitro group:

asymmetric: in non-polar solvents	1523±8 cm^{-1}
as solids	1525±10 cm^{-1}
symmetric: in non-polar solvents	1344±7 cm^{-1}
as solids	1339±7 cm^{-1}

These bands shift under the influence of several factors.

According to Brown [23], Kross and Fassel [30] and Conduit [7], the asymmetric frequence is considerably reduced from cu. 1534 cm^{-1} (e.g. to 1510 cm^{-1}) under the influence of a powerful electron-donor such as NH_2.

Conduit classified the asymmetric frequencies according to the number of nitro groups :

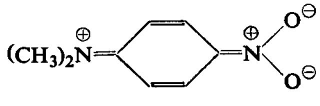
mononitro	1509-1540 cm^{-1}
dinitro	1539-1552 cm^{-1}
trinitro	1554-1567 cm^{-1}

The only discrepancy in the above correlation arises when a dinitro compound also contains strong electron-donor groups (e.g. NR_2.

Lippert [31] draws attention to the fact that the nitro group frequencies can be shifted under the influence of a solvent. They are decreased in polar solvents and their intensity increases. This effect is particularly strong when the nitro compounds contain strong electron-repelling groups. Thus *p*- nitrodimethylaniline gives bands in non-polar CCl_4 and strongly polar CCl_3CN as shown below:

	CCl_4	CCl_3CN
asymmetric vibrations	1506 cm^{-1}	1332 cm^{-1}
symmetric vibrations	1496 cm^{-1}	1320 cm^{-1}

Lippert [31] tried to explain this phenomenon by assuming that a polar solvent enhances the stability of the resonance structure of a solute

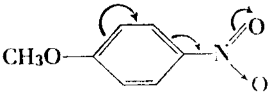


An increase in the number of molecules of this polar structure results in increasing the negative charge of the acceptor group, i.e. NO_2, hence in a decrease of frequency and a rise of intensity of absorption.

A number of authors have found that conjugation of double bonds lowers the frequency of NO_2 bands. Shechter and Shepherd [25], Fieser et al. [32], Eckstein, Kraczkiewicz, T. Urbanski and Wojnowska [33] have all reported that this occurs with nitro-olefins.

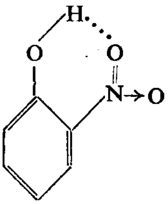
A similar phenomenon was noticed in the case of aromatic compounds. Thus, Bellamy [24] has pointed out that in polynitro compounds when one nitro group remains coplanar whilst another is twisted out of the plane of the ring under the influence of steric hindrance, the degree of aromatic conjugation is reduced and a new higher frequency band appears.

Frank, Hörman and Scheibe [34] also found that asymmetric NO_2 vibrations could be shifted towards lower frequencies under the influence of conjugation in aromatic compounds. They examined their substances in potassium bromide. A number of aromatic nitro compounds in dilute solutions were recently examined by T. Urbanski and Dabrowska [35]. They found that when a nitro group was placed in the *para* position with respect to another group, its symmetric stretching modes were of a lower frequency than in the *meta* position. This was most likely due to the strong conjugation of substituents with the ring:



The nitro group in the *ortho* position also gave a higher frequency. Thus for instance in the case of *o*-, *m*- and *p*- nitroanisoles the frequencies were 1352, 1347 and 1341 cm^{-1} respectively. In the case of *m*- and *p*- nitrophenol the frequencies were 1349 and 1339 cm^{-1} respectively.

The frequency of the nitro group in *o*- nitrophenol was markedly reduced, to 1320 cm^{-1}, as the result of hydrogen bonding between the nitro and phenolic group:



Bellamy [34] pointed out that in polyaromatic compounds multiple peaks can occur if hydrogen bonds are attached to the nitro group.

Steric effects of bulky substituents in the *ortho* position to the nitro group (such as I) can reduce the frequency of the *p*- nitro group vibrations, as shown by Perret and Holleck [36] (Table 24).

The authors explain that the strong steric effect on *o*- nitro groups produced by the halogens, particularly iodine, is superposed upon the induction effect of the *o*- nitro groups. Hence a reduction in the frequency of *p*- nitro group vibrations occurs. This is in agreement with an observation by Golder and Zhdanov [37] who found that the C-N bond in the *para* position in picryl chloride is considerably shortened (1.38 Å), and thus approaches the value of a double bond. The *ortho*-situated C-N bonds are of a normal length (1.46 Å).

TABLE 24

Substances	Asymmetrical vibrations, cm^{-1}	Position of the nitro group
sym-Trinitrobenzene	1558	*o*- and *p*-
Picryl chloride	1550 1560	*p*- *o*-
Picryl iodide	1543 1558	*p*- *o*-

In the case of 2,4,6-trinitrobenzoic acid, the frequency of all the nitro groups remains unchanged (1553 cm^{-1}). However, the presence of nitro groups increases the C=O frequency of the carboxylic group to 1733 cm^{-1} (as against 1698 cm^{-1}

TABLE 25

SPECTRAL CHARACTERISTICS OF MONO-, DI- AND TRINITRO COMPOUNDS

Nitro compounds	Bands, cm^{-1}
o- Mononitro containing any one of the following groups *ortho* to the nitro: CH_3, C_2H_5, CHO, NH_2, COOH	787-781
p- Mononitro containing the same group as above *para* to the nitro	1111
m- Dinitro containing the following additional group: CH_3, C_2H_5, OH, NH-NH_2, COOH, CHO. OCH_3, CH_3NH, C_2H_5NH, NO_2 (trinitro) in sym-trinitro compounds	930-922† 939-909
m- Dinitro containing other additional groups *ortho* to the nitro	840-836
sym-Trinitro which have the additional groups: CH_3, C_2H_5, OH, OCH_3, OC_2H_5, COOH, NH	1081†

† These bands are the most important for diagnostic purposes.

in benzoic acid). According to Perret and Holleck [36], this is due to the out-of-plane deformation vibrations of the carboxylic group which occur under the influence of the nitro groups.

An extensive study of the infra-red absorption spectra of nitro compounds was reported recently by Pristera, Halik, Castelli and Fredericks [37a]. The following are bands which are valuable in the structural investigation of unknown nitro compounds and their mixtures (Table 25).

Recently a number of authors (Holder and Klein [38], Ogg Jr. and Ray [39] have examined certain nitro compounds, particularly in comparison with the nitrite ion (NO_2^-).

NUCLEAR MAGNETIC RESONANCE AND X-RAY EXAMINATION OF NITRO COMPOUNDS

The major application of nuclear magnetic resonance spectroscopy to organic chemistry involves the study of proton shifts (the “chemical shift” of proton),

The aromatic proton frequencies of substituted benzenes fall between 2.0 and 3.5 according to the number and nature of the substituents. Corio and Dailey [39a] have examined a number of monosubstituted benzenes.

The proton frequency of benzene was found to be 2.73.

In nitrobenzene the frequencies of the *meta* and *para* protons are lowered by the figures of the same order (-0.30 and -0.42 respectively), whereas the *ortho* protons are of much lower frequency (-0.97).

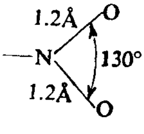
A similar phenomenon was found with COOH, COCl, $COOCH_3$ and CCl_3, whereas CN lowers the frequency by 0.30 equally in all three positions: *o*-, *m*- and *p*-.

Schmidt, Brown and D. Williams [40] examined the nuclear magnetic resonance of ^{14}N in three aromatic nitro compounds: nitrobenzene, nitrobenzoic acid, dinitrobenzoyl chloride.

In all three compounds the ^{14}N peak was observed. In each case the peak was not so wide as in NO_2^- ion and considerably wider than that in the NO_3^- ion. The broadness occurring with nitro groups (and even greater broadness in the NO_2^- ion) was indicative of large electric asymmetries at ^{14}N in these groups.

The shifts measured ranged from 165 milligauss in an ether solution of $(NO_2)_2C_6H_3COCl$ to 230 milligauss in $C_6H_5NO_2$, in a field of 10,700 gauss (NH_4^+ as a standard).

X-ray investigations indicate that the nitro group has a planar or near-planar structure, and that the atom distances and the bond angles for the nitro group of dinitrobenzene are:



The N-O angle for various compounds varies from 125° to 134°, and the distances between nitrogen and oxygen atoms from 1.17 to 1.30Å

The structural configuration of *p*- dinitrobenzene was the one most fully examined in investigations of the structures of aromatic compounds by X-rays. Among the first to carry out this research were Hertel [41], Bannerjee [42] and James, King and Herrocks [43]. The last group of investigators determined the structure by means of two-dimensional series and projections onto the principal planes. Because of limited accuracy attainable with the technique all that time the pattern obtained was not clear enough. The molecule was not planar, the benzene ring was distorted, and the N-O, bonds differed in length. It was only when Llewellyn's investigations [44] were published in 1947, in which a complete three-dimensional Fourier synthesis was applied, that a definite pattern was obtained as shown in Fig. 44. The accuracy of determination of the bond length was ±0.02Å and that of the angles ±2°. The molecule proved to be exactly planar with the benzene ring undistorted, and the lengths of the N-O. bond equal.

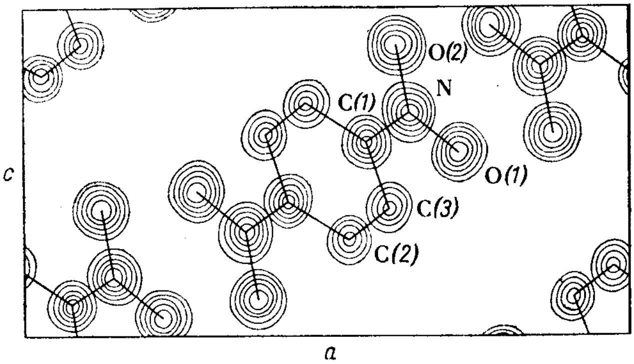


FIG. 44. Electrons density of *p*- dinitrobenzene(Llewellyn [44]).

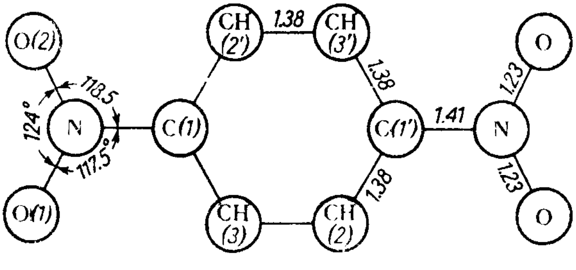


FIG. 45. Bond distances and angles of p-dinitrobenzene (Llewellyn [44]).

The structure of m-dinitrobenzene has been established by X-ray analysis by Archer [45], utilizing Fourier analysis. The author proved the benzene ring to be a regular hexagon with sides of 1.41Å. The C-N bonds do not lie in the plane of the ring but make an angle of 15° with it. The C-N bond length is 1.54Å and the N-O distance has been found to be 1.20 Å. The distance between the atoms of oxygen in the nitro group is 2.17 Å.

The structure of *m*- dinitrobenzene, as established by Archer [45], is shown diagrammatically in Fig. 46.

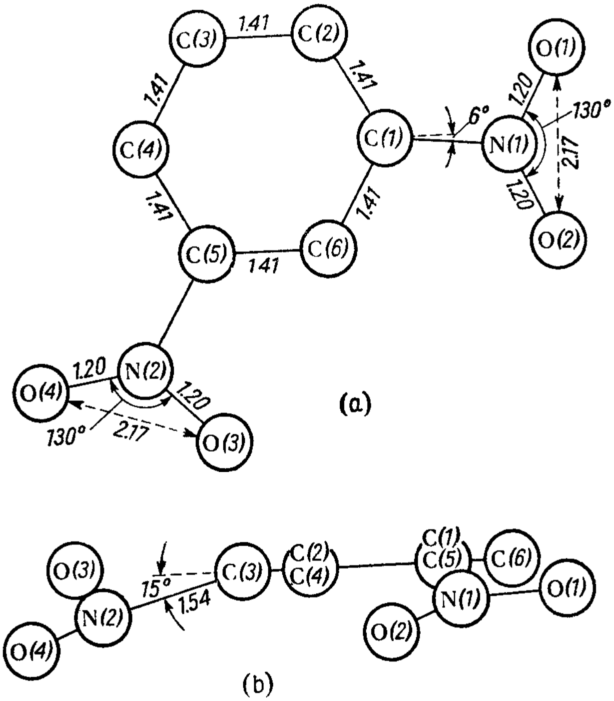


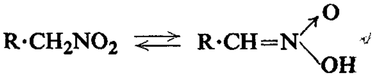
FIG. 46. Bond distances and angles of *m*- dinitrobenzene (Archer [45]).

Structures of the simplest compounds containing the nitro group, such as for example, NO_2, N_2O_4, HNO_3 and NO_2^+, have already been discussed. The N-O distances for nitromethane are 1.21 Å and the bond angle 127° (Brockway, Beach and Pauling [46] and Rogowski [47]).

CHEMICAL PROPERTIES OF NITRO COMPOUNDS

PRIMARY, SECONDARY AND TERTIARY NITRO COMPOUNDS

The chemical properties of primary and secondary nitro compounds differ considerably from those of tertiary nitro compounds. This is due to the presence of active hydrogen atoms in the first two. The difference appears most clearly when nitro compounds are treated with alkalis. As long ago as 1872 Meyer [48,48a] observed that certain nitroparaffins were soluble in sodium hydroxide solutions. In 1888 Michael [49], and later Nef [50], suggested that the salt formed in the process was one of the tautomeric forms assumed by the nitro compound, so-called aci- or iso-nitro form (Ia):



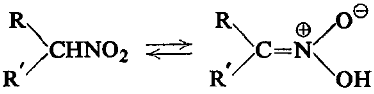
$$R\cdot CH_2NO_2 \rightleftarrows R\cdot CH{=}N\begin{matrix}\nearrow O\\ \searrow OH\end{matrix}$$

I Ia

Experimental evidence of the existence of aci-forms has soon been provided. In 1895 Holleman [51] found that *m*- nitrophenylnitromethane yielded a yellow salt, which under the influence of hydrochloric acid was converted initially into a yellow substance having a high electrical conductivity. After some time, the product changed into a colourless substance, showing no electrical conductivity. The aci-structure was assigned to the yellow substance, and that of a pseudoacid to the colourless one.

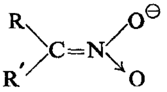
This observation was confirmed by Hantzsch and Schultze [52] in 1896 with phenylmtromethane. The aci-form of phenylnitromethane is a crystalline product. Its melting point is 84°C. It charges spontaneously into the normal, liquid form. Aci-forms differ from the normal ones in that they turn brown-red with ferric chloride.

Secondary nitroparaffins behave similarly :

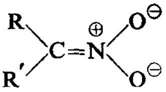


II Ha

Thus the anion of the aci-form of nitroparaffins can be written in two ways: IIIa and IIIb



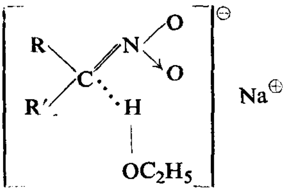
IIIa



IIIb

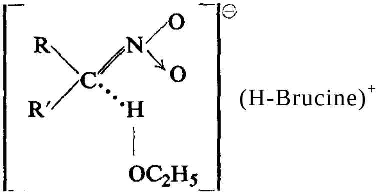
However, these structures were in doubt for a number of years. Strong evidence for criticizing them was given in 1927 by Kuhn and Albrecht [53]. They reported that optically active D- and L-2-nitrobutanes can be converted into their optically active sodium salts and then regenerated without complete racemization. This was confirmed by Shriner and Young [54] who found that 2-nitrooctane behaves similarly. Subsequently the structures Ia and IIa for the aci-forms and IIIa and IIIb for the aci-anion appeared to be excluded as they cannot correspond to dissymmetric configurations. If they were correct, the regenerated nitro compounds should be racemic.

Shriner and Young tried to explain this behaviour of nitroparaffins by postulating the "normal" structure of anion "stabilized" by combination with the solvent, e.g. ethanol, through a hydrogen bond (IV):



IV

This appeared to be supported by the findings of Ray and Palinchak [55] who resolved 9-nitro-2-benzoylfluorene with brucine. The brucine salt contained alcohol of crystallization and could probably be represented by the formula V:



V

The theory of “solvated asymmetric anion” therefore appeared to be admissible [56].

However, in 1947 Kornblum et al. [57] showed that the apparent incompleteness of racemization is due to incomplete neutralization and also to the presence of optically active impurities in the nitro compounds used. He found that the complete neutralization of the pure nitro compounds always leads to complete racemization. This was also confirmed by Theilacker and Wendtland [58]. The results of Komblum and the latter authors evidently supports the formulae Ia and IIa.

Generally speaking it is now admitted that primary and secondary nitroparaffins exist in normal and aci-forms and that there is an equilibrium between them.

The two forms may be distinguished from each other by the fact that aci-form absorbs bromine and gives characteristic colour reaction with ferric chloride. The equilibrium constant depends on the solvent used, and mainly on its basicity. Thus *p*- nitrophenylnitromethane contains 0.18% of aci-form in ethyl alcohol, 0.79% and 16% in aqueous methyl alcohol and pyridine respectively [59].

Tertiary nitro compounds, of course, do not undergo tautomeric transformation, and they might be expected to be resistant to alkalis. Nevertheless aromatic nitro compounds, and polynitro-ones in particular, are very sensitive to alkalis, and undergo transformation when treated with them. For example, sym-trinitrobenzene and also α– trinitrotoluene, when reacted with potassium hydroxide in methyl alcohol solution, form dark addition products (see also p. 202). Under certain conditions the nitro group can break off to form high molecular compounds.

Nitro derivatives of benzene, when boiled with sodium hydroxide in methyl alcohol solution are reduced to azoxy compounds (pp. 31, 237, 251). Nitro derivatives of toluene under these conditions are oxidized to nitro derivatives of stilbene (pp. 70, 283, 302).

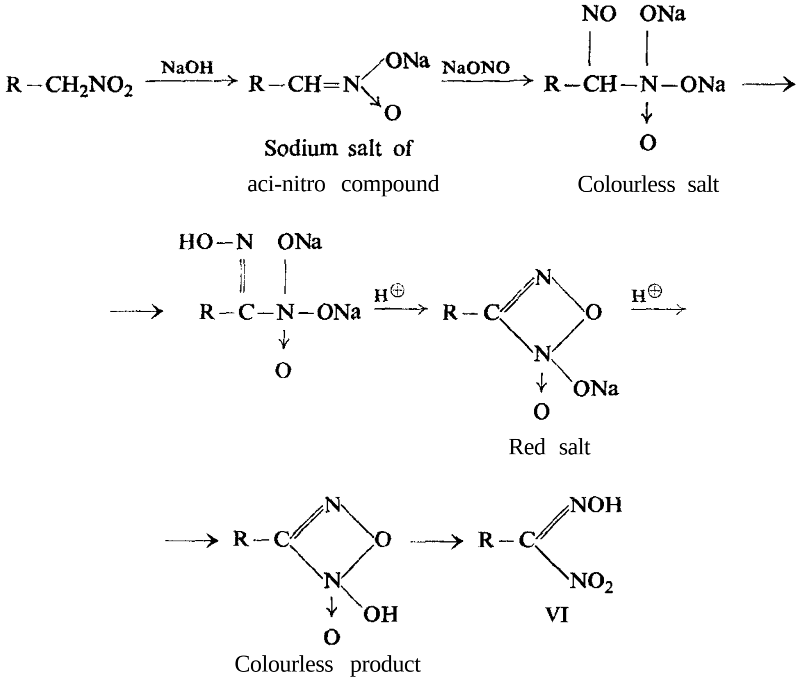
Both cryometric (Gillespie [60]) and spectrographic (Brand, Horning and Thornley [17]) investigations of nitro compounds indicate that in sulphuric acid solutions mononitro compounds behave like weak bases (p. 174). Thus it follows from cryometric measurements that nitromethane in 100% sulphuric acid solution is 20% ionized, and nitrobenzene 40%. Nitrobenzene is a stronger base than nitromethane.

The pale yellow colour of nitrobenzene or *p*- nitrotoluene turns more intense when the compound is dissolved in sulphuric acid, while solutions of nitromethane and other nitroparaffins are colourless. The yellow colour of the aromatic nitro compounds is due presumably to an ionic structure containing a quinonoid ring.

Primary and secondary nitro compounds also react with acids, while tertiary compounds show considerable resistance to them.

Primary nitro compounds, when treated with nitrous acid, give nitrolic acids (VI).

The reaction leading to the formation of nitrolic acids was described for the first time by V. Meyer [49]. The compounds are formed by treating aci-forms of primary paraffins with $NaNO_2$, followed by acidification of the whole mass. According to Veibel [61], the mechanism of the reaction may be presented by the following multistage scheme :

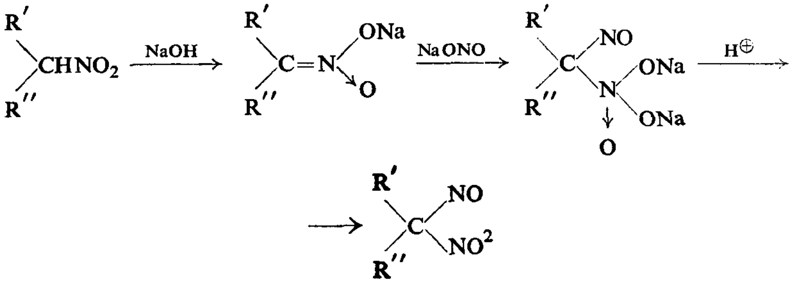


(4)

Nitrolic acids, when reacted with sodium or potassium hydroxide, produce a reddish-brown colour. The reaction is used for the detection of primary nitroparaffins. Secondary. nitroparaffins form pseudonitroles with nitric acid (VII)

Again V. Meyer was the first to describe the reaction. As in the formation of nitrolic acids, here also it is the aci-form of the secondary nitro compound that takes part in the reaction. It reacts with sodium nitrite to give a compound which. after acidification, forms pseudonitrole.

According to Veibel [61], the formation of pseudonitrole can be explained by the following reaction series :

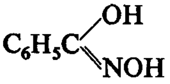


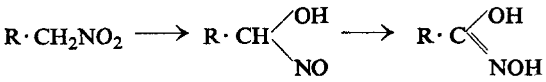
VII

(5)

Pseudonitroles are crystalline, colourless products. They exist probably as dimers. But when molten or in solutions they turn blue, and are probably present as monomers. The reaction is utilized for the detection of secondary nitro compounds.

Heating the primary nitroparaffins with sulphuric acid of a concentration over 50% results in their isomerization to hydroxamic acids (IX).

From phenylnitromethane, Bamberger [62] obtained benzhydroxamic acid,  $C_6H_5C\begin{smallmatrix}OH\\NOH\end{smallmatrix}$ and explained the mechanism of the isomerization reaction as:



VIII IX

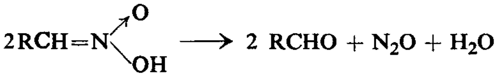
(6)

A blue hydroxynitroso compound (VIII) is formed as an unstable Intermediate product.

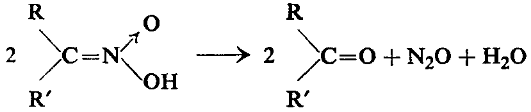
T. Urbanski [63] and T. Urbanski and Gurzydska [64] found that isomerization also occurs under the influence of acetic anhydride or ketene in the presence of a basic agent such as sodium acetate or pyridine.

In some cases hydroxamic acid hydrolyses to form hydroxylamine. The reaction has been utilized by Turski [65] for direct amination of aromatic hydrocarbons. Primary nitroparaffins were used in place of hydroxylamine, and sulphuric acid and a catalyst (e.g. V_2O_5) were present.

When a salt of the aci-form of a primary or secondary nitroparaffin is treated with an acid, it may decompose, evolving nitrous oxide and yielding an aldehyde or ketone:



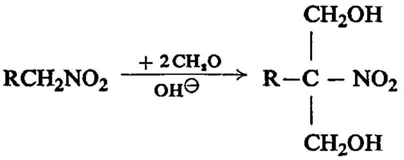
(7a)



(7b)

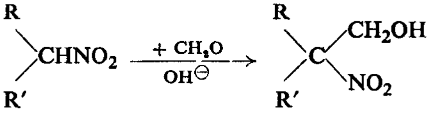
The reaction was discovered by Nef [50] and was investigated later by Nametkin [66], and by Johnson and Degering [671.

A very characteristic feature of primary and secondary nitro compounds is their ability to add on aldehydes in a weak basic medium to form nitroalcohols (X, XI). Formaldehyde is particularly readily added:



$$RCH_2NO_2 \xrightarrow[OH^{\ominus}]{+\,2CH_2O} R-\overset{\displaystyle CH_2OH}{\underset{\displaystyle CH_2OH}{C}}-NO_2 \qquad (8a)$$

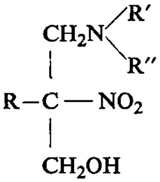
X



(8b)

XI

Nitroalcohols X and XI may be utilized as starting materials for the manufacture of nitric acid esters having explosive properties (see Vol. II). In the presence of primary or secondary amines or ammonia the reaction leads to formation of aminonitroalcohols (XII)

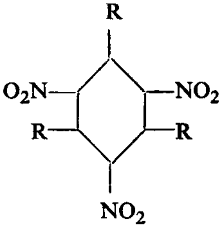


XII

When R' = H (i.e. in the case of primary amines), the product may react further with formaldehyde to form a tetrahydro-1,3-oxazine ring, or with an amine and formaldehyde to form a hexahydropyrimidine ring. When using ammonia, (R' = R" = H), the same rings may be formed (Hirst, J. K. N. Jones, T. Urbanski *et al.* [68]).

All nitro compounds, even the tertiary ones, which contain no "active hydrogen" atoms, react with the Grignard reagent (Oddo [84]). Thus, according to Gilman and Fothergill [69], nitrobenzene reacts in the Zerevitinov reaction as if it contained two active hydrogen atoms. Further studies of Gilman and Fothergill have proved that the nitro group itself gives the Zerevitinov reaction, even when a compound does not contain hydrogen at all, as for example, tetranitromethane, pentabromonitrobenzene, etc.

According to several authors (e.g. Moureu [85], Bewad [86], Kharasch and Reinmuth [70]), the Grignard reagent may react with nitro groups reducing them to amino- or hydroxyamino groups (NHOH). However, this is not the only way the Grignard reagent reacts with aromatic nitro compounds. Thus Severin [71] has established that sym-trinitrobenzene reacts with magnesium alkyl bromide to form a yellowish precipitate of an addition product which, with aqueous acetic acid, gives colourless crystals of 1,3,5-tri-alkyl-2,4,6-trinitrocyclohexane



R = C_2H_5 (m. p. 276°C)
R = C_4H_9 (m. p. 258°C)

Polarographic reduction of nitro compounds is a subject matter of a recent monograph by Strading [87].

HETEROCYCLIC NITRO COMPOUNDS

Heterocyclic nitro compounds have no practical importance in the technology of explosives, either because the raw materials are too expensive, or because it is difficult to introduce the nitro group into them. For example, pyridine and its homologues, the most easily obtainable heterocyclic compound, are nitrated only with the greatest difficulty, and the most powerful nitrating agents give 3-nitropyridine only in low yield (e.g. 6%) [89].

When nitrated in the gaseous phase with nitrogen dioxide at temperatures of 115-120°C, pyridine gives also 3-nitropyridine (Shorygin and Topchiyev [74]) in the same yield. See also Schofield [90].

Alkylpyridines (picolines, and especially lutidines) can be nitrated much more readily, as Plazek [75] has shown. Introduction of the nitro group is greatly facilitated by the presence of the hydroxyl group in the pyridine ring. For example, 3-hydroxypyridine can be nitrated to 2-nitro-3-hydroxypyridine in good yield (Plazek and Rodewald [76]). It may be further nitrated to the dinitro derivative. From this, 3,5-dinitropyridine can be obtained (Plazek [77]).

It has been shown recently by den Hertog and Overhoff [78] that N-pyridine oxide can readily be nitrated with a nitric and sulphuric acid mixture. 4-Nitropyridine is formed in good yield-about 81%.

Another heterocyclic compound obtainable in considerable quantities-quinoline-nitrates in the isocyclic ring. Indole and carbazole behave in a similar way. Nitro derivatives of these compounds have not yet found practical application.

Dinitro derivatives of thiophene described by Steinkopf have recently been obtained in a pure form by Blatt and co-workers [80] by nitrating 2- and 3-nitrothiophenes in nitric acid-acetic anhydride mixture, according to Steinkopf. A good yield of 2,4-dinitrothiophene (m.p. 49-50°C) was obtained. In the case of nitrating 3-nitrothiophene a smaller proportion of 2,5-dinitrothiophene (m.p. 78-82°C) was also formed.

The ability of the substances of being nitrated depends on many factors which exercise their influence upon the activity of the compounds. For example cyclopentadiene, C_5H_6 can readily be nitrated with ethyl nitrate (Thiele [72]). Titov [73] explained this fact by suggesting that the hydrocarbon forms readily the anion $C_5H_5^-$ which possesses a high potential π.

On the contrary, ferrocene, $(C_5H_5)_2Fe$, can be nitrated with difficulty. This is explained by formation of cation $(C_5H_5)_2Fe^+$ with reduced activity towards electrophilic agents.

NITRO COMPOUNDS AS EXPLOSIVES

Among aliphatic nitro compounds nitromethane was only recently recognized as an explosive. Tetranitromethane is not explosive but can form an explosive when mixed with combustible substances. Tetranitromethane possesses here a character of an oxygen carrier.

Nitro derivatives of aromatic compounds as explosives are of greatest practical importance.

It is usually considered that only those nitro compounds possess explosive properties which contain at least two nitro groups attached to one benzene ring. However, Berthclot [81] noticed as long ago as 1887 that the presence of even one nitro group is sufficient to increase the ease of thermal decomposition of the aromatic compound. This was later confirmed by Datta and Chatterjee [82], and Condit and Haynor [83] when studying the temperatures of thermal decomposition of nitro compounds. Nevertheless, among aromatic nitro compounds only those which have three or more nitro groups for one benzene ring (and some of those which have two) exhibit distinctly marked explosive properties. Among the compounds with two nitro groups, only dinitrobenzenes and dinitrotoluenes are recognized as explosives while dinitronaphthalenes are on the borderline between explosive and non-explosive substances. Trinitronaphthalene has explosive properties similar to those of dinitrobenzene, since the ratio between the number of nitro groups and carbon atoms is approximately the same for both compounds.

For this reason, mononitro compounds will be described only from the viewpoint of their utilization as intermediates for the preparation of higher nitrated products.

Explosive nitro compounds exhibit a high degree of chemical stability and undergo no changes during storage. They differ from other explosives by possessing a low sensitivity to impact and friction.

Aromatic nitro compounds are obtained from the corresponding aromatic compounds by classic nitration methods using mixtures of nitric and sulphuric acids. The methods will be discussed in further chapters.

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CHAPTER VI

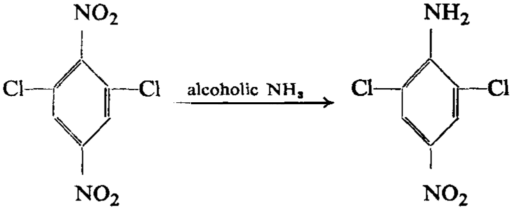
AROMATIC NITRO COMPOUNDS

REACTIVITY OF THE NITRO GROUP

AROMATIC nitro compounds which are of course tertiary, form a separate group of compounds, differing from the aliphatic nitro derivatives in many respects. For this reason they deserve special attention.

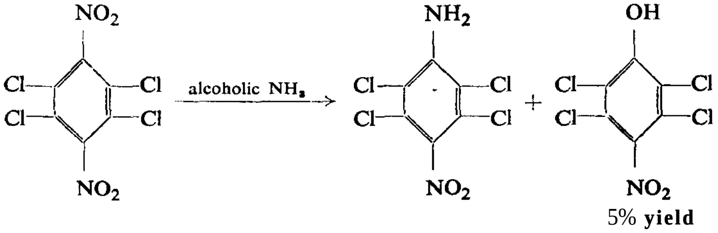
The attachment of nitro groups to the aromatic ring affects their reactivity. For example, nitro groups in *ortho* or *para* position in relation to each other are rather reactive, and one of them can be substituted relatively easily. Only the nitro groups in the *meta* position to each other are stable. Thus, one of the nitro groups in the unsymmetrical trinitrotoluenes (isomers of TNT) can readily be substituted. This is a consequence of the substitution rule, that the nitro group directs a new entrant group towards *meta* position. If in an aromatic compound two nitro groups, i.e. meta-orienting groups, are in a different - *ortho* or *para* position in relation to each other, the system must be unstable.

A nitro group may also become mobile under the influence of a large number of substituents in the same ring. The following reaction was observed by Körner and Contardi [1] as early as 1914:



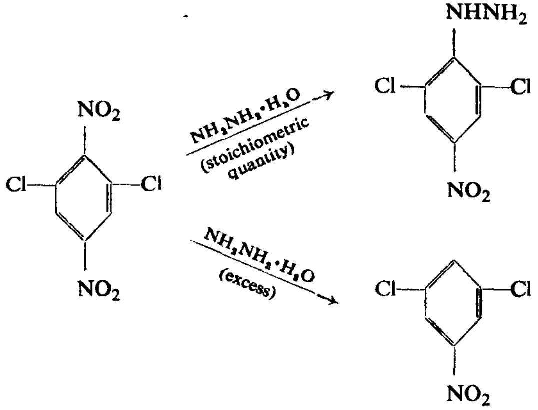
(1)

Peters, Rowe and Stead [2] observed a similar reaction, accompanied by hydrolysis as a side-reaction:



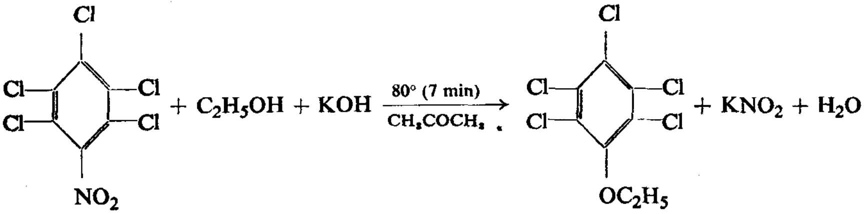
5% yield

A number of reactions on the mobility of the NO_2 group have been carried out by Qvist and his co-workers [3,4,5]:



(3)

In presence of an excess of hydrazine, denitration occurs, probably because of the reducing action of this reagent. Pentachloronitrobenzene (a well known fungicide "Terraclor") hydrolyses to form pentachlorophenol or its ethers:



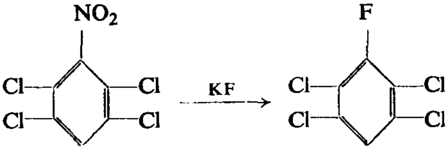
"Terraclor" Pentachlorophenetole

The yield of the reaction amounts to 50% and it can be utilized for quantitative analysis of pentachloronitrobenzene by determining the quantity of KNO_2 split off (Ackermann ***et al.*** [6]).

On mobility of nitro groups, see also Loudon and Robson [158].

Nitro groups can be replaced by chlorine and bromine on drastic action of phosphorous pentachloride (Ganguly [6a]) or chlorine [151] and bromine [152] respectively.

A nitro group adjacent to chlorine atoms in the *ortho* and *meta* position can be replaced by fluorine on heating with potassium fluoride at 147°C:

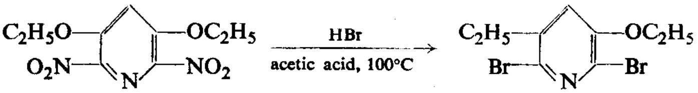


(5)

The reaction yield is 10%. It may be increased up to 37% by heating in dimethylformamide solution (Finger and Kruze [7].)

On vigorous reaction with basic reagents (sodium hydroxide or sodium alcoholate), a nitro group located symmetrically, in the *meta* position to other nitro groups and, hence of relatively low reactivity, may also be substituted. Thus, for example, from sym-trinitrobenzene, 3,5-dinitrophenol or its ethers may be obtained (p. 251).

An interesting example of the replacement of a nitro group in the *meta* position by a bromine atom can be observed in the case of the pyridine derivatives (Koenigs, Gerdes and Sirot [8]):



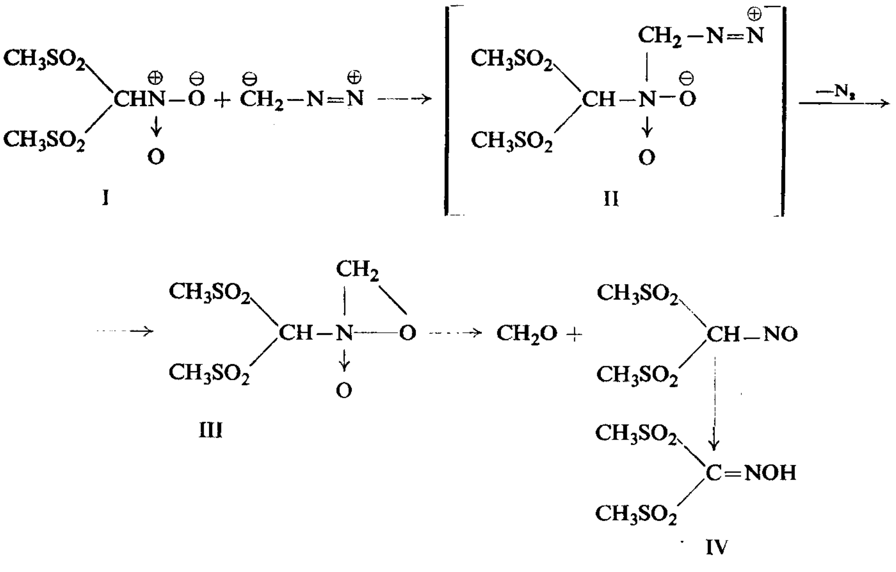
(6)

Also the nitro group in 4-nitropyridine-N-oxide is very mobile (den Hertog and Combé [8a]).

The nitro group itself exhibits a certain reactivity which is not confined to the liability to reduction or to the formation of addition products.

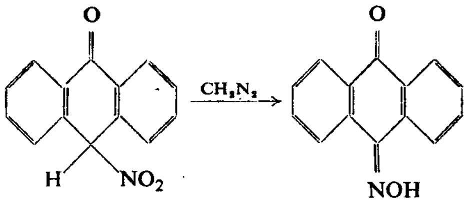
Thus, Backer [9] explained that in certain cases an aliphatic nitro group could react with such a typical methylating agent as diazomethane. For example, bis-(methylsulphonyl)nitromethane (I), when reacted with diazomethane, formed a crystalline product which was found to be an oxime (IV). Simultaneously formaldehyde was formed, doubtless from the methylene group of diazomethane.

Backer explained the reaction assuming the following mechanism:



(7)

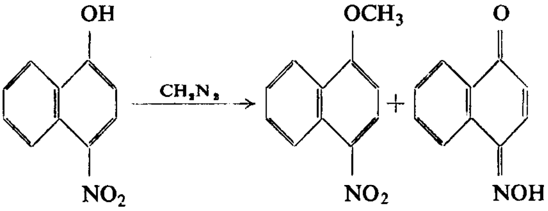
The observation that a nitro group of an aliphatic character in an aromatic molecule could react with diazomethane was confirmed by Edwards [10] for nitroanthrone, which reacted with diazomethane to form anthraquinone oxime (VI):



V VI

(8)

According to that author, such a typical aromatic nitro compound as 4-nitro-1-naphthol (VII) when reacted with diazomethane, formed not only methyl ether (VIII) but also quinone oxime (IX) in lower yield (16%):

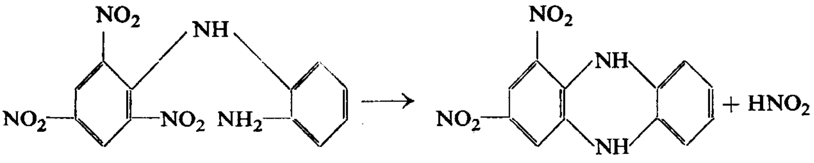


VII VIII IX

(9)

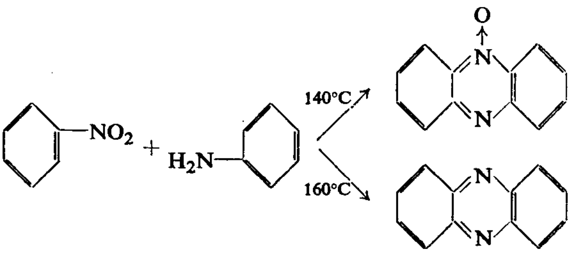
From these examples one could infer that diazomethane would react with those nitro compounds which contain a reactive hydrogen atom. With that respect particularly important is recent work of de Boer [160].

The nitro group can take part in the formation of heterocyclic nitrogen-containing rings. For example, one of the well known methods for the preparation of phenazine derivatives consists in heating derivatives of 2-nitro-2'-aminodiphenylamine at high temperature (Kehrmann et al. [11]) :



(10)

The synthesis of phenazine derivatives and phenazine oxide based on the condensation of aromatic nitro compounds with aromatic amines in an alkaline medium (sodium hydroxide), reported for the first time by Wohl [12] in 1901, was of similar character :

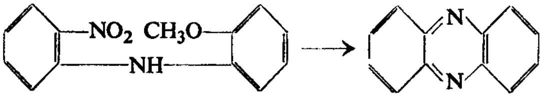


(11)

at 140°C phenazine and its oxide were formed, while at 160°C phenazine only was obtained. The yield of the reaction was insignificant.

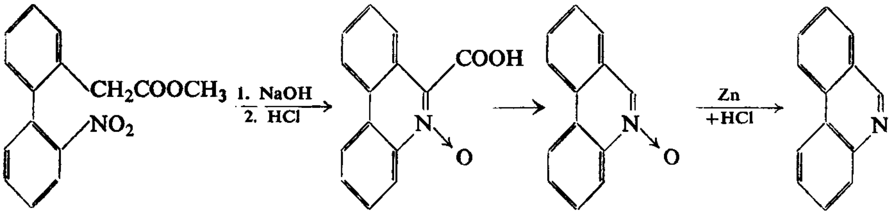
The reaction was improved and its mechanism partly elucidated by several Russian investigators (Pushkareva and Agibalova [13], Chernetskii, Kipryanov, Serebrianyi and others [14-17] and Abramova and Postovskii [18]).

It is interesting to note an example of cyclization by the elimination of a methoxy group by means of a nitro group (Slack and Slack [19]) :



(12)

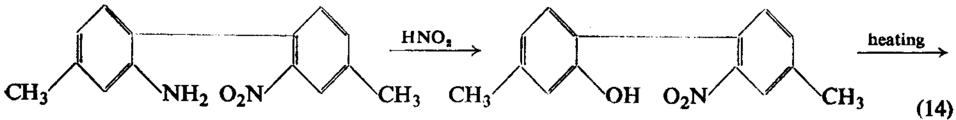
Among more recent examples of cyclization through a nitro group the reaction of preparation of phenanthridine might be referred to (Muth, Ellers and Folmer [20]) :



(13)

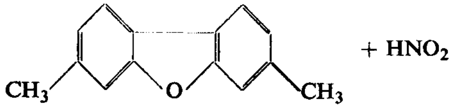
The known reduction of two nitro groups to an azoxy group by acting with strong alkali on nitro compounds (p. 183) can yield cyclic azoxy compounds, according to Knueppel [153].

A rather unusual example of cyclization by means of a nitro group can also be referred to in which the nitro group is separated as a molecule of nitrous acid (Turpin [20a], Angeletti and Brambilla [21]), e.g.:



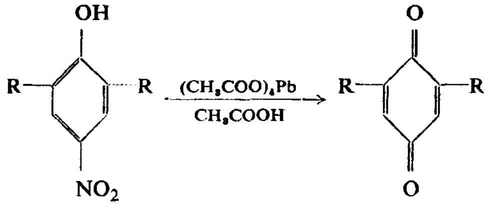
(14)

2-Amine-2'-nitro-4,4'-dimethyldiphenyl



3,7-Dimethyldiphenylene oxide

An interesting instance of elimination of a nitro group was given by Kenner and co-workers [21a,21b]. It consists in oxidation of 2,6-disubstituted derivatives of *p*- nitrophenol by lead tetraacetate at room temperature to form derivatives of *p*- benzoquinone in excellent yields:



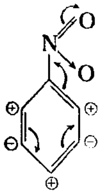
(15)

(R are alkyls)

The reactivity of the nitro group is also manifested by the ease of its reduction. Thanks to this, aromatic compounds (e.g. nitrobenzene) can be used as oxidizing agents in the well known Skraup reaction.

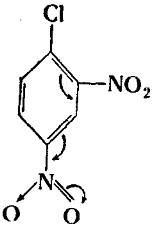
INFLUENCE OF NITRO GROUPS ON REACTIVITY OF HYDROGEN ATOMS AND SUBSTITUENTS. NUCLEOPHILIC REACTIONS

The fact that the nitro group is a meta-orienting one can be explained by the induction effect, caused by its electron attracting properties (I):



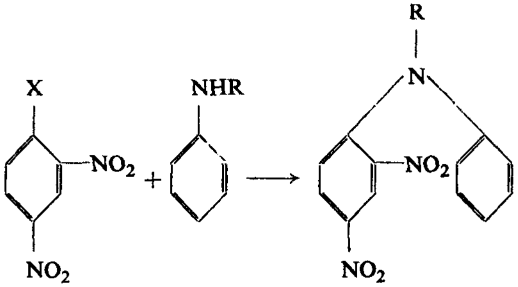
In practice, *ortho* and *para* substitutions also occur to a lesser extent along with the ***meta*** substitution in relation to the nitro group. Some deviations from the rule of substitution in the *meta* position are also encountered.

The nitro group has a considerable influence on the properties of the whole molecule of an aromatic compound. For example, owing to the presence of the nitro group, nitrobenzene does not take part in the Friedel-Crafts reaction. The reactivity of a chlorine atom, brought about by the presence of a nitro group in the *ortho* or *para* position, may be represented by a diagram based on the induction effect (Ia).



Ia

A halogen atom in the *ortho* or *para* position to the nitro group can readily undergo nucleophilic displacement. The higher the polarization ability of a halogen, the more readily it enters into substitution reactions. Therefore the common rule that the atoms of the lighter halogens are more reactive is not followed here. For example, the reaction of halogeno-2,4-dinitrobenzene with N-alkylaniline in nitrobenzene solution runs with the greatest rapidity in the case of bromine, and with the lowest in the case of fluorine, i.e. the reactivity varies according to the order: Br>Cl>F:



(16)

This was formerly considered to be one of the most typical examples of nucleophilic displacement.

However, several exceptions to this rule have recently been observed.

According to Beckwith, Miller and Leahy [22], the rates of the nucleophilic displacement of halogeno-2-dinitrobenzenes with sodium methoxide or sodium *p*- nitrophenate for the F, Cl, Br and I derivatives can be expressed by the figures 2880, 1, 0.690, 0.154 respectively.

However, this sequence may be altered as a result of changes in the nucleophilic agent and the solvent. Thus Hammond and Parks [23] noticed the rate of reaction of halogeno-2,4-dinitrobenzenes with aniline in ethanol to be the highest with fluorine and the lowest with chlorine : F> Br> Cl. When N-methylaniline in nitrobenzene solution was used the sequence was Br>Cl>F - as mentioned above (Fierens and Halleux [24]).

Temperature can also influence the rate of this nucleophilic displacement and alter the rate of reaction of different halogens. Brieux and Deulofeu [25] made the important observation that the temperature change may. affect the rate of reaction of various halogens differently. Thus the halogeno-2,4-dinitrobenzenes react with piperidine at the rates which can be arranged:

as Br>Cl>I at 75°C

and

as Br>I>Cl at 100°C

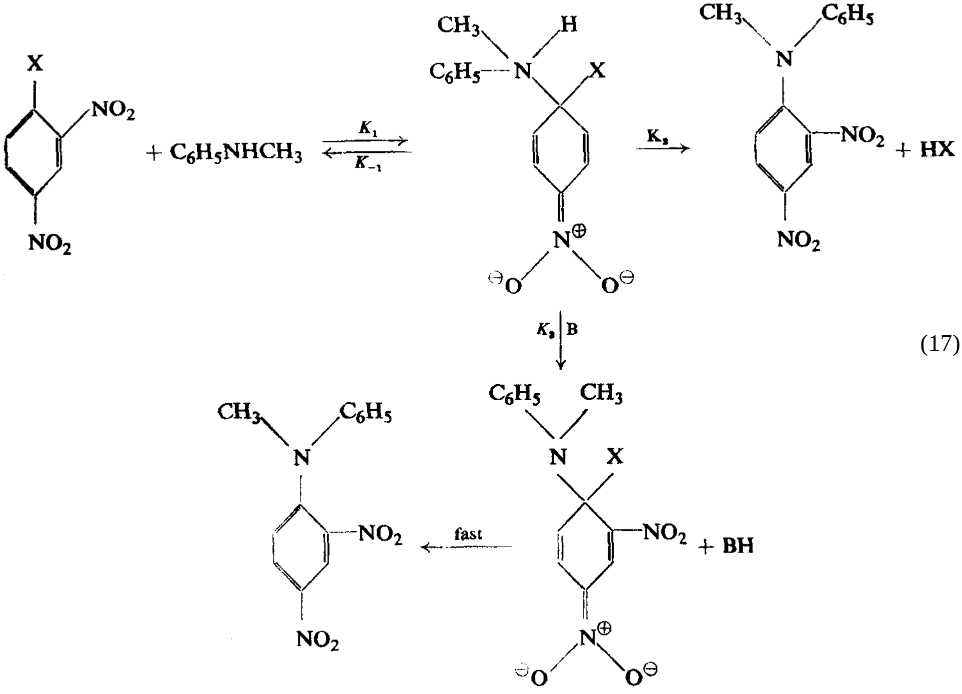
This would explain the discrepancy between the data of different authors. (Brewin and Turner [26] and Sandin and Liskear [27] examined the rate of reaction with piperidine in benzene. The temperature of a boiling solution in benzene is in the region where a change in the order of reactivities may take place.)

Plazek [28,28b] and Plazek and Talik [28a] stated recently that the reactivity of halogens in nitro derivatives of pyridine is much higher than in the similar benzene derivatives. Thus, at 20°C where only 0.5% of chloro-2,4-dinitrobenzene was subjected to nucleophilic displacement of chlorine by the amino group, the figure was 98.3% for 2-chloro-3,5-dinitropyridine.

In water, after 5 hr of boiling, the following figures for percentage reacted were recorded :

ca.	1.0%,	of chloro-2,4-dinitrobenzene
	26.2%	of chloro-2,4,6-trinitrobenzene
	98.4%	of 2-chloro-3,5-dinitropyridine
	99.7%	of 2-bromo-3,5-dinitropyridine

Bunnet and Randall [29] suggest a two-stage mechanism involving a nucleophitic reaction of the formation of a metastable intermediate complex according to the diagrammatic presentation:



(17)

Bases (e.g. alcoholic potassium acetate) were found to catalyse the reaction when X= F, but they do not catalyse it when X= Cl.

Bunnet and Randall suggest the following equation for the rate of reaction K:

$$K = \frac{K_1K_2 + K_1K_3(B)}{K_{-1} + K_2 + K_3(B)}$$

(See also Knowles, Norman and Prosser [159]).

S. D. Ross [30] studied the nucleophilic displacement reaction in aromatic systems by examining the rate of reaction of chloro-2,4-dinitrobenzene with n-butylamine and with OH^- in dioxane-water (50/50). The results suggest that the reaction with the amine is catalysed by both n-butylamine and OH^- ions.

Plazek and L. Kuczyriski [31] investigated the reactivity towards ammonia of bromine atoms in *o-*, *m-* and *p-* bromonitrobenzene. The bromine atom in a position *ortho* to the nitro group is the most reactive, while the bromine atom in the *meta* position is the least so. However, in the presence of copper catalyst ($CuSO_4.5H_2O$) there is not much difference between the reactivity of *meta-* and *para-* bromine atoms. The bromine atom in the *ortho* position remains the most reactive in the presence of a catalyst.

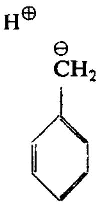
Hawthorne [31a] arrived at a similar conclusion when investigating the rate of reaction of *o-* and *p-* chloronitrobenzene with piperidine. The displacement of the chlorine atom from the *ortho* compound by piperidine at 116°C proceeds 80 times more rapidly than the similar reaction of the *para* compound. He also observed that substitution of D for H in the amino group in the nucleophile (piperidine) did not alter these rates of reaction.

Recently Reinheimer and his co-workers [31b] found that a number of salts have a marked effect on the rate of reaction of chloro-2,4-dinitrobenzene with sodium methoxide to yield 2,4-dinitroanisole. Thus, lithium salts slowed the reaction, sodium salts did not change the rate of reaction while potassium salts increased the reaction rate. These results were interpreted on the basis of the ion pairing of Na^+ and OCH_3^- ions in solution. Addition of another M^+ from added salt would affect the equilibrium

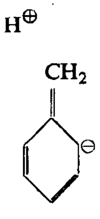
$$M^+ + OCH_3^- \leftrightarrow M\text{-}OCH_3$$

The carboxyl group of trinitrobenzoic acid is also mobile and can readily be liberated as CO_2 simply by heating.

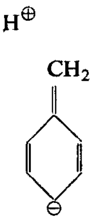
The fact that nitro groups attached to an aromatic ring increase the reactivity of the hydrogen atoms of a methyl group, can also be explained by the induction effect strengthening the effect of hyperconjugation of the molecule of toluene. According to the concept of hyperconjugation, the ionized states of toluene can be written as II, III and IV:



II



III

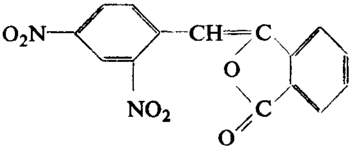


IV

(see for instance Waters [32], E. Müller [33]).

This would explain a number of reactions of the methyl group in nitro derivatives of toluene, particularly in trinitrotoluene. For example, formaldehyde can be added relatively easily to the methyl group of trinitrotoluene, resulting in the formation of the trinitro derivative of phenylethyl alcohol (Vol. II).

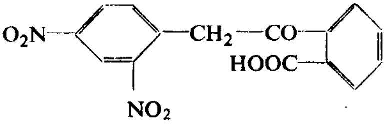
The methyl group in nitrotoluenes reacts with benzaldehyde much more readily than that of toluene itself, giving the corresponding derivatives of stilbene. Mono-, di- and tri-nitrotoluenes also react with *p*- nitrosodimethylaniline to form the corresponding anils. Such a product is not obtained in the case of toluene (Sachs and Kempf [34]). The methyl group of 2,4-dinitrotoluene also reacts with pyridine N-oxide in the presence of iodine to yield 2,4-dinitrobenzaldehyde [155]. Poray-Koshits and Chizhevskaya [35] found that di- and trinitrotoluenes react with phthalic anhydride to form nitro derivatives of benzylidenephthalide:



Mononitrotoluene is not subject to this reaction.

The compounds obtained are crystalline products and may be utilized for the identification of di- and tri-nitro compounds containing a methyl group.

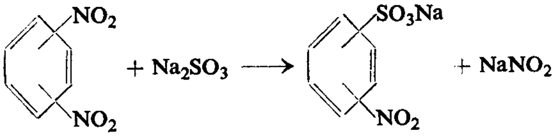
On heating with an aqueous solution of NaOH the benzylidenephthalide derivatives hydrolyse to form ketoacids:



2,4-Dinitrotoluene also reacts with pyridine and iodine to yield 2,4-dinitrobenzylpyridinium iodide [156].

On boiling nitro derivatives of toluene with sodium hydroxide, their methyl group is readily oxidized, forming a methine group and nitro derivatives of stilbene.

One of the typical reactions of aromatic nitro compounds with two or more nitro groups is that with sodium sulphite. Here one of the nitro groups is replaced by a sulphonic group (as its sodium salt) and sodium nitrate is formed:



(18)

The reaction occurs particularly readily with nitro groups that are in the o- and *p*- position to each other, i.e. with “mobile nitro groups”. As to *meta*- nitro groups they react less readily and require a higher temperature. Nitro derivatives of higher homologues of benzene with two or three nitro groups (such as di- and tri-nitro derivatives of *m*- xylene also react less readily, and trinitromesitylene does not react with sodium sulphite [35a].

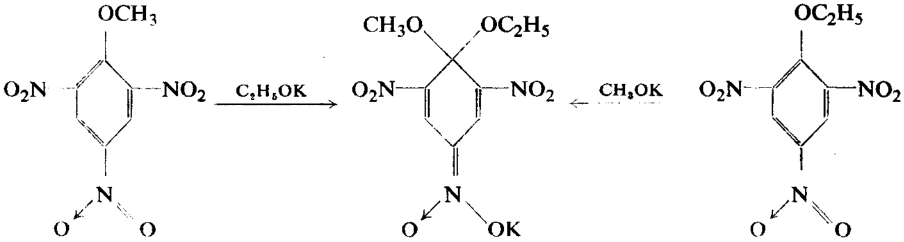
The reaction is of great practical importance and is described in detail in the appropriate places (pp. 231, 308, 332 and 379).

It is well known that the presence of nitro groups in aromatic amines makes diazotization of the amino group more difficult.

The presence of nitro groups in diazonium compounds considerably facilitates coupling to yield azo-compounds. For example the diazonium salt of picramide couples readily with mesitylene [157].

A nitro group attached to an aromatic ring may activate the ring. Owing to this the nitro-substituted aromatic ring can take part in reactions in which it usually remains more or less inactive. Nucleophilic reactions of nitro compounds should be mentioned here first.

Nitro compounds, particularly the higher nitrated derivatives, readily enter into nucleophilic reactions. The reactions of aromatic halogenonitro compounds with bases (p. 453), as well as the addition of potassium methoxylate on to sym-trinitrobenzene resulting in the formation of an anisole derivative will be discussed below. Similar addition reactions of potassium methoxylate to trinitrotoluene (p. 301) and trinitroanisole (p. 546) are also known. These reactions were described in detail by Meisenheimer [36-38]. Confirmation of such an interpretation of the reaction is provided by the fact that in the reaction of potassium ethoxylate with trinitroanisole the same dark coloured product (I) is obtained, as when potassium methoxylate is reacted with trinitrophenetole:



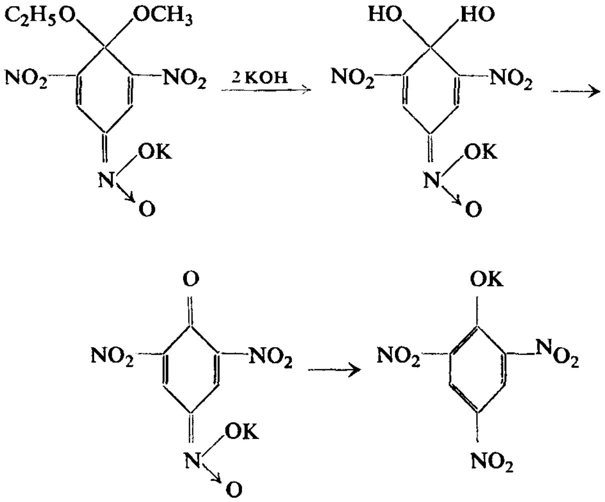
(19)

When treating the addition product (I) with dilute sulphuric acid, Meisenheimer obtained a mixture containing trinitrophenetole. Jackson and Earle [39] confirmed Meisenheimer's results as regards the preparation of the product.

Hammick and Foster [40] investigated the infra-red absorption spectra of the products obtained by both routes. The visible spectra were examined by Foster [41]. Both spectra were found to be identical in each case.

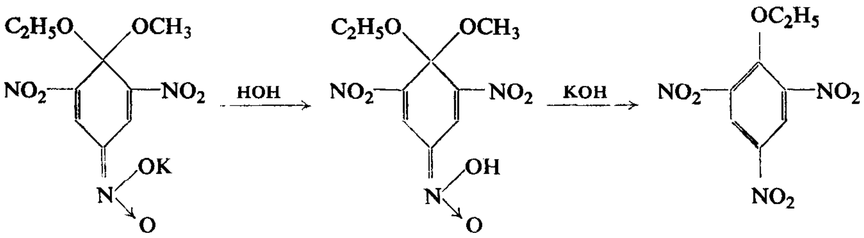
Gitis and Glaz [42] also confirmed Meisenheimer's view. They found that the ultra-violet spectrum of the addition product resulting from the reaction of potassium ethoxylate with trinitroanisole was identical with that of the addition product of potassium methoxylate and trinitrophenetole. Both products showed an absorption maximum at 485 mμ.

Moreover, the same authors found that heating the product with potassium hydroxide resulted in the formation of potassium picrate, presumably according to the scheme:



(20a)

At a low temperature the reaction occurred without complete hydrolysis of the ether group, and the ethyl ether of picric acid was formed:



(20b)

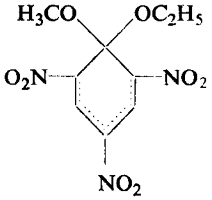
When products of the reaction of higher alcoholates with trinitroanisole were hydrolysed, ethers of higher alcohols were formed. According to the authors, this could be a convenient method of preparing higher ethers of picric acid.

The kinetics and mechanism of Meisenheimer's reaction has been studied by Caldin and Ainscough [43] who utilized the reactions of addition of sodium ethoxylate to trinitroanisole, trinitrobenzene and trinitrotoluene. By using temperatures in the range from -70°C to -100°C they were able to reduce the reaction rate to a measurable value. On treating the addition product with acetic acid at temperatures ranging from -50°C to -80°C they obtained the starting product. Thus, the reaction was proved to be reversible, as for example in the case of trinitroanisole (TNA) :

$$\mathrm{TNA} + \mathrm{OC_2H_5^-} <\!-\!> [\mathrm{TNA,OC_2H_5^-}] <\!-\!> [\mathrm{TNA^-.OC_2H_5}] \qquad (21)$$

Addition product (II)

The authors consider that the addition product may exist as a complex, in which a transfer of charge has taken place, while the structure of the true addition product is III.



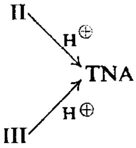
III

The reaction of the formation of product II is fast. while that of product III is slow:

$$\text{TNA} + \text{OC}_2\text{H}_5^- \leftrightarrow \text{II}$$

$$\text{II} \xrightarrow{\text{slow}} \text{III}$$

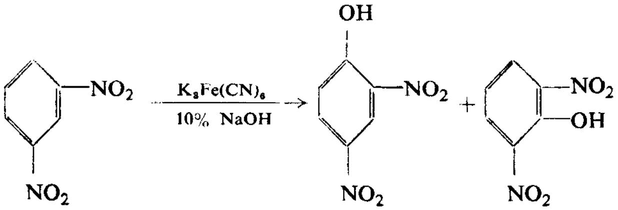
On treating both products, (II) and (III), with acetic acid the authors were able to regenerate the original nitro compound:



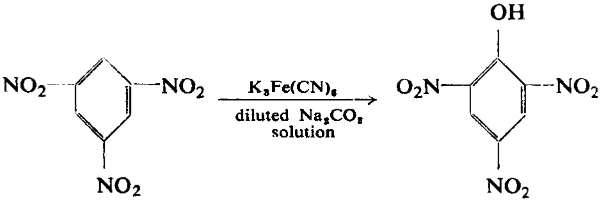
(22)

The products of type III obtained from various other nitro compounds, are discussed further under the heading of the individual nitro compounds (see also Farmer [44]).

Oxidation of nitro compounds to nitrophenols is another example of a nucleophilic reaction. Thus, *m-* dinitrobenzene and *sym-* trinitrobenzene were oxidized in an alkaline medium when boiled with potassium ferricyanide solution (Hepp[45]) :



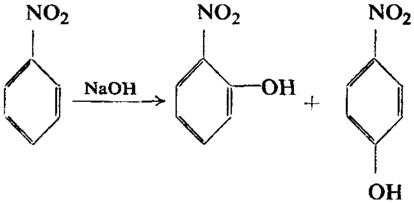
(23)



(24)

This reaction does not occur with nitrobenzene.

The oxidation of nitrobenzene to *o*- nitrophenol (with traces of the *p*- isomer) when mixed with dry sodium hydroxide, and slightly heated, may be another example of the oxidation of nitro compounds by nucleophilic substitution (Wohl [46]):

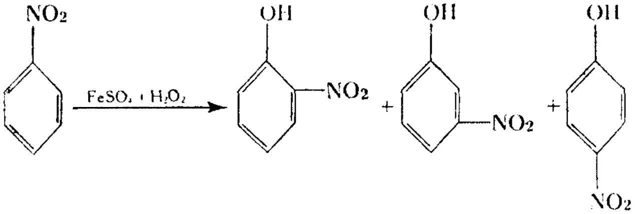


(25)

The yield of *o*- nitrophenol in this reactions amounts up to 50% of the theoretical value.

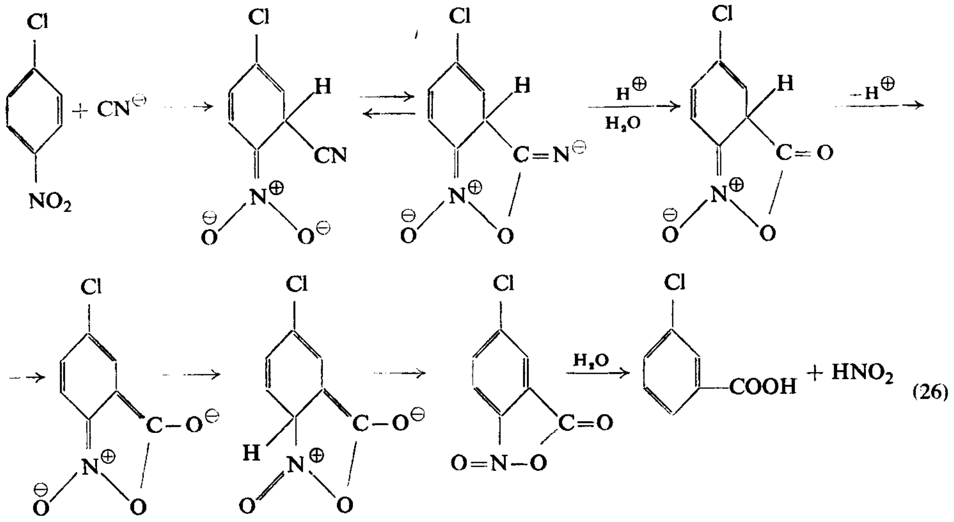
A specific feature of these reactions is that the substitution occurs in the ortho and *para* positions. This is typical of nucleophilic reactions whereas the *meta*-orienting influence of the nitro group (i.e. the conventional substitution rule) can be observed when electrophilic substitution occurs.

Another example of nucleophilic hydroxylation of nitro compounds is the formation of nitrophenols by the action on nitrobenzene with aqueous ferrous sulphate in the presence of hydrogen peroxide in a yield of *ca.* 3% [46a] (Fenton's reagent) [46b] ; Weiss *et al.* [46]) and by the action of ionizing radiations on aqueous solution (Weiss and Stein [46c]) *:*



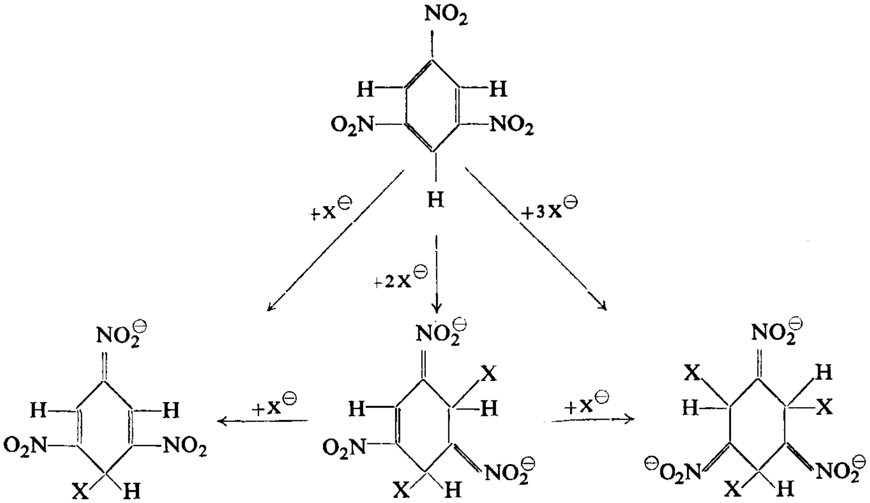
Aromatic hydroxylation is known to take place in animal and human organisms and therefore it is of great importance to know the metabolism of various aromatic compounds including drugs (D. Robinson, J. N. Smith, R.T. Williams [47]). The presence of the nitro group in a molecule, resulting in its activation, may sometimes lead to a rather unusual course of reaction. The Richter [48] reaction might be taken as an example, in which *m*- bromobenzoic acid may be obtained by reacting potassium cyanide with *p*- nitrobromobenzene. Likewise, when reacting potassium cyanide with *m*- nitrobromobenzene, a mixture of *o*- and *p*- bromobenzoic acids are formed.

According to Bunnett and his co-workers [49,50,50a] the reaction is of the nucleophilic substitution type and may be represented by the following scheme:

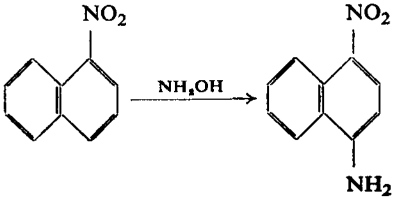


(26)

Holleck and Perret [51] gave the following diagrammatic presentation of nucleophilic addition of the OH⁻ or CN⁻ ion to *sym*- trinitrobenzene in alkaline medium (X=OH⁻ or CN⁻):

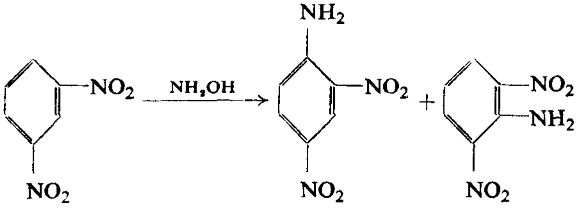


According to Angeli and Angelico [52], and later Meisenheimer [38], aromatic nitro compounds react with hydroxylamine to form aminonitro derivatives. Thus, Angeli obtained 1-nitro-4-naphthylamine from 1-nitronaphthalene:

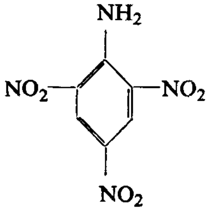


(27)

In the case of nitro derivatives of benzene at least two nitro groups should be present on the ring. Here are the most typical reactions, as suggested by Meisenheimer :



(28)



(28a)

Here the amino group enters the *ortho* or *para* position in relation to the nitro groups.

The reaction of sulphitation of polynitro compounds is also a nucleophilic substitution reaction. It is dealt with more fully on pp. 237, 308 and 332.

The so-called Janovsky reaction [53] is a very characteristic one for many higher nitrated benzene derivatives. It is probably also of nucleophilic character. It consists in treating a diluted di- or tri-nitro compound solution in acetone with a concentrated solution of potassium or sodium hydroxide (generally of 30% concentration). The acetone solution turns bright coloured. Red to violet colours may appear according to the nitro compound present.

Thus, as Janovsky [53] reports, *m*- dinitrobenzene produces a reddish violet colour, 2,4-dinitrotoluene a blue one, 1,3-dinitronaphthalene a bluish-red.

Bitt6 [54] stated that di- and tri-nitro compounds give colour reactions with a number of aliphatic and aromatic aldehydes and ketones in the presence of alkalis.

Thus, *m*- dinitrobenzene produces the following colours:

with pulegone	hyacinth red
with carvone	blue pink
with camphor (in nitrobenzene solution)	brown red
with propionic aldehyde	dark brown

No colour appears with some aldehydes, for example, furfural and cinnamic aldehyde. Bittó has suggested this reaction may be used for the identification of aldehydes and ketones (see also p. 239).

The Janovsky reaction and its Bittó modification were investigated by Reitzenstein and Stamm [55]. Both these as well as other authors (Bost and Nicholson [56], Nisida [57], Canäck [58]) stated a number of irregularities.

Thus, nitro compounds with a great number substituents, for example trinitromesitylene, do not give any colour reactions. Compounds with nitro groups located in the 2,4-positions, produce colours that depend to a considerable extent on the substituent in position 1. The presence of the OH or NH_2 group interferes with the colour reaction. The situation remains unchanged after both of the groups have been acylated, while alkylation of a phenol restores the ability to produce colour.

Newlands and F. Wild [59], when investigating maxima of the absorption spectra of coloured solution, obtained with various dinitro compounds, found that some of them produce two maxima.

T. Urbanski, Kwiatkowska and Kutkiewicz [60] came to similar conclusions. Table 26 lists some of the results obtained.

TABLE 26

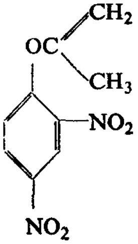
ABSORPTION SPECTRA OF COLOURED COMPOUNDS PRODUCED BY THE JANOVSKY REACTION

Compound	Colour	Absorption maxima mµ	Reference
m- Dinitrobenzene	violet	570-573	[60]
o- Dinitrobenzene	none		[60]
p- Dinitrobenzene	none		[60]
2,4-Dinitrotoluene	bluish-violet	570-575	[60]
3,5-Dinitrotoluene	reddish-violet	450-460 and 575	[60]
1,3,5-Trinitrobenzene	reddish-violet	562 and 573	[60]
1,2,3-Trinitrobenzene	reddish-violet	562	[60]
1,2,4-Trinitrobenzene	red	525	[60]
2,4,6-Trinitrotoluene	blood red	460 and 540	[60]
2,3,4-Trinitrotoluene	violet	550	[60]
2,4,5-Trinitrotoluene	yellow-green	425-430 and 630	[60]
1-Fluoro-2,4-dinitrobenzene	greenish-blue	430 and 550	[59]
1,3-Dichloro-4,6-dinitrobenzene	deep blue	640	[59]
2,4-Dinitrophenetole	reddish-violet	560	[59]
2,4-Dinitroaniline	red	560	[59]
2,4-Dinitrophenylamine	red	590	[59]
2,4-Dinitrophenylhydrazine	blood red	570	[59]

Abe [61] investigated the rate of the colour development with *m*- dinitrobenzene in acetone in the presence of sodium hydroxide by examining the intensity of the band 560 mµ against time. The maximum intensity occurs after 9 min. The more concentrated the solution of sodium hydroxide the more quickly the colour fades.

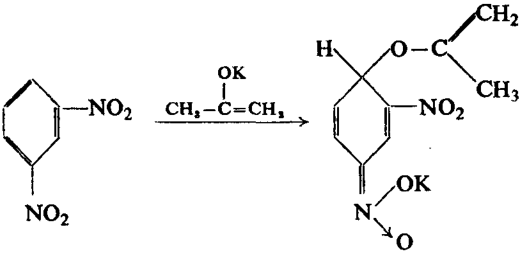
According to Cone [62] it is advisable to use butanone (methyl ethyl ketone) instead of acetone, because the former gives a more stable colour and the reaction can be used for colorimetric determination of TNT in air.

The nature of the Janovsky's colour reaction is not sufficiently understood. Reitzenstein and Stamm [55] were the first to try to establish the structure of the compounds formed. They were able to isolate from an acetone solution a brown product (IV), resulting from the reaction of 1,2,4-chlorodinitrobenzene with the enolic form of acetone:



IV

Quite recently Gitis [42] isolated a number of coloured products formed by polynitro compounds with acetone in the presence of sodium hydroxide. The author, like Reitzenstein and Stamm, postulated that it was the enol form of acetone that reacted with a nitro compound, products of nucleophilic substitution of the type described by Meisenheimer [36-38] (p. 202), being formed:



V

(29)

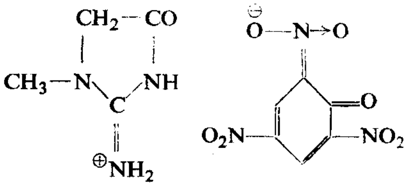
Gitis believes that compounds of the V type are the main products of the Janovsky reaction.

The formula V is not in agreement with the views expressed by various authors on the structure of the coloured products obtained by adding substances containing an active methylene group to higher nitrated aromatic compounds, starting from *m*- dinitrobenzene. A number of papers have been published on the subject. They originated from the Jaffe-Folin [63,64] reaction for quantitative calorimetric determination of creatinine. The reaction consists in the development of a red colour when solutions containing creatinine are treated with aqueous picric acid and a few drops of alkali at room temperature. Many (but not all) compounds with active CH_2 group are capable of giving this reaction.

Several red compounds have been isolated from the red solution obtained from creatinine, picric acid and alkali. By acidification a red powder was isolated by Greenwald and Gross [65]. On boiling with water (Anslow and King [66]) or on heating to 139°C this was transformed into the usual yellow creatinine picrate.

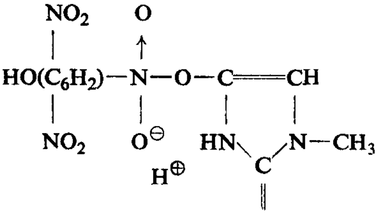
It was considered originally to be a tautomer of the picrate. More recently, by treating aqueous solutions of creatinine picrate of different compositions with alcohol, several crystalline compounds have been obtained (Bollinger [67]).

The formula VI was originally suggested for the red tautomer of creatinine picrate



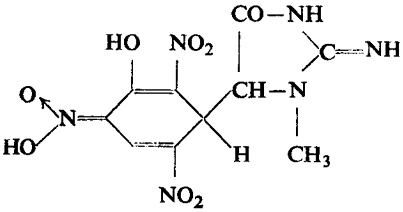
VI

Because non-basic substances may also produce a similar reaction, it was later suggested by Anslow and King [66] that the enolate anion of creatinine forms a coordinate bond with the positively charged nitrogen atom of one of the nitro groups. The structure of the compound they postulated is VII:



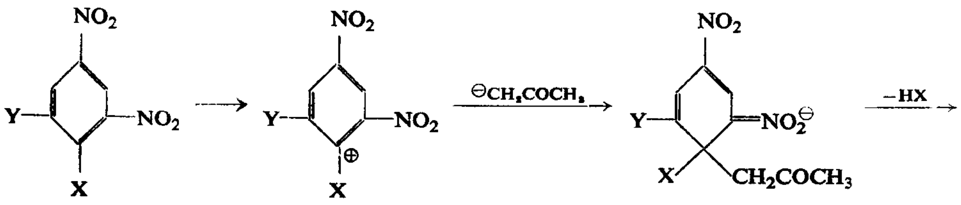
VII

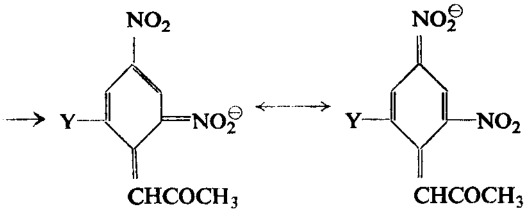
According to the most recent suggestion (Kimura [69]), the product of the reaction of picric acid with creatinine is not a substitution but an addition product VIII:



VIII

With regard to the other coloured compounds formed from *m*- dinitrobenzene or *sym*- trinitrobenzene, it was claimed that the carbanion of active methylene compounds condenses with the nitro compound in terms of nucleophilic substitution :





IX X

(30)

X = H, OH, Cl
Y = H, NO_2

This mechanism was suggested by Ishidata and Sagakuchi [68].

The formula X may be considered to correspond with the coloured products of the Janovsky reaction.

Recently T. Urbanski [70] established that an alcoholic solution of *m*- dinitrobenzene is coloured pink with primary nitroparaffins in the presence of sodium hydroxide. The colour is very intense when nitromethane is used. The spectrum of the solution shows a maximum of absorption near 550 mμ.

The formation of the coloured products is most likely due to the presence of the active methylene group in the primary nitroparaffins. Secondary nitroparaffins do not give this reaction.

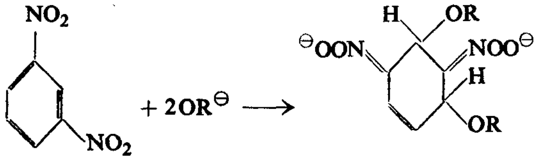
The reaction can be used to detect the presence of nitromethane (T. Urbanski and Kwiatkowska [70a].

2,4-Dinitrotoluene does not give this reaction. Trinitro compounds (such as *sym*-trinitrobenzene and α– trinitrotoluene) also give the colour reaction but this is less typical, as the trinitro compounds give a similar colour with alcoholic NaOH alone without primary nitroparaffins.

The reaction of nucleophilic substitution described above admit the ease of formation of quinoid ring. The problem of quinoid ring formation was recently examined by Perret and Holleck [47]. On the basis of their spectroscopic ultraviolet investigations using visible and infra-red techniques and their polarographic investigations, Perret and Holleck came to the conclusion that differently substituted derivatives of *sym*- trinitrobenzene possess different abilities to form a quinoid structure. Trinitrotoluene belongs to those derivatives which behave in a polarograph in much the same manner as *sym*- trinitrobenzene because the methyl group does not take part in the formation of quinoid structure. On the contrary OH groups promote the formation of quinoid structures.

The ability of higher nitrated aromatic compounds to form dark coloured products in alkaline medium can be used for the titration of certain weak acids with bases. For example trinitrobenxene acquires an orange and red colour at pH 12.2 and 13.6 respectively.

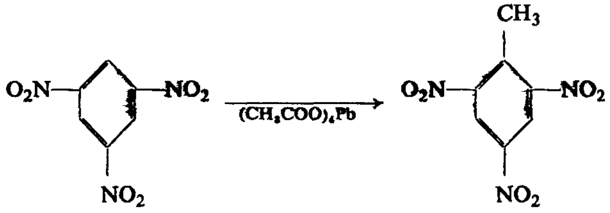
The formation of coloured compounds was used by Brockmann and Meyer [71] for the quantitative determination of polynitro compounds. The di- or trinitro compound is dissolved in ethylenediamine and titrated potentiometrically with an 0.1 N solution of sodium colamate. The nitro compound behaves as a Lewis acid:



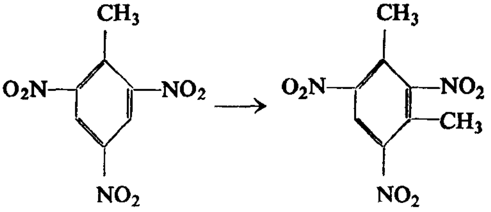
m- Dinitrobenzene and α– trinitrotoluene require two and three equivalents of colamate respectively. On reaction of polynitrocompounds with diazomethane-see [160].

FREE RADICAL REACTIONS

Nitro groups also enable free radical reactions to occur with aromatic rings. As Fieser's investigations [71a] have shown, aromatic nitro compounds can be methylated when reacted with lead tetraacetate:



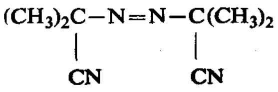
(31)



(32)

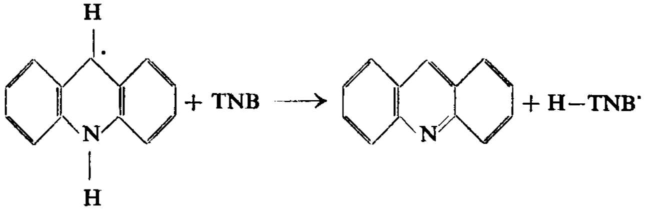
The reactions probably involve free radicals. The lead tetraacetate liberates the methyl radical, which reacts with the aromatic free radical.

It is characteristic that the new entrant methyl group assumes the ortho position to the nitro group and thus a substitution occurs which is similar to nucleophilic attack. Recently it has been found by Jackson and Waters [72] that higher nitrated benzene derivatives such as *m*- dinitrobenzene, or 1,3,5-trinitrobenzene, become homolytic hydrogen acceptors at temperatures of 80-100°C especially in the presence of the 2-cyano-2-propyl radical, which is formed by thermal decomposition of a,a'-azo-bis-isobutyronitrile



$$\underset{\displaystyle CN}{(CH_3)_2\overset{}{C}}-N=N-\underset{\displaystyle CN}{C}(CH_3)_2$$

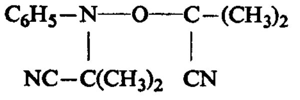
Owing to this, an acrydane, for example, can be converted under the influence of *m*- dinitrobenzene or 1,3,5-trinitrobenzene into acridine in the presence of the above mentioned radical :



(33)

In the presence of 2-cyano-2-propyl, using 0.72 mole of trinitrobenzene, acridine can be obtained in 64% yield, whereas without the radical the yield is only 4%.

This reaction suggests that free radicals may act as reducing agents (Haines and Waters [73]). Indeed, Inamoto and Simamura [74] have recently proved that the 2-cyano-2-propyl radical can react with nitrobenzene to give small quantities of O,N-di(2-cyano-2-propyl)-N-phenylhydroxylamine (I).

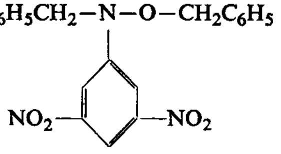


$$\begin{array}{lcl} C_6H_5-N & -O- & C-(CH_3)_2 \\ | & & | \\ NC-C(CH_3)_2 & & CN \end{array}$$

I

Thus it has been found that the free radical attacks the nitro group resulting in its partial reduction. Apart from this acetone is also formed.

Jackson, Waters and Watson [75] found that the free benzyl radical (prepared by the method reported by Beckwith and Waters [76] in 1957, which consists in heating dibutylperoxide with toluene to the boiling point of the latter under a nitrogen atmosphere) reacts with 1,3,5-trinitrobenzene, to form O,N-dibenzyl-3,5-dinitrophenylhydroxylamine (II) in 28% yield. In addition to this, benzaldehyde was formed though it was never produced in the absence of trinitrobenzene.



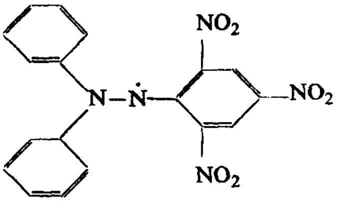
II

The overall equation is:

$$C_6H_3(NO_2)_3 \ + \ 4C_6H_5CH_2^* \ \text{->} \ II \ + \ C_6H_5CHO \ + \ C_6H_5CH_3 \qquad (34)$$

It follows from the above equation that one nitro group destroys four free radicals. A further conclusion is that the complete reduction of a nitro group to an amino group would destroy six free radicals.

Recently Eley and Parfitt [77] discovered that a,a'-diphenyl- β -picrylhydrazyl (DPPH) (III) is one of the best organic semiconductors with an energy gap of only 0.26 eV.



III

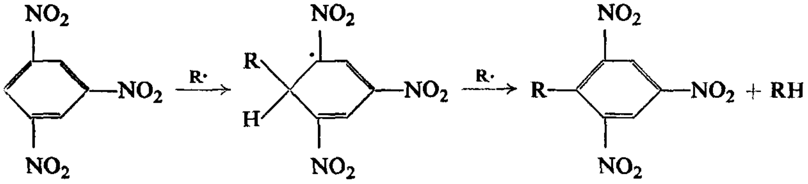
The mobile electron is most likely that associated with the free valency on the N atom.

INHIBITING ACTION OF NITRO COMPOUNDS ON POLYMERIZATION

Another example of the homolytic reaction of nitro compounds with free radicals is their inhibiting effect on addition polymerization of vinyl compounds, especially by the higher nitrated compounds which have the most pronounced inhibiting properties.

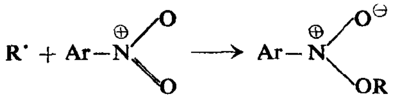
This property of nitro compounds was first observed by Foord [78] with regard to *o*- nitrophenol, 2,4-dinitrophenol, picric acid, *m*- dinitrobenzene, 2,4-dinitrotoluene, 1,3,8-trinitronaphthalene, 2,4-dinitroaniline and other higher nitrated aromatic compounds.

Subsequently Price and Durham [79] stated their view regarding the inhibition of polymerization, which, according to them, consisted in a free radical reaction, analogous to the reaction of alkylation of trinitrobenzene, discovered by Fieser and his co-workers [71a], which has already been described. Price [80] suggested the following mechanism for the reaction, assuming that two molecules I and II were formed from a polymerizable radical k:

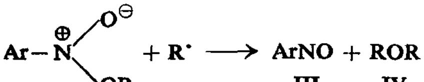


I II

However, Bartlett and his co-workers [81,82] provided evidence, based on the study of the reaction kinetics, which proved that inhibition of polymerization started at the oxygen atom of a nitro group:



$$R^{\cdot} + Ar-\overset{\oplus}{N}O_2 \longrightarrow Ar-\overset{\oplus}{N}(O^{\ominus})OR \qquad (35a)$$



$$Ar-\overset{\oplus}{N}(O^{\ominus})OR + R^{\cdot} \longrightarrow \underset{\text{III}}{ArNO} + \underset{\text{IV}}{ROR} \qquad (35b)$$

Stopping the polymerization consisted here in the formation of a nitro compound (I) and an ether (IV).

Bartlett and Kwart [81] gave the figures referring to the so-called inhibition constants in the polymerization of vinyl acetate under influence of various substances, and mainly nitro compounds (Table 27).

TABLE 27

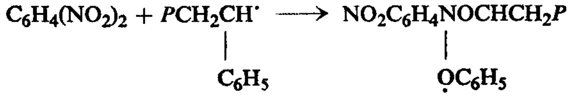
INHIBITION CONSTANTS IN THE POLYMERIZATION OF VINYL ACETATE AT 45°C

Inhibitor	Z_1 (initial inhibition constant)
Nitrobenzene	38
p- Nitrotoluene	40
Dinitrodurene	2.5
o- Dinitrobenzene	96
m- Dinitrobenzene	105
p- Dinitrobenzene	267
sym-Trinitrobenzene	890
Sulphur	410

More recent investigations by Ihrig and Wong [83] in which the authors used optically active nitrodiphenyl derivatives for studying the mechanism of the reaction, confirmed the second scheme, i.e. the attack on a growing radical by a nitro group.

Recently Inamoto and Simamura [74] investigated the interaction of l-cyano-1-methylethyl radicals and various nitro compounds (nitrobenzene, *m*- dinitrobenzene, nitromethane, tetranitromethane) and Bevington and Ghanem [84] have studied the effects of picric acid and *m*- dinitrobenzene on the sensitized radical polymerization of styrene. Picric acid proved to be a rather inefficient inhibitor. *m*- dinitrobenzene was found to be a polymerization retardant. By using ^{14}C-labelled specimens of the nitro compounds the authors determined the amounts of nitro compounds incorporated in the polymer. The average number of retardant molecules per polymer molecule was found to be 0.5-0.7.

On the basis of these experiments and of those of Inamoto and Sinamura, Bevington and Ghanem suggest the interaction of polymer radical with *m*- dinitrobenzene is likely to be:

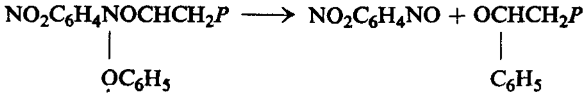


$$C_6H_4(NO_2)_2 + PCH_2\underset{\substack{|\\ C_6H_5}}{C}H^{\cdot} \longrightarrow NO_2C_6H_4\underset{\substack{|\\ \underset{\cdot}{O}C_6H_5}}{N}OCHCH_2P \qquad (36a)$$

V

where *P* represents a polystyrene chain with a terminal initiator fragment.

The next stage would be the formation of the nitroso compound:



$$NO_2C_6H_4\underset{\begin{array}{c}|\\ OC_6H_5\end{array}}{N}OCHCH_2P \longrightarrow NO_2C_6H_4NO + O\underset{\begin{array}{c}|\\ C_6H_5\end{array}}{C}HCH_2P \qquad (36b)$$

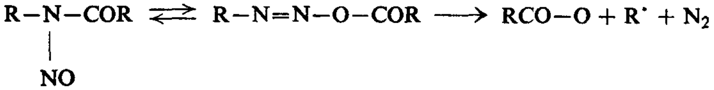
VI VII

Next, various interactions between V, VI, VII and free radicals would occur.

As Kite [85] observed, aromatic nitro compounds inhibited the polymerization of vinyl acetate more strongly than that of methyl methacrylate.

It is interesting to see, that C-nitroso- and N-nitroso compounds (e.g. nitrosoacetanilide, N-nitrosoacylarylamines) catalyse polymerization reactions (Hey [86-88], Blomquist, Johnson and Sykes [89]).

Hey suggested in 1947 the following plausible scheme for the action of N-nitrosoacylarylamine :



$$R-\underset{\begin{array}{c}|\\ NO\end{array}}{N}-COR \rightleftarrows R-N=N-O-COR \longrightarrow RCO-O + R^{\bullet} + N_2 \qquad (37)$$

This action is similar to that of benzoyl peroxide.

VULCANIZATION OF RUBBER WITH AROMATIC NITRO COMPOUNDS

Ostromyslensky [90] observed that rubber could be vulcanized in the absence of sulphur or its compounds if small quantities of aromatic nitro compounds, e.g. nitrobenzene, dinitro- or *sym*- trinitro-benzene, tetranitronaphthalene plus certain oxidizing compounds, such as benzoyl peroxide, were added to it. The resultant vulcanized rubber had mechanical properties not inferior to those of a product vulcanized by sulphur alone, and when free from accelerators it exhibited a greater resistance to ageing. Some metal oxides, such as PbO, CaO, BaO, promoted vulcanization by nitro compounds. Urea played the role of an accelerator of vulcanization. These observations have been confirmed in more recent studies by other workers.

The action of *m*- dinitrobenzene chiefly as a vulcanizing agent, has been studied by Wright [91] and Blake [92] who found that all the *m*- dinitrobenzene entered into reaction with rubber when added in the proportion of 6%. Blake failed to obtain hard rubber (“ebonite”) that way. A method for obtaining hard rubber by using *m*- dinitrobenzene was, however, described by Wright [91]. Rubber vulcanized by nitro compounds has the advantage of not corroding metals (Koshelev [93]).

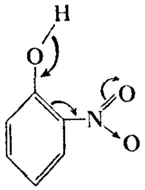
The investigation of sulphurless vulcanizing agents, including the use of polynitro derivatives of benzene, has been completed by Mark and his co-workers [94]).

The hypothesis has been advanced that during the vulcanization of natural rubber by means of polynitro compounds, a partial reduction of polynitro- to nitroso compounds takes place, the latter being known as vulcanizing agents.

In practice, the application of nitro compounds (e.g. *m*- or *p*- dinitrobenzene) in the vulcanization of rubber is limited to butyl rubber, as may be seen from the patent literature [94a].

INFLUENCE OF NITRO GROUPS ON SOME PHYSICO-CHEMICAL PROPERTIES OF PHENOLS AND AMINES

The nitro group enhances the acidic properties of phenols, possibly due to the influence of the induction effect (p. 197):



The comparison of dissociation constants (K) of several phenols in aqueous solution with those of their nitro derivatives (Table 28) illustrates this effect of the nitro group.

TABLE 28

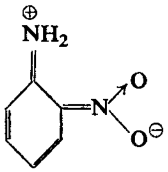
Phenol	K	Reference
Phenol	1.2×10^{-10}	[82]
o- Nitrophenol	6.8×10^{-8}	[82]
m- Nitrophenol	5×10^{-9}	[82]
p- Nitrophenol	7×10^{-8}	[82]
2,4-Dinitrophenol	5.6×10^{-4}	[83]
2,6-Dinitrophenol	1×10^{-4}	[84]
Catechol	3.5×10^{-10}	[82]
3-Nitrocatechol	1.88×10^{-6}	[84]
Hydroquinone	4.5×10^{-11}	[82]
Nitrohydroquinone	1.01×10^{-6}	[84]

A nitro group ortho to the phenol group can form a chelate through an internal hydrogen bond (p. 177, see also p. 171).

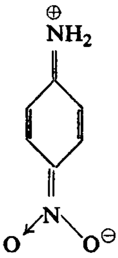
This structure accounts for certain properties of *o*- nitrophenol, and namely those by which it differs from its ***m***- and *p*- isomers. For example, *o*- nitrophenol is volatile in steam. This may be explained by the fact that owing to the presence of an internal hydrogen bond, the intermolecular links which are responsible for molecular association are either weakened or non-existent. This is the reason why the phenolic group in *o*- nitrophenol is not capable of molecular association, unlike *m*- and *p*- nitrophenols.

The nitro group also strongly influences the amino group present in the ring, reducing its basic properties. This influence is strongest when it is in the *ortho* or *para* position to the amino group. The reactivity of the amino group is so enhanced that *o*- or *p*- nitroaniline, when boiled in a aqueous solution of sodium hydroxide, are hydrolysed to form *o*- or *p*- nitrophenol. *m*- Nitroaniline is not subject to this reaction.

This specific property of *o*- and *p*- nitroaniline may be explained by assuming the structure of an amphoteric ion:



I



II

However, this formula for *m*- nitroaniline cannot be accepted as it requires the assumption of the *m*- quinone structure which is unknown at present.

To confirm the formula II, reference is made to the fact that the dipole moment of *p*- nitroaniline ($\mu = 6.45$) is much higher than that which would be deduced from the total of the dipole moments of aniline ($\mu = 1.52$) and nitrobenzene ($\mu = 3.96$).

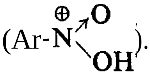
The nitro group may, in some cases, form a hydrogen bond with a primary or secondary amine group in the ***ortho*** position to the nitro group. Thus, Hathway and Flett [98], on the basis of their investigations of the infra-red absorption spectra of 1,2- and 2,1-nitronaphthylamines, inferred that such a bond might exist.

However, more recent studies by Dyall and Hambly [99] as well as by T. Urbanski and Dabrowska [100] with nitro derivatives of aniline have shown that in *o*- nitroaniline such a bond cannot be confirmed so that for the time being we can go no farther than speaking of an ion bond.

BEHAVIOUR OF NITRO COMPOUNDS IN CONCENTRATED ACIDS

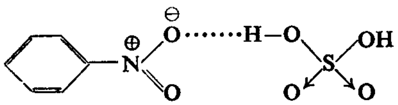
As stated by Hantzsch [101] on the basis of cryometric measurements, the nitro group itself could be of a basic character. The author had studied the behaviour of nitromethane, *p*- nitrotoluene, *m*- dinitrobenzene and 2,4,6-trinitrotoluene in oleum solutions. Among all the compounds investigated, only *p*- nitrotoluene behaved abnormally, as its molecular weight increased with the increase of the concentration of solution. Hantzsch suggested that an addition compound, ($ArNO_2.H_2SO_4$), was formed by adding a sulphuric acid molecule on to the nitro group, as if it had a basic character.

The investigations were continued by Hammett [102] and by Gillespie [103, 103a]. This work established that if oleum of high concentration was used as a solvent, higher nitrated aromatic compounds also exhibited basic properties.

These results were not quite in agreement with those of spectrophotometric investigations reported by Brand and his co-workers [104]. Brand suggested that the difference was due to insufficient knowledge of the true form of nitro compounds in the solutions under consideration. He assumed that nitro compounds in sulphuric acid solutions became cations  $(\text{Ar-}\overset{\oplus}{\text{N}}{\nearrow \text{O} \atop \searrow \text{OH}})$. That was in agreement with an earlier hypothesis (Masson [105], Hetherington and Masson [106]) on the mechanism of aromatic nitration.

In support of Hantzsch's view reference should be made to the fact that Metro compounds can form addition products with sulphuric acid. Thus, Cherbuliez [107] isolated $C_6H_5NO_2.H_2SO_4$ (m. p. 11.6°C) as the product of addition of nitrobenzene to sulphuric acid. This was later supported by Masson [105] who assigned a salt structure to the product $[C_6H_5NO_2H^+]$ $[HSO_4^-]$.

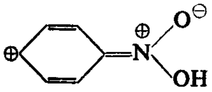
Gillespie and Millen [108] assumed that in such a substance both molecules were linked by a hydrogen bond:



Confirmation of that view has been provided by Hammett and Chapman's work [109]. They inferred from their examination of the solubilities of various organic compounds, among others nitrobenzene, in mixtures of sulphuric acid and water that this form of hydrogen bonding could exist. It might be that similar hydrogen bonds were also formed between *m*- dinitro- or *sym*- trinitro-benzene and sulphuric acid. Gillespie and Millen [108] had drawn attention to that, basing their supposition on the observation by Klough, Savage and van Marl [110], that the solubilities of higher nitro compounds increased rapidly with increase in the concentration of sulphuric acid.

Also Hammond and Medic [111] on the basis of analysis of the ultra-violet spectrum, advanced the hypothesis that sulphuric acid combined with the nitro group through a hydrogen bond. Liler and Kosanovic [150] came to the same conclusion on the basis of their experiments on viscosities, electrical conductivities and refractivities of solution of nitro compounds in sulphuric acid.

On the other hand it should be emphasized that solutions of aromatic nitro compounds, especially mononitro derivatives are distinctly coloured, as already observed by Hantzsch [101]. The yellowish colour of nitrobenzene and *p*- nitrotoluene becomes more intense under the influence of sulphuric acid. That is ascribed to the formation of the quinonoid ion:



in the protonizing medium of sulphuric acid.

ADDITION COMPOUNDS OF AROMATIC POLYNITRO COMPOUNDS

The ability to form addition compounds, especially with aromatic hydrocarbons composed of condensed rings, is one of the specific properties of aromatic polynitro compounds. For example, compounds of trinitrobenzene or picric acid with naphthalene, as well as with other hydrocarbons with condensed rings, are very characteristic. Generally they are intensely coloured.

The nature of the bonds forming molecular addition compounds has been investigated by several workers, but up to now it has not been made sufficiently clear. Pfeiffer [112] held that complex formation was due to the mutual saturation of "residual valencies", but Briegleb [113,114] advanced the theory that addition compounds should be regarded as "polarization aggregates" which owed their stability to electrostatic interactions, possibly due to polarization of one component by the other. Thus, in the case of polynitro compounds, their strongly polar mole cules influence the non polar molecules of the hydrocarbon. Further, no covalent bonds exist between these two kinds of molecules. This hypothesis has received considerable support and a new development.

The experimental observations which support this point of view are as follows:

(1) The interatomic distances between the two components were found by X-ray analysis to be of the order 3.0-3.5 Å (Powell and Huse [115]; Rapson, Saunder and Stewart [116]). This is too long for covalent bonds.

(2) Molecules of 1,3,5-trinitrobcnzene or *p*- dinitrobenzene have no electric dipole moments but they have moments in solutions where molecular compounds are formed. For example they have no moments in carbon tetrachloride or chloroform, but they do have moments in benzene, naphthalene, or dioxane.

(3) Molecular addition compounds are readily formed and decomposed, e.g. by acting with a suitable solvent, which would dissolve one of the components and extract it. For example addition compound formed between picric acid and a hydrocarbon can be split into its components by extracting the picric acid with alcohol while the hydrocarbon remains undissolved. Another fact also indicative of the instability of the addition products is that those of picric acid may be decomposed by treating their solutions with saturated solution of potassium chloride. Potassium picrate is then precipitated, while the other component remains in solution (Taben and Kosak [117]). Generally speaking, the organic addition compounds

are dissolved in solution to a considerable extent. All this would be impossible if they were formed by covalent bonds.

(4) Measurable, although small, conductivities have been observed for some molecular addition compounds (picric acid-naphthalene and 1,3,5-trinitrobenzene--naphthalene) in liquid sulphur dioxide, according to Weiss [118]. He suggests that the complex molecule is essentially ionic in character, being formed by electron transfer from the hydrocarbon (donor A) to the polynitro compound (acceptor B), according to the diagrammatic reaction ("charge transfer compounds"):

$$\mathbf{A} + \mathbf{B} \rightleftarrows \mathbf{A}^{\oplus}\mathbf{B}^{\ominus}$$

A number of authors have studied the emission spectra characteristics of many complexes of sym-trinitrobenzene (TNB) with aromatics (Reid [119]; Bier and Ketelaar [120]; Bier [121]; Czekalla, Briegleb ***et al.*** [122]; McGlynn and Boggus [123]). These experiments led to the conclusion that in most complexes the emission is a charge transfer (E -> N) emission.

McGlynn and Boggus describe the phenomenon thus: absorption in the charge transfer band is followed either by the converse emission or by intersystem crossing (according to Kasha [124]) to a dissociative level of the complex which yields the aromatic in its first excited triplet state. The aromatic hydrocarbon then phosphoresces.

(5) It is now recognized that electron transfer from one component to another is responsible for the change of colour noticed in some molecular compounds (cf. Orgel [125]).

Brackman [126] showed that it was possible to arrange the components of the molecular compounds in such a way that if the colours of the molecular compounds were plotted against the nitro compound, a series of roughly parallel straight lines was obtained (Fig. 47†). It will be noted that an increase in the number or power of the electron-attracting groups in the nitrobenzene nucleus produces a bathochromic effect (a shift towards longer waves), while an increase in the number of electron-repelling groups has the opposite effect (hypsochromic effect).

(6) The magnetic susceptibility of some addition compounds, such as naphthalene picrate, is nearly additive, i.e. equal to the sum of the components (Le Fèvre [127], Baddar and Mikhail [128]). This would suggest that the molecules are held by weak electrostatic forces.

(7) The ultra-violet absorption spectra of the addition compounds have been found to be additive, i.e. equal to the sum of the spectra of components, according to Friedel and Orchin [129]. This would also support the theory of ionic bond between the components.

(8) The stability of an addition compound (A^+B^-) is affected by the Presence of strong donor and acceptor groups. Thus electron-donor groups in molecule A and/or electron-acceptor groups in B lead to a greater binding energy be-

---

† Here not only aromatic nitro compounds are given, but also aliphatic such as nitromethane, tetranitromethane and also chloranil, benzoquinone, maleic and phthalic anhydrides.

tween A and B (Buehler *et al.* [130]). This would explain the superiority of trinitrobenzene over picric acid as a complex forming agent.

(9) The heat of formation in solution of the addition compound of picric acid and naphthalene determined by Brönsted [131], using e.m.f. measurements, was found to be 2.15 kcal/mole. Similar figures were obtained by cryometric measurements (Brown [132]), and solubility measurements (Moore, Shepherd, Goodall [133]). However, all these measurements have neglected the heat of solution. Briegleb [114] applied another method which gave more exact figures. He took advantage of the fact that most of the addition compounds were strongly coloured and measured the colour change of the solutions with temperature. He found that the heats of formation of compounds of 1,3,5-trinitrobenzene with various hydrocarbons in carbon tetrachloride varied between 1.5 and 4.5 kcal/mol.

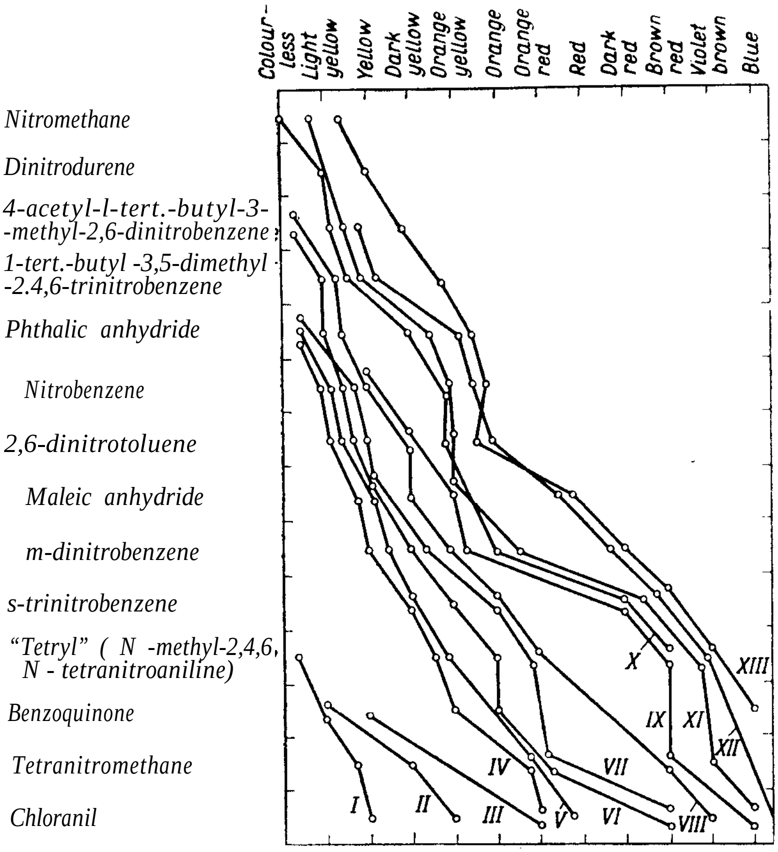


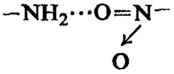
FIG. 47. Colours of addition products of various nitro compounds with hydrocarbons and amines: I - Benzene; II - Xylene; III - Durene; IV - Naphthalene; V - Acetanilide; VI - Phenanthrene;VII - Tribromoaniline; VIII - Safrole; IX - Anthracene; X - Aniline; XI - Diphenylamine; XII - Benzidine: XIII -Dimethylaniline (Brackman [126]).

He also studied the effect of the solvent and found that it should not be neglected:

	Heats of formation	
	in $CC1_4$	in $C_2H_2Cl_4$
anthracene-m-dinitrobenzene	2.2 kcal/mole	1.5 kcal/mole
anthracene-sym-trinitrobenzene	4.4 kcal/mole	3.6 kcal/mole

Ross and Labes [I34] determined the heats of formation of the addition compounds: 1,3,5-trinitrobenzene-naphthalene and -aniline, and found them to be 3.3 and 5.1 kcal/mole respectively.

According to Kross and Fassel [135], addition compounds between nitro compounds and amines can be formed through hydrogen bonds of the type:



$$\begin{array}{r} -NH_2\cdots O=N- \\ \swarrow\; \\ O\;\; \end{array}$$

This was based on the shift in frequency of the nitro group bands in the infra-red absorption spectrum.

It has also been suggested that 1,3,5-trinitrobenzene and *m*- dinitrobenzene may react with amines to form addition compounds by a proton transfer reaction (Lewis and Seaborg [136], Farr, Bard, and Wheland [137]).

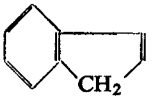
However, Field, W. G. Garner and Smith [138] had concluded earlier that proton transfers do not occur in liquid ammonia solutions of *m*- dinitrobenzene. On the basis of ultra-violet and visible absorption spectra and electrical conductance measurements of the products of interaction of polynitroaromatic compounds with a variety of amines, Miller and Wynne-Jones [139] came to the conclusion that:

(a) Proton transfers do not appear to be involved in the formation of complexes by 1,3,5-trinitrobenzene but electron transfers probably occur.

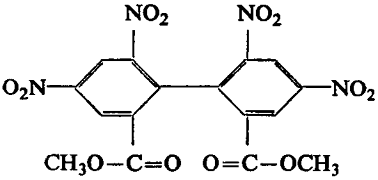
(b) Both proton transfers and electron transfers occur when 2,4,6-trinitrotoluene and 2,4,6-trinitro-m-xylene react with amines.

Steric factors in addition compounds also ought to be referred to when considering formation of addition compounds. X-ray diffraction studies (e.g. Powell and Huse [115], Rapson, Saunder and Stewart [116]) have shown that in general the crystalline addition compounds consist of alternate layers of the two components. The approach of the acceptor molecule can be sterically hindered if the donor molecule is non-planar. Hence complex formation is difficult as the non-planarity increases the distance between the components. For example, trans-stilbene forms a picrate, but the cis-isomer does not. The planar molecule of 2-phenylnaphthalene also forms a picrate, while its non-planar isomer, 1-phenylnaphthalene, fails to do so.

Hammick and Sixsmith [140] found that indene (X) and dimethyl-4,6,4’,6’-tetranitrodiphenate (XI) formed an addition compound at a relatively low rate, which could be measured.



X



XI

This means that steric barriers exist which must be overcome to form an addition compound owing to nonplanarity of the nitro compound. The steric factor could also explain the fact that the addition compound reacts only slowly with bromine, whereas indene itself rapidly adds bromine to form a dibromide.

A detailed list of addition compounds formed by *sym*- trinitrobenzene, 2,4,6-trinitrotoluene, picric acid and other polynitro compounds is given in the appropriate paragraphs devoted to these nitro compounds.

It is important to add that some molecular addition compounds of *sym*- trinitrobenzene with hydrocarbons can serve for identification and purification of hydrocarbons (Veibel [141]). Trinitrofluorenone seems to be of particular value (Orchin and Woolfolk [142], Lepley [154]).

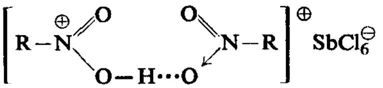
As shown by T. Urbanski [143] between 1933 and 1937, there is a group of molecular addition compounds whose existence cannot be explained by all the points mentioned above. They are addition compounds of certain nitro compounds with esters of nitric acid. Thus many aromatic mononitro compounds form addition compounds with mannitol hexanitrate, and some aromatic trinitro compounds do so with erythritol tetranitrate (Vol. II). On the basis of these facts the author suggests that two main reasons are responsible for the formation of these addition compounds :

(1) Assembly of a great number of nitro groups in both components: nitric ester and nitro compound. Incidentally the sum of these groups is eight in the above mentioned examples.

As shown by Hackel [144] glycerine trinitrate (nitroglycerine) does not form addition compounds with any of the aromatic nitro derivatives (mono-, di- or tri-nitro compounds). This is probably due to the inadequate number of nitro groups in nitroglycerine.

(2) The polarity of nitric ester. All esters forming addition compounds possess high polarity. On the contrary, the ester of low polarity-penthaerythritol tetranitrate does not give addition compounds with any of the above mentioned aromatic nitro derivatives.

Complex compounds between nitro compounds and $SbCl_5$ and HCl possess a quite different and clearly ionic character (Klages, Mühlbauer and Uhl [145]). They are stable below 0°C and at 0°C they readily lose HCl. The heat of decomposition (5-6 kcal/mole) suggests that a hydrogen bond is present in the complex to stabilize the salts. The authors suggest the structure



OTHER REACTIONS OF NITRO COMPOUNDS

All aromatic. nitro compounds yield chloropicrin when treated with alkaline solutions of hypochlorous acid salts. The reaction occurs at room temperature or below (the lower the temperature the higher the yields).

The reaction was first observed by Stenhouse [146] in 1847, when treating picric acid with a hypochlorite. According to A. W. Hofmann [147], a 114 wt. % yield could be obtained in the reaction. As Gardner and Fox [148] reported, the yield could be increased up to 180 - 190%. A yield of chloropicrin amounting to about 200% can be obtained by introducing gaseous chlorine into a suspension of sodium picrate in a solution of sodium carbonate at 0°C (Orton and McKie [149]).

It can be assumed that complete transformation of the nitro groups to chloropicrin takes place in the reaction:

$$C_6H_2(NO_2)_3OH + 11Cl_2 + 5H_2O \rightarrow 3CCl_3NO_2 + 13HCl + 3CO_2 \qquad (37)$$

At higher temperatures side reactions occur, among others the formation of nitric acid, while the yield of chloropicrin decreases.

Orton and McKie give the following maximum yields of chloropicrin, obtained from various nitro compounds:

from picric acid	96-97%	of	the	theoretical	yield
from 2,4-dinitrophenol	50%	”	”	”	”
from *p*- nitrophenol	33-34%	”	”	”	”
from *o*- nitrophenol	10%	”	”	”	”
from 2,4,6-trinitrotoluene	82-84 wt. %				
from 1,3,5-trinitrobenzene	53 ” %				

For the last two compounds the yields are given in wt. %, since the stoichiometry of the reactions is not known accurately.

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CHAPTER VII

NITRO DERIVATIVES OF BENZENE

One or two nitro groups can be introduced by the direct nitration of benzene. The introduction of a third can be accomplished only with great difficulty and the yield obtained is relatively poor. For this reason trinitro derivatives of benzene are prepared by indirect methods. Higher nitrated derivatives of benzene-tetra- and hexanitrobenzene-are also known; they can be obtained by special methods. Dinitrobenzene is the most important of them as an explosive. It was the most used substitute for trinitrotoluene.

NITROBENZENE

PHYSICAL PROPERTIES

Nitrobenzene is a highly toxic, pale, yellow liquid, having a specific smell of bitter almonds. It melts at +5.7°C, and boils at 210.9°C. It was first obtained by Mitscherlich [1] in 1834. The compound is widely used in organic industry as a starting material for the preparation of aniline, benzidine and other intermediates for the manufacture of dyes, medicinals, etc. It is also used for the preparation of dinitrobenzene and as a component of liquid explosives.

TABLE 29

SOLUBILITY OF NITROBENZENE IN SULPHURIC ACID ALONE, AND IN THE PRESENCE OF HNO_3, AT 43°C

H_2SO_4 concentration %	$C_6H_5NO_2$ content in the solution, %	Concentration of H_2SO_4, containing 0.2% HNO_3, %	$C_6H_5NO_2$ content in the solution, %
1-6	0.02	-	-
40	0.015		-
50	0.02	40-50	ca. 0.015
60	0.03	60	ca. 0.02
70	0.04	75	completely soluble
80	completely soluble	-	-

The solubility of nitrobenzene in water and in spent nitrating acid is its most important property, which should be borne in mind in its manufacture on account of the possible loss of the product and the toxicity of the waste water.

The relevant data, reported by Groggins [2] are tabulated above (Table 29).

In waste acid of the composition: 0.5% of HNO_3, 74.5% of H_2SO_4, and 25% of H_2O, nitrobenzene dissolves to the extent of 0.03%. The solubility varies little with temperature over the range of 4.4 to 82°C.

The solubility of nitrobenzene in water is given below (Table 30).

TABLE 30

SOLUBILITY OF NITROBENZENE IN WATER

Temperature °C	Quantity of nitrobenzene dissolved, %
4.4	0.08
21.1	0.085
43.3	0.090
71.1	0.095

In aqueous solutions of $NaHCO_3$, nitrobenzene dissolves with greater difficulty than in water. The values for 43°C are given below (Table 31):

TABLE 31

SOLUBILITY OF NITROBENZENE IN AQUEOUS SOLUTIONS OF $NaHCO_3$

Concentrations of aqueous solutions of $NaHCO_3$, %	Nitrobenzene dissolved %
1	0.024
3	0.023
7	0.020
10	0.018

The thermochemical properties of nitrobenzene are given on pp. 259-262.

CHEMICAL PROPERTIES

Nitrobenzene is resistant to acids. Bases at certain concentrations and temperatures do not affect nitrobenzene. Only when boiled with NaOH in alcoholic solution, is nitrobenzene reduced to form azoxybenzene. Nitrobenzene does not react with Friedel-Crafts reagents and can be used as solvent in Friedel-Crafts reactions.

The reduction of nitrobenzene may lead to various products, depending on the reaction conditions and on the reducing agent. The subject is dealt with in detail in organic chemistry textbooks.

TOXICITY OF NITROBENZENE

The toxicity of nitrobenzene consists primarily in the formation of methaemoglobine in the blood. It is also toxic for the nervous system and the liver. At concentrations in air exceeding 5 mg/m^3 it is considered dangerous. Poisoning by nitrobenzene may be caused either by its direct contact with the skin or when it is inhaled as vapour. Symptoms of slight poisoning include nausea, headache, dizziness, and disturbed functioning of the stomach. A blue tinge of the lips and face - cyanosis - is one of the most characteristic symptoms. In acute poisoning, these symptoms are very severe and heart palpitation, loss of consciousness, cramps, and disturbance of vision may also appear. In women it may cause severe menstrual bleeding. The urine of people suffering from nitrobenzene poisoning contains the blood pigment. Chronic poisoning by nitrobenzene may cause anaemia and liver damage.

PREPARATION OF NITROBENZENE

Nitrobenzene is prepared by the nitration of benzene with mixtures of nitric and sulphuric acids of the composition ranging from:

27 to 28% of HNO_3
56 to 58% of H_2SO_4
14 to 17% of H_2O

By the end of the reaction the temperature rises to 70°C.

The quantity of nitrating mixture is calculated with a small excess of HNO_3 (1%), or the nitration is carried out with a volume of mixture insufficient for complete nitration (e.g. 95-97.5%). In the latter case the spent acid does not contain any nitric acid or nitrogen oxides. Nitrobenzene, together with unreacted benzene, is separated from the spent acid. Then benzene is separated from nitrobenzene by distillation. The yield generally amounts to 98% on a large scale, and to about 95% in the laboratory.

At present the nitration of benzene is one of the simplest processes in the organic chemical industry. Nevertheless, the safety factor should not be neglected. The explosion in Rummelsburg of the plant for the nitration of benzene to nitrobenzene, described earlier (p. 152), was the result of defective operation of the nitrator.

The manufacture of nitrobenzene on an industrial scale in the Griesheim (I. G. Farbenindustrie) plant is described below:

2300 kg of benzene is fed to the nitrator and 6500 kg of the nitrating mixture of the composition:

HNO_3	28%
H_2SO_4	58%
H_2O	14%

is added gradually, with vigorous stirring.

At the beginning of acidification a temperature of 25°C should be maintained. During the addition of the first 4000 kg of acid the temperature is allowed to rise up to 35°C. On adding a further 2500 kg of acid the temperature rises up to 60°C. Then the whole is mixed for an hour at 70°C. After cooling, the layer of nitro compound is separated from that of the acid. The spent acid is shaken with benzene to remove any nitrobenzene, nitric acid and nitrogen oxides that may be left. Then the spent acid is transferred to a distillation plant, where it is subjected to concentration up to 70% of H_2SO_4. The benzene from the extraction is either recycled to the nitration plant or is distilled off to separate it from nitrobenzene.

However, the nitrobenzene obtained still contains some acid. To remove it the product is washed with water, then with a 3.0-3.3% solution of sodium hydroxide. The quantity of NaOH used for washing comprises 0.5% of the nitrobenzene weight. In this way not only the remaining acid (which of course is harmless if the nitrobenzene is to be used for further nitration) can be removed, but also any nitrophenols formed in the nitration process. The latter are particularly undesirable impurities in the product. Finally the nitrobenzene is washed once more with water and dried under reduced pressure.

The Leverkusen (I. G. Farbenindustrie) process differs in that it uses a slightly different mixed acid and a rather lower nitration temperature.

The nitrating acid had the composition:

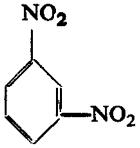
HNO_3	35.5%
H_2SO_4	52.5%
H_2O	12.0%

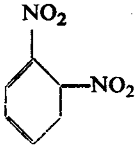
The nitrator (7 m^3 capacity) is fed with 2200 kg of benzene. Mixed acid (4900 kg) is run in for 10 hr, allowing the temperature to rise gradually from 20 to 45°C, which is maintained for further 1 hr with stirring. A sample is taken for a quick test. The density of a crude unwashed sample of nitrobenzene should be 1.200 g/cm^3 at 15°C The waste acid should have the following characteristics: density at 15°C 1.610-1.620 g/cm^3, HNO_3 below 0.2%, HNO_2 below 0.5%. Generally the last two figures are 0.0% and 0.3% respectively.

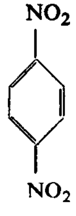
If the test is satisfactory the contents of the nitrator are transferred into another vessel where separation is performed. Three batches are collected in a washing tank, washed with water until neutral to Congo Red and then with water containing ca 0.5% of Na_2CO_3 until strongly alkaline to phenolphthalein. The product is stream distilled until the density of the oil coming over is 1.2. The oil with density < 1.0 is collected and nitrated when a sufficient quantity of it is available for a batch. The oil with a density over 1.0 and below 1.2 is steam distilled with the next batch. The product, freed from unnitrated material, is washed with 3000 1. of water to which 10 kg of a 30% NaOH solution has been added to remove phenols. Then all is washed until neutral and dried at 90°C under reduced pressure. The yield is 98% of the theoretical. The waste acid contains ca. 70% H_2SO_4.

DINITROBENZENES

There are three known isomers of dinitrobenzene - *meta, ortho* and *para:*







PHYSICAL PROPERTIES

The boiling points of the *ortho-*, *meta-*, and *para- isomers* are 319°C, 303°C, and 299°C respectively. The corresponding melting points are 118°C, 91°C and 172°C.

They are all crystalline, pale yellow products, highly toxic, the *ortho-* and *para-* isomers even more than *m-* dinitrobenzene, according to existing data.

Commercial dinitrobenzene is a mixture of the m-dinitro compound, as a principal component, with some 8.0% the *ortho-* and *para-isomers.* It melts at 80-82°C. The melting point of dinitrobenzene for military purposes (as a substitute for TNT) should be 88-89°C.

Dinitrobenzene is of great importance in the organic chemical industry as a raw material for the manufacture of *m-* nitroaniline, *m-* phenylenediamine, sulphur dyes etc.

Dinitrobenzene was used during World War I as a substitute for TNT, since the raw material benzene, necessary for its production, was more readily available than that for trinitrotoluene, and the production process itself was more economical.

Dinitrobenzene was used in Russia (1914-1918) for filling naval mines, in Germany, where it was known as DiFp (Di-Füllpulver), for filling various shells, and in Switzerland.

Even earlier (1879-1880) liquid explosives known as Hellhoffites (Vol. III) had been tried as high explosives. They consisted of nitric acid and dinitrobenzene.

When in the molten state, *m-* dinitrobenzene freezes to form a product having a density of approximately 1.5 g/cm^3. The specific gravity of *m-* dinitrobenzene at different temperatures is given in Table 32 according to Orlova [3]. By compressing powdered *m-* dinitrobenzene, pellets of various densities can be obtained. For example Kast [3a] using pressures of 290 kg/cm^2 and 585 kg/cm^2 obtained products of density 1.29 and 1.44 g/cm^3 respectively.

TABLE 32

SPECIFIC GRAVITY OF *m-* DINITBOBENZENE

Temperature, °C	20	90	120	140	160
Specific gravity	1.577	1.3644	1.3349	1.3149	1.2957

The viscosity [3] of molten m-dinitrobenzene is 0.02528 P at 90°C.

m- Dinitrobenzene is readily soluble in acetone, benzene and toluene and less so in ethyl alcohol. The solubility of the dinitrobenzenes is shown in Table 33, and the solubility of *m-* dinitrobenzene in sulphuric acid in Table 34 [3].

m- Dinitrobenzene forms eutectics with higher nitrated aromatics and with nitric esters. Some of them have been suggested as low melting and low freezing mixtures respectively (Vol. III).

Here are the most important data (Table 35).

TABLB 33
SOLUBILITY OF DINITROBENZENES

Solvent	Temperature °C	100 g of solvent dissolve		
		ortho 8	*meta* g	*Para* g
Methanol	20.2	3.3	6.75	0.69
Ethanol	20.5	1.9	3.5	0.40
Propanol	20.0	1.09	2.4	0.30
Carbon disulphide	17.6	0.24	1.35	0.14
Chloroform	17.6	27.1	32.4	1.82
Carbon tetrachloride	16.5	0.14	1.18	0.12
Benzene	18.2	5.68	39.45	2.56
Toluene	16.5	3.63	30.66	2.36
Ethyl acetate	18.2	12.96	36.27	3.56
Water	20.0	0.01	0.02	0.01
Water	100.0	0.30	0.32	0.30

TABLE 34
SOLUBILITY OF *m*- DINITROBENZENE (%) IN SULPHURIC ACID OF VARIOUS CONCENTRATIONS

Temperature °C	Concentration of sulphuric acid in % H_2SO_4		
	70	80	90
0	0.60	1.4	7.15
10	0.65	1.4	7.2
25	0.75	1.7	7.9
40	0.90	1.8	9.0
50	1.00	2.2	10.1
60	1.15	2.7	11.25
70	1.40	3.5	13.40
80	1.85	4.0	16.0
90	2.05	4.8	18.6
100	3.00	6.5	22.3

TABLE 35
EUTECTICS WITH *m*- DINITROBENZENE

The second component	Weight % of *m*- DNB	m.p. °C	Author
Cyclonite	92	85.5	Urbanski and Rabek-Gawronska [4]
Nitroglycerine	17.1	5.0	Kurita and Hagui [5]
	17.5	5.0	Hackel [6]
Pentaerythritol tetranitrate	47.5	65.5	Urbanski [7]
Picric acid	66	63	Kremann and Pogantsch [8]
Tetryl	54	65.5	Jefremov and Tikhomirova [9]
sym-Trinitrobenzene	53	61.9	Hammick, Andrews and Hampson [10]
Trinitro-m-cresol	44.8	54.4	Jefremov [11]
α -Trinitrotoluene	45.5	51	Hrynakowski and Kapuscinski [12]
Trinitro-m-xylene	82.2	76.4	Jefremov and Tikhomirova [9]

Three-component systems with *m*- dinitrobenzene have been studied by Khaibashev and Bogush [12a]. They found ternary eutectics:

(1) 9% trinitro-m-xylene, 9% tetryl, 82% m-dinitrobenzene, m.p. 80.6%.
(2) 18.5% 1,8-dinitronaphthalene, 7% tetryl, 74.5 *m*- dinitrobenzene, m.p. 74.5°C.
(3) 8.5% trinitro-m-xylene, 16% pentaerythritol tetranitrate, 75% *m*- dinitrobenzene. m.p 79.5%.
(4) 16.5% 1,8-dinitronaphthalene, 12.5% pentaerythritol tetranitrate, 71% *m*- dinitrobenzene, m.p. 69°C.
(5) 5% trinitro-m-xylene, 43% picric acid, 52% *m*- dinitrobenzene, m.p. 57.6°C.

m- Dinitrobenzene can be separated from the *o*- isomer by paper-chromatography (Franc [13]), the mobile phase being composed of ethyl alcohol, water and acetic acid.

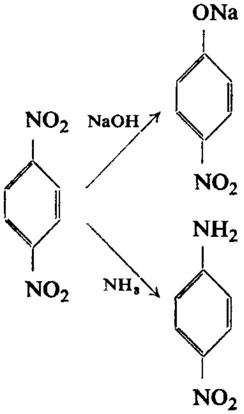
The thermochemical properties of dinitrobenzene are given on pp. 259-262 (Fig. 50).

CHEMICAL PROPERTIES

m- Dinitrobenzene is the least reactive of the three isomeric forms of dinitrobenzene, because its nitro groups are in the *meta* position to each other.

Like most nitro compounds all three isomers are resistant to concentrated acids, and fairly sensitive to alkalis.

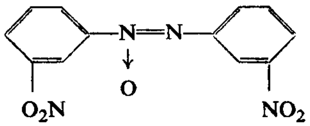
When treated with alkalis, *o*- and *p*- dinitrobenzenes are slowly converted to *o*- and *p*- nitrophenols, while with ammonia they form *o*- and *p*- nitroaniline. These reactions proceed slowly at room temperature, and more rapidly on heating.



(1)

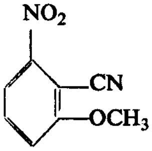
m- Dinitrobenzene does not undergo this reaction. This property was utilized in the past for separating *m*- dinitrobenzene from its isomers. Crude dinitrobenzene was shaken up with a 0.5-1.0% NaOH solution at about 80°C and the *o*- and *p*- isomers were partly extracted as corresponding nitrophenates. However, this method was not very efficient as the purified dinitrobenzene had a low melting point (80°C). It has now been replaced by sodium sulphite method.

m-Dinitrobenzene reacts with a 20% solution of sodium hydroxide only when boiled. One of its nitro groups is reduced and 3,3'-dinitroazoxybenzene is formed (Klinger and Pitschke [14]):

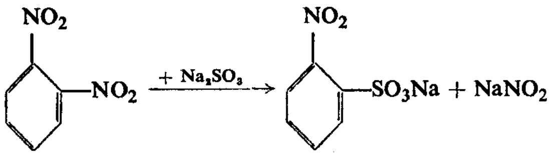


When in alcoholic solution, a molecule of *m*- dinitrobenzene adds a molecule of sodium ethoxyde to form an addition product with the formula $C_6H_4(NO_2)_2 \cdot$ $.C_2H_5ONa$ (Giua [15]).

m- Dinitrobenzene reacts with potassium cyanide in methyl (or ethyl) alcohol solution, methoxynitrobenzonitrile being formed (de Bruyn [16], 1904) :



Ortho- and *p*- dinitrobenzene react with sodium sulphite toform the correspending nitrosulphonic acids:



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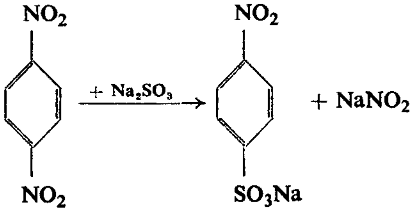
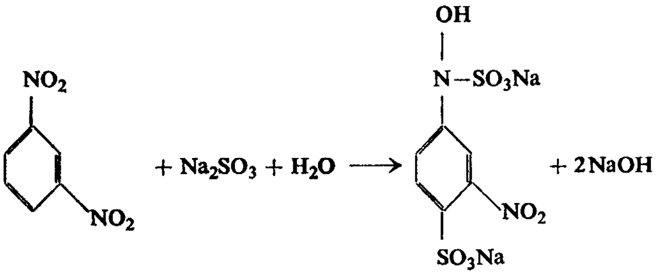
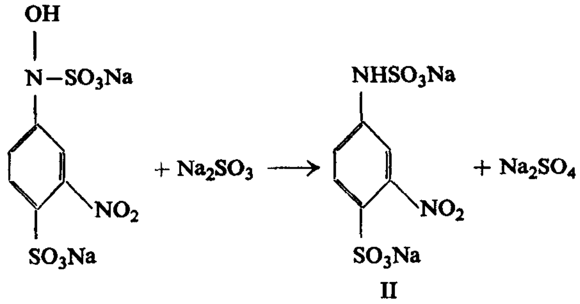


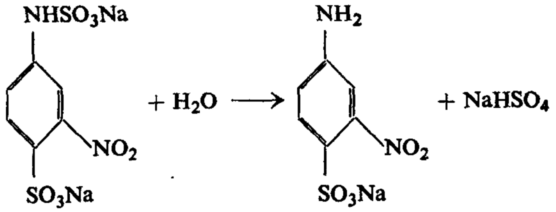
(3)

According to Golosenko (after Orlova [3]), *m*- dinitrobenzene reacts with sodium sulphite at 70°C according to the scheme:



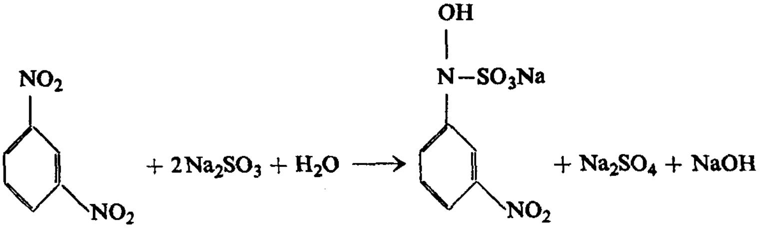
(4a)



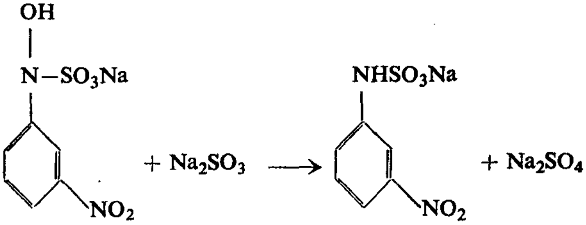


(4c)

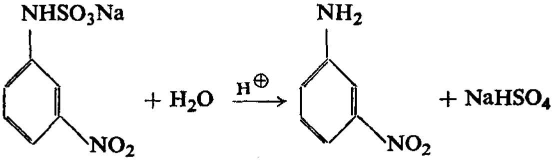
A side reaction yields *m*- nitroaniline:



(4d)

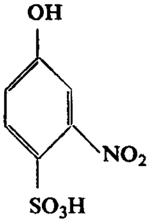


(4e)



(4f)

Also as result of hydrolysis of I and II a nitrophenolsulphonic acid (V) can be formed :



V

The proportion of the compounds is: III-80%, IV-13%, V-7%.

As *m*- dinitrobenzene reacts with sodium sulphite with more difficulty, this reaction is now used for removing the *o*- and *p*- isomers from commercial dinitrobenzene (pp. 246-248).

TABLE 36

ADDITION PRODUCTS OF DINITROBENZENE ISOMERS

Second component	*o*- Dinitrobenzene		*m*- Dinitrobenzene		*p*- Dinitrobenzene	
	composition of the products	m.p. °C	composition of the products	m.p. °C	composition of the products	m.p. °C
Acenaphthene	none	—	1:1	72.3	none	
Phenanthrene	none	—	none	-	1:3	81.5
Naphthalene	none	—	1:1	50.5	1:1	ca. 117
Aniline	none	—	1:1	41.5	none	-
o- Phenylenediamine	none	—	3:2 (unstable)	58.3	none	-
m- Phenylenediamine	none	—	1:2 (unstable)	36.2	1:2	
p- Phenylenediamine			none	-	1:1	114
α -Naphthylamine	none	—	none	-	1:1	81
β -Naphthylamine	none	—	1:1	63.8	1:1	91

m- Dinitrobenzene is used for the identification of some ketosteroids (androsterone, estrone, pregnandione, cortisone etc.). A blue colour develops in the presence of potassium hydroxide. This is a modification of the Janovsky reaction suggested for this particular purpose by Zimmermann [17] (p. 207).

m- Dinitrobenzene reacts with liquid ammonia to give a purple solution containing an addition anion [68].

Dinitrobenzenes form addition products with hydrocarbons with condensed rings, as well as with aromatic amines, *p*- nitrobenzene entering the reactions the most readily, and *o*- dinitrobenzene - the least so. The addition products formed by dinitrobenzenes with various compounds have been extensively studied by Kremann and co-workers [18], Szperl and co-workers [19-20b], Giua [15]. Jefremov [9,11], Hrynakowski and KapuScinski [12].

Some of the addition products are shown in Table 36.

m- Dinitrobenzene also forms an addition product with nitrobenzene which, according to Lehmstedt [21], contains 1 mol. *m*- dinitrobenzene and 2 mol. of nitrobenzene. Its melting point is 25°C.

TOXICITY OF DINITROBENZENE

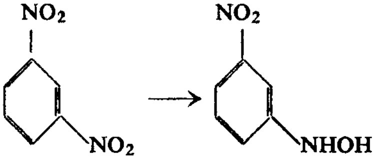
Dinitrobenzene-the commercial product consists mainly of *m*- dinitrobenzene-is one of the most toxic industrial poisons and has been the cause of a great number of fatal cases. Poisoning may be caused by inhaling the vapours or by absorption through the skin. Although dinitrobenzene has relatively little volatility, a concentration as low as 1 mg/m^3 may be sufficient to cause acute poisoning, so great care should be taken to avoid toxic concentrations.

Dinitrobenzene is a strong poison, affecting the blood and the liver. It causes the formation of methaemoglobin, which can be seen in the intense blue discolouration-cyanosis-of the lips, mucous membranes and the face of the victim.

Kiese and his colleagues [22] working with dogs, found that subcutaneous injections of *m*- dinitrobenzene given in quantities of 0.2-6 mg/kg over a long period caused anaemia, cramps, paralysis and liver damage. When experimenting on rats they were able to establish that animals suffering from chronic alcoholic poisoning, were more sensitive to *m*- dinitrobenzene than normal rats. The reverse was also true-the narcotic action of alcohol was stronger when the rats were victims of chronic *m*- dinitrobenzene poisoning.

According to Koelsch [23], chronic industrial poisoning by dinitrobenzene may appear in two forms. One of them causes degeneration of haemoglobin and in most cases recovery follows within 1-2 weeks. In exceptionally acute cases the symptoms appear rapidly and are often followed by death within a few hours.

Another form of dinitrobenzene poisoning is characterized by delayed symptoms which may appear from 1 to 3 months after exposure. Within 1-3 weeks after the first symptoms are manifested, degeneration of the liver takes place. Women are particularly liable to this form of poisoning. The illness may last for about 2 weeks in mild cases, while severe but not-fatal ones may last for 2 months. Some of the dinitrobenzene is excreted unchanged with the urine, while some of it undergoes a partial reduction in the body to a still more poisonous hydroxylamine derivative :



(5)

The medical literature (Staub [24]), dealing with industrial aspects of hygiene, reports that in the one year 1900 in a German explosives factory, 41% of the workers were poisoned by dinitrobenzene.

During World War I when dinitrobenzene was manufactured and widely used cases of poisoning in Germany were exceptionally numerous. Poisoning cases, often fatal, would occur despite the fact that the workshops were thoroughly ventilated and the workers took such safety measures as wearing protective gloves and using helmets against inhaling the dust and vapours of the substance.

No statistical data are available for the whole period of the war. Neverthe less there are numerous fragmentary pieces of information about cases of poisoning in the manufacture and application of dinitrobenzene. For example, of about 4000 workers at one of the ammunition plants in Bavaria, nearly 2000 persons were poisoned by dinitrobenzene. In one of the workshops of another factory, within one month of the year 1917, 30 cases of poisoning were recorded, which corresponded to 46.8% of the personnel.

TABLE 37

STATISTICS OF CASES OF POISONING CAUSED BY DINITROBENZENE

Year	Month	Poisoned by dinitrobenzene	
		number	% of the personnel
1917	March	16	16.6
	April	15	13.6
	May	12	13.8
	June	24	30.8
	July	14	12.6
	August	19	21.2
	September	17	12.2
	October	9	8.2
	November	5	4.6
	December	3	2.3
1918	January	10	7.3
	February	19	12.5
	March	19	10.0
	April	16	11.7
	May	21	16.4
	June	19	13.3
	July	20	10.0
	August	27	17.4
	September	2	1.4
	October	6	5.8

It has been observed that poisoning occurs more often on hot days than on cooler ones owing to the higher vapour pressure of the compound at higher temperatures. For example, in one of the German factories using dinitrobenzene for filling shells, the numbers of poisoning cases recorded in several months of 1917 find 1918 are given in Table 37.

Observations by several authors have shown that women are more sensitive to dinitrobenzene than men. Poisoning by dinitrobenzene results in increased sensitivity and hence makes the sufferer more liable to repeated poisoning, especially in less resistant persons. Out of 179 workers of a German factory who were poisoned in the year 1918, 146 of them were poisoned for the first time, 10 for the second time, 12 for the third time, and 2 women for the fourth time.

EXPLOSIVE PROPERTIES OF DINITROBENZENE

One of the characteristics of *m*- dinitrobenzene is that it shows an exceptionally low sensitivity to impact and friction. For this reason attempts have been made to use it in armour-piercing shells. However they have failed due to its two serious disadvantages; namely its great toxicity and the difficulty of effective complete detonation by initiation with an ordinary detonator. Thus, *m*- dinitrobenzene, even when compressed to a density of 1.44, requires an additional, secondary detonator.

Sensitivity to impact. According to Wöhler and Wenzelberg [25], energy of impact per unit area required to initiate 50% explosions is 19.5 kgm/cm^2 Other authors report that the relative value of the energy necessary for initiation by impact is 120 as compared with 100 for picric acid.

The explosive decomposition of dinitrobenzene may proceed, as Kast [3a] assumes, according to the equation:

$$16C_6H_4(NO_2)_2 = 10CO_2 + 38CO + 10CH_4 + C_2H_2 + HCN + 5.5H_2 + 14.5N_2 + \\ + 2NH_4HCO_3 + 33C + Q \qquad (6)$$

where Q is 870 cal/kg
V_0 is 670 l./g
t is 2500°C
f is 7035 m
Lead block expansion is 250 cm^3
The highest rate of detonation is 6100 m/sec.

PREPARATION OF DINITROBENZENE

Deville [26] first prepared dinitrobenzene in 1841 by treating benzene with concentrated nitric acid and heating it to the boiling point. Soon after that Mus-Pratt and Hofmann [27] obtained it, using a mixture of nitric and sulphuric acid for the nitration.

For a long time it was thought that a uniform substance was produced. However, m 1874 Rinne and Zincke [28], and also Körner [29] found that the *o*- and *p*- isomers are also formed along with large quantities of *m*- dinitrobenzene.

The conditions for preparing dinitrobenzene were described more fully by Beilstein and Kurbatov [29a] in 1875. They dissolved 1 part by volume of benzene in 2 parts by volume of nitric acid (sp. gr. 1.52). After cooling, 3.3 parts by volume. of sulphuric acid were added.

The possibility that a certain quantity of trinitrobenzene may be formed, as an impurity in dinitrobenzene, was reported by Hepp [30] in 1882.

Holleman and de Bruyn [31] investigated the influence of the nitration conditions on the quantity of isomers formed. When nitrating nitrobenzene with nitric acid or a nitrating mixture at temperatures below and above room temperature, they obtained the following percentages of isomers (Table 38).

Clearly, higher temperatures enhance the formation of the o-isomer at the expense of the *m*- isomer. The presence of sulphuric acid in the nitrating mixture results in a slight increase of the quantity of *m*- isomer formed and a corresponding decrease in the production of the *o*- isomer.

TABLE 38

RESULTS OF THE NITRATION OF NITROBENZENE TO DINITROBENZENE UNDER VARIOUS CONDITIONS

Nitrating agent	Temperature °C	Isomer content, %		
		meta	ortho	para
Nitric acid	0	93.2	6.4	0.5
	30	90.9	8.1	1.0
Nitric and sulphuric	0	93.9	4.8	1.7
	40	91.8	6.8	1.4

Wyler [32] has carried out a vast amount of work on the nitration of benzene. He found that in the nitration of benzene or nitrobenzene on an industrial scale, a product was obtained containing up to 12% of the *o*- and *p*- isomers. This was contrary to the generally held opinion that dinitrobenzene contains only 1% of *o*- and 3% of *p*- dinitrobenzene.

Wyler proved by a number of experiments with the nitration of nitrobenzene to dinitrobenzene, that the content of the *o*- and *p*- isomers in the product may vary from 5 to 15%, depending on the reaction conditions. At a low temperature, e.g. -17°C, equal amounts of the *o*- and *p*- isomers were formed, while higher temperatures favoured the formation of the *o*- isomer, this being on the whole in agreement with the earlier observations by Holleman and de Bruyn [31].

The results obtained by Wyler are shown in Table 39.

TABLE 39

RESULTS OF THE NITRATION OF NITROBENZENE UNDER VARIOUS CONDITIONS (WYLER)

Nitration tempera-ture, °C	Weight of nitroben-zene g	Nitrating mixture				Period of nitration hr	m.p. °C	Composition of the product		
		Sulphuric acid		Nitric acid						
		g	Concen-tration %	g	Concen-tration %			meta	ortho	para
-17 to -10	24.6	150	105	25	96	4.00	86.9	95.1	2.5	2.4
- 5	-5	,,	,,	,,	,,	2.00	86.8	94.7	3.5	1.8
25-29	,,	,,	,,	,,	,,	1.75	85.0	92.6	5.0	2.4
65-69	,,	500	100	250	,,	1.5	83.0	89.7	7.7	3.0
65-75	,,	900	98	284	88	1.5	82.1	89.2	8.7	2.1
90-100	,,	,,	,,	,,	,,	1.50	80.0	87.0	11.8	1.2
108-113	,,	,,	,,	,,	,,	1.25	81.2	87.6	10.2	2.2
124-129	,,	,,	,,	,,	,,	0.75	79.9	85.7	13.9	0.4

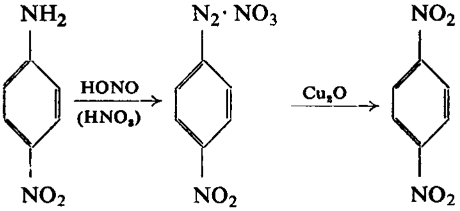
In 1933, Hetherington and Masson [33] made a systematic study of nitration of nitrobenzene to dinitrobenzene using a wide range of mixtures of sulphuric and nitric acids and water. They plotted their results on a curve of "limiting compositions" beyond which the reaction does not occur (Fig. 27, p. 154). They also showed the change in molar composition of the acid during nitration (Fig. 48). For example, an acid of initial composition will nitrate nitrobenzene until its composition moving along the parallel XY reaches Y, when it practically ceases to react. Figure 49 gives the molar compositions of the acid present in both the organic and acid layer. The rate of nitration was given in Fig. 28 (p. 155).

In practice, for the nitration of nitrobenzene, a nitrating. mixture of the composition:

HNO_3	18%
H_2SO_4	80%
H_2O	2%

is generally used, in about 10% excess over the theoretical amount.

Pure *o*- and *p*- dinitrobenzenes may be obtained from the corresponding nitroanilines in two ways: either by diazotization (Meisenheimer and Patzig [34],) or by oxidation (Bamberger and Hübner [35], Witt and Kopetschni [36]):



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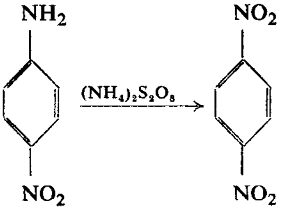


(8)

Nitration in two stages in two nitrators. In industrial practice the preparation of dinitrobenzene is commonly carried out by nitration in two stages:

Benzene -> Nitrobenzene -> Dinitrobenzene

In this way, operating conditions are safer during the process and acid control can be made more efficient.

The first operation, i.e. the nitration of benzene to nitrobenzene, has been already described (pp. 232, 233). The second stage of the process, i.e. the nitration of nitrobenzene to dinitrobenzene by the method used at Höchst (I. G. Farbenindustrie) is described below.

Nitrobenzene is pumped into a measuring tank of 5 m^3 capacity, lined with sheet lead. 3660 kg of nitrobenzene is fed from the tank to a nitrator of 10 m^3

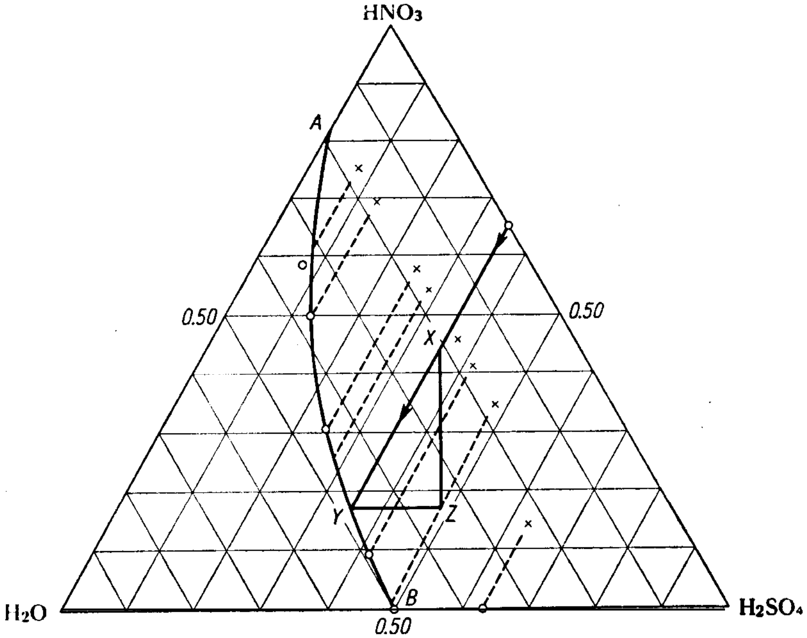


FIG. 48. Change in molecular composition of acids during nitration. AB - the curve of limiting compositions (Hetherington and Masson [33]).

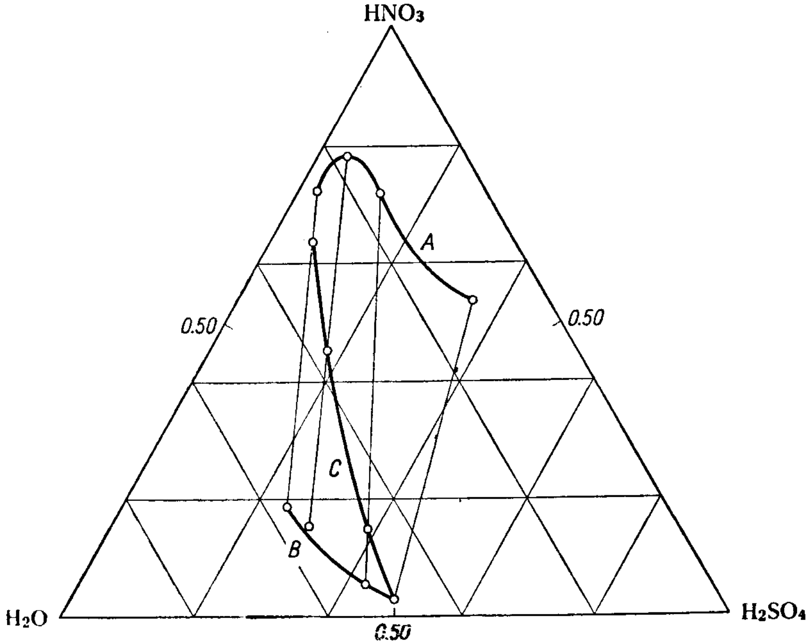


FIG. 49. Molecular compositions of acid present in the organic layer (A), acid layer (B), and in the aggregate (C). The tie-lines show the conjugate layers (Hetherington and Masson [33]).

capacity already containing the spent acid from the previous nitration. The mixture is stirred at high speed. During this operation the extraction of dinitrobenzene from the spent acid is taking place. After one hour of stirring the nitrator contents are allowed to remain at rest for 1 hr during which separation of the liquid into two layers takes place. The lower, acid layer is drained off to a spent acid tank of 25 m^3 capacity; then 6500 kg of nitrating mixture of the composition:

HNO_3	30%
H_2SO_4	67%
H_2O	3%

is fed slowly into the nitrator over a period of 4 to 5 hr. The nitrator contents are then cooled and stirred at high speed. A temperature below 40°C is maintained during the addition of acid. By the end of the operation a rise in temperature up to 80°C may be allowed. After all the acid has been added the contents of the nitrator are stirred again at 80-90°C until the nitration of nitrobenzene to dinitrobenzene has been completed. This can be achieved within 1 to 2 hr. Nitrobenzene is tested for by smelling.

After the nitration has been completed, 1000 l. of water is added gradually during 1 hr, the temperature being maintained at 80-90°C. The nitrator contents are allowed to remain at the above temperature for 1 hr. Then the lower layer, i.e. the spent acid, is drained off to a tank from which it can be transferred by compressed air to the nitrator for the next nitration operation. The product left in the nitrator is passed to a purification plant, where it is washed with alkali and purified by sulphitation. Finally the product is dried.

Purification. Washing dinitrobenzene with a solution of sodium hydroxide is carried out in the following way. The crude, molten dinitrobenzene in the nitrator is run in a tightly closed, brick lined iron vessel, heated internally by a stainless steel steam coil. From this vessel it is transferred in steam heated, stainless steel pipes to a washing tank of 16 m^3 capacity, filled with 3-4 m^3 of water and 400 1. of a 33% solution of sodium hydroxide, heated to 50°C. The dinitrobenzene is run in the washing tank over a period of half an hour and this is accompanied by continuous vigorous stirring. The temperature should not rise above 80-85°C. All the time the solution in the washing tank should be alkaline (phenolphthalein test). If all the sodium hydroxide is used up, an additional quantity of it must be added. After all the crude dinitrobenzene has been introduced to the washing tank its contents are stirred for a further period of 30 min to one hour.

Sulphitation of dinitrobenzene (Griesheim method) is carried out in the same washing tank. Cold water is run in until the temperature falls to 66°C. Then a solution of sodium sulphite, prepared by mixing 1000-1100 l. of a 40% solution of sodium hydrogen sulphite with 400-500 kg of 33% sodium hydroxide, is added.

During sulphitation a temperature of 66-73°C is maintained. After 2 hr of mixing at this temperature the contents of the vessel are cooled to 50°C. The purified dinitrobenzene crystallizes in rather large crystals. The melting point of the product should be 88-89°C. The mother liquor is pumped off through a pipe closed by a wire gauze, which retains the dinitrobenzene crystals, while the liquor runs into an outlet pipe, through a separator where any crystals which have been carried over are retained. The dinitrobenzene in the vessel is thoroughly washed by repeated rinsing with water, which is then pumped away.

The dinitrobenzene, which is now well washed and free from the sodium sulphite and sodium nitrite formed during sulphitation, is melted and introduced to a special vessel of 15 m^3 capacity, where it is separated from residual water by decantation. It is tested to ensure that washing has been fully effective, by boiling a sample with water, followed by cooling and filtering. The filtrate should not decolorize a solution of $KMnO_4$ during a 10-min test period.

The tinal product is dried at 135°C under reduced pressure in the molten state in a drying vat of 16 m^3 capacity.

The product is cast in blocks. From the quantities of raw materials given above, 4100 kg of dinitrobenzene, melting at 88-89°C, are obtained.

Nitration in two stages in one nitrator. The Griesheim (I. G. Farbenindustrie) process for the manufacture of dinitrobenzene differs from that of Höchst since in the latter the whole nitration starting from benzene is carried out in one cast iron nitrator of 8 m^3 capacity. The nitrator is equipped with a stirrer, rotating at 110 r.p.m., a jacket having a cooling area of 8 m^2 and a lead cooling coil of 16 m^2 area.

2200 kg of the waste acid from the previous batch are left in the nitrator and to this 1900 kg of nitrating mixture is added, the composition of which is as follows:

HNO_3	88%
H_2SO_4	11%
H_2O	1%

2200 kg of benzene are run in during a period of 4 hr while the temperature rises from 25°C to 40°C. Then the temperature is allowed to rise gradually to 60°C over a period of 1 hr. Then the stirrer is stopped, the contents are allowed to settle and the waste acid is run off to a lead lined washing vessel (A) of 12 m^3 capacity, where it is washed with benzene or nitrobenzene.

To the crude nitrobenzene left in the nitrator 5000-6000 kg of a nitrating mixture are then added gradually over 3 hr, the temperature rising from 25°C to 40°C. The mean composition of the mixture is:

HNO_3	33%
H_2SO_4	67%

The temperature should rise to 90°C and be maintained there for 1 hr. A sample is then tested by steam distillation for the presence of nitrobenzene. The amount of nitrating mixture used depends on the actual amount of HNO_3 in it and on the result of the test.

When the batch has settled the waste acid is run into a washing tank (A) where the acid from three or four nitrations has been collected and where the whole is washed with nitrobenzene.

Next the dinitrobenzene is run to a tile-lined stainless steel washing tank (B) of 12 m^3 capacity, where it is washed with 4000 l. of hot water and then with a further 4000 l. containing sufficient NaOH to give a neutral reaction. Finally it is washed with water, and then transferred in a molten state to a purification unit. where it is dried at 120°C and 15 mm Hg. The product is crude dinitrobenzene. The amount of H_2SO_4 in the waste acid from dinitration is about 80%. After mixing with nitric acid it can be used for mononitration.

Purification. 4500 kg of molten dinitrobenzene (i.e. one charge of the nitrator) are run into a washing tank (C). The tank of 12 m^3 capacity must be made of stainless steel, lined with tiles, and fitted with a lead coated lid and a lead coated stirrer. 3000 1. water at ca. 80°C are run into it over the dinitrobenzene, with constant stirring. The whole is allowed to cool until granulation begins at ca. 70°C, the exact temperature depending on the stirrer and on the quality of the dinitrobenzene. Immediately granulation begins, 650 kg of sodium sulphite are introduced at a rate of 100 kg per 15 min. The temperature rises to 78°C and stirring must be continued for another 3 hr.

Samples should be taken, filtered, washed and dried. The setting point should not be lower than 88.5°C. If it is too low, 25-30 kg more of sodium sulphite are added.

The contents of the washing tank are cooled by circulating water within the jacket to 20-25°C. The mother liquor is pumped off through a wire gauze and the product is washed with cold water. Washing is continued until the colour changes from dark red to light yellow. The dark wash-liquors are discarded, the light ones being kept for the next batch.

The washed product is heated to 95°C and when in a molten state it is dried under reduced pressure. The drier consists of a jacketed cylindrical vessel of 12 m^3 capacity. Finally, the pure dried product is turned into flakes.

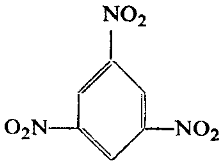
The product has the setting point 88.5-89°C.

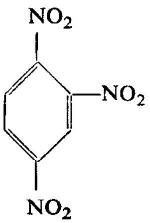
The yield is 100 kg of crude dinitrobenzene from 48 kg of benzene (96.7% theoretical). 100 kg of pure dinitrobenzene are obtained from 118 kg of crude product. This makes an overall yield of 81.9% calculated on benzene.

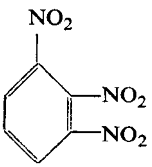
The crude product, according to Griesheim's experience, contains: 85% of *meta*-, 13% of *ortho*- and 2% of *para*- isomers.

TRINITROBENZENES

Three isomers of trinitrobenzene are known: 1,3,5-trinitrobenzene (sym-trinitrobenzene), 1,2,4-trinitrobenzene and 1,2,3-trinitrobenzene:







Their melting points are: 122°C, 62°C and 127.5°C respectively.

All the isomers are crystalline, pale yellow products and are poisonous. In addition, sym-trinitrobenzene causes severe irritation of the skin. 1,3,5-Trinitrobenzene can be formed in poor yield by the action of a mixture of anhydrous nitric acid and fuming sulphuric acid on *m*- dinitrobenzene, the 1,2,4-isomer also being formed in a very small quantity. The 1,2,3-isomer can be obtained only by indirect methods.

sym-Trinitrobenzene, though the most readily obtainable as well as chemically the most stable of the three isomers, has not found practical application, although it is a powerful explosive, with an explosive power slightly higher than that of TNT. Its preparation is too expensive. In the organic chemical industry sym-trinitrobenzene is used only for the manufacture of certain intermediates. e.g. phloroglucinol.

PHYSICAL PROPERTIES OF SYM-TRINITROBENZENE

According to Jefremov and Bogoyavlenskii [37] sym-trinitrobenzene exists in two isomorphic forms, which melt at 122.5°C and 106.3°C respectively.

It forms eutectics with other high nitrated aromatic compounds and certain nitric esters (Table 40). (See also Burkhardt [65].)

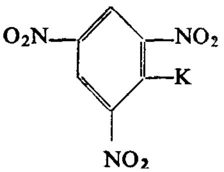
The solubility of sym-trinitrobenzene in various solvents according to Orlova [3] is given in Table 41.

The solubility of sym-trinitrobenzene in sulphuric acid of various concentrations is given in Table 42 (according to Orlova [3]).

CHEMICAL PROPERTIES OF SYM-TRINITROBENZENE

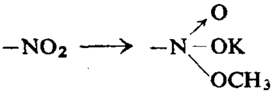
Reactions with alkalis. sym-Trinitrobenzene like other polynitro-compounds. exhibits high resistance to acids, while it reacts readily with alkalis.

It was Hepp [30] in 1882 who first found that sym-trinitrobenzene forms a dark coloured substance with sodium alcoholate. V. Meyer [38] isolated a similar substance in 1896 when treating sym-trinitrobenzene with potassium alcoholate, and assigned the following structure to it:



However, the formula could not be accepted, as, according to observations of de Bruyn [16] in 1895, the product is formed only in the presence of alcohol, and its empirical formula is $C_6H_3(NO_2)_3.CH_3OK$.

Angeli [39] suggested in 1884 that the addition of potassium alcoholate occurs through one of the nitro groups:



$$-NO_2 \longrightarrow -N\begin{matrix}\nearrow O \\ -OK \\ \searrow OCH_3\end{matrix}$$

TABLE 40

EUTECTICS WITH SYM-TRINITROBENZENE

The second component	Weight % of TNB	m.p. °C	Author
m- Dinitrobenzene	47	61.9	Hammick, Andrews and Hampson[10]
Nitroglycerine	17.5	5.0	Hackel [6]
Pentaerythritol tetranitrate	70	101.1	T. Urbanski [7]

TABLE 41

SOLUBILITY OF SYM-TRINITROBENZENE

(g) $C_6H_3(NO_2)_3$ IN 100 g OF SOLVENT

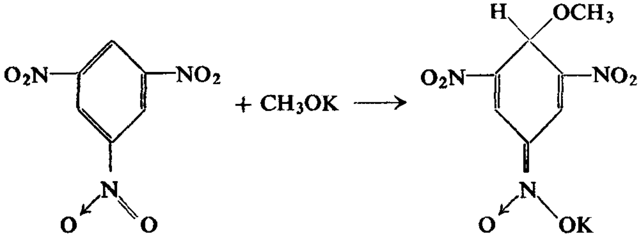
Solvent	Temperature, °C		
	17	50	100
Methanol	3.76	7.62	
Ethanol	2.09	4.57	
Ether	1.70	2.72 (at 32°)	
Acetone	59.11	160.67	
Carbon disulphide	0.24	0.44 (at 33°)	
Chloroform	6.24	18.42	
Benzene	6.18	25.70	
Toluene	11.86	46.31	
Pyridine	112.60	194.23	
Ethyl acetate	29.83	52.40	
Water	0.03	0.10	0.50

TABLE 42

SOLUBILITY OF SYM-TRINITROBENZENE IN SULPHURIC ACID

Temperature °C	Solubility (%) in sulphuric acid of concentration in % H_2SO_4			
	70	80	90	100
25	0.5	1.05	7.8	21.5
40	0.75	1.75	8.6	24.0
50	0.9	1.9	11.3	26.5
60	1.15	2.3	11.65	28.0
70	1.2	2.95	12.05	32.0
80	1.5	3.75	14.75	34.3
90	2.0	4.15	17.75	37.0
100	2.5	5.90	21.30	42.4

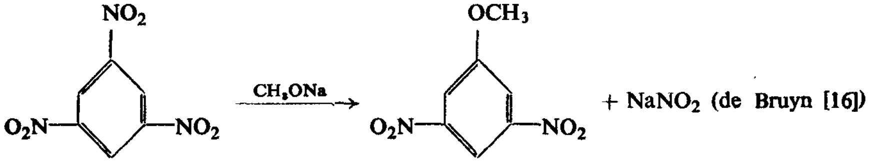
The problem was finally solved by Meisenheimer [40] in 1902, who found that by the addition of CH_3OK to trinitrobenzene an anisole derivative was formed:



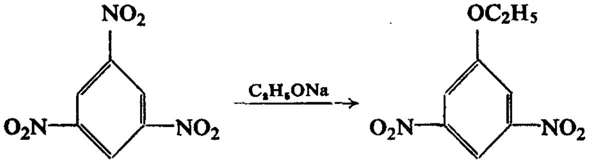
(9)

According to Meisenheimer, this formula was confirmed by the fact that the product of the addition of potassium ethoxide to trinitroanisole is identical to the product of the addition of potassium methoxide to trinitrophenetole. Meisenheimer's view was later confirmed by a number of workers, as for example Busch and Kogel [41], Bölian [42] and others (p. 203).

The reaction proceeds differently when sym-trinitrobenzene is heated with sodium ethoxide. One of the nitro groups is substituted by a methoxy or ethoxy group, 3,5-dinitroanisole or 3,5-dinitrophenetole being formed:



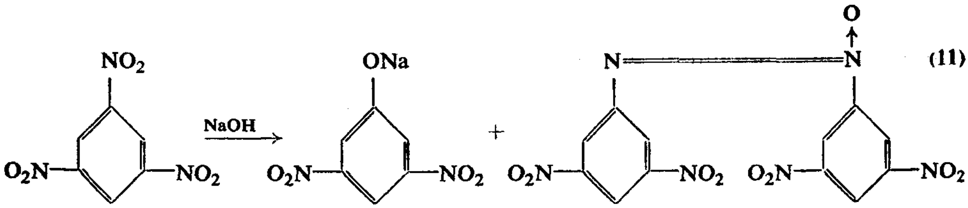
(10a)



+ $NaNO_2$ (Blanksma [43])

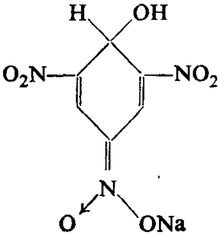
(10b)

Similarly, when trinitrobenzene is boiled with an aqueous solution of NaOH, sodium 3,5-dinitrophenate is formed along with some tetranitroazoxybenzene (de Bruyn [16]):



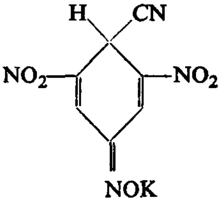
(11)

At a low temperature sym-trinitrobenzene may form an addition product with NaOH (Giua [15]). Giua ascribed to it a structure based on Meisenheimer's proposals :



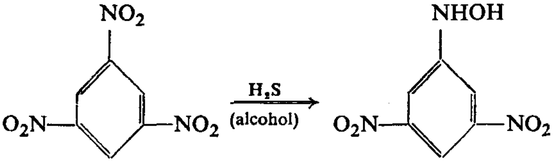
It seems possible that the products of the reaction of sym-trinitrobenzene with NaOH or alkali ethoxides are not individuals but mixtures of several compounds. For example, Busch and Kögel [41] found that sym-trinitrobenzene was able to add on not only one, but also two or three molecules of an ethoxide.

Trinitrobenzene combines with potassium cyanide to form a blood red addition product, to which Meisenheimer [40] ascribed the structure:



Oxidation. Mild oxidizing agents, such as potassium ferricyanide, convert trinitrobenzene into picric acid (p. 204).

Reduction. sym-Trinitrobenzcne, when reduced with sodium- or ammonium sulphide, forms 3,5-dinitroaniline. By treating it with hydrogen sulphide in alcoholic solution dinitrophenylhydroxylamine may be formed:



(12)

With sodium polysulphide, sym-trinitrobenzene yields tetranitroazoxybenzene along with dinitroaniline. All three nitro groups can be reduced by tin or iron in hydrochloric acid, triaminobenzenc being formed, which is the starting material for the manufacture of phloroglucinol. sym-Trinitrobenzene can react with sodium borohydride to yield trinitrocyclohexane (Severin [66]).

Reaction specific to sym-trinitrobenzene. Sym-trinitrobenzene in acetone solution rapidly produces a red colour with alkali hydroxides or ammonia. In the absence of the solvent the colour develops slowly.

Addition compounds. sym-Trinitrobenzcne readily forms well defined, often coloured compounds with hydrocarbons with condensed rings. Kremann and co-workers [18,44], Jefremov and co-workers [9,11,44a], Sudborough and Beard [44b] and their co-workers have studied most of these systems, containing sym-trinitrobenzene, by thermal analysis.

Similar compounds, for the most part coloured, are formed with aromatic artlines as well as with some phenols and aromatic alcohols.

TABLE 43
MOLECULAR COMPOUNDS WITH SYM-TRINITROBENZENE

Second component	Molecular proportion†	m.p., °C
Naphthalene	1:1	151
Anthracene	1:1	165
Acenaphthene	1:1	161
Phenanthrene	1:1	125
Fluorene	3:2	105
Aniline	1:1	125
p- Naphthylamine	1:1	161
o- Phenylenediamine	1:1	163
m- Phenylenediamine	1:1	168
p- Phenylenediamine	1:1	145.5
Diphenylamine	2:1	100.3
m- Nitroaniiine	1:1	97.5
Carbazole	1:1	203
Hydroquinone	1:1	131
Resorcinol	2:1	103
Triphenylcarbinol	3:2	134.5

† The first figure is for trinitrobenzene.

sym-Trinitrobenzene forms also an addition compound with nitrobenzene, the molecular proportion being 1:1. The product melts at 66.3°C (Hammick, Andrews and Hampson [10]).

sym-Trinitrobenzene also forms an addition product with pyridine N-oxide (Ross, Kelley and Labes [45]).

The addition products are generally unstable and can be dissociated simply by dissolution in solvents, e.g. benzene. They decompose completely into their components when treated with acids. For example, dilute acid causes quantitative separation of the amine from the nitro compound.

The cause of the colour intensity of the addition products of trinitrobenzene, as well as of other higher nitrated aromatic hydrocarbons with amines has already been discussed (pp. 221-222).

EXPLOSIVE PROPERTIES OF SYM-TRINITROBENZENE

According to Kast [3a], the explosive characteristics of sym-trinitrobenzene are exposed in the following figures:

density	1.63 g/cm^3
heat of explosion	1065 kcal/kg
volume of gases, V_0	670 I./kg
explosion temperature	3540°C
maximum rate of detonation	7000 m/sec
specific pressure, f	9665 m

The lead block test is 330 cm^3, and compared with picric acid (taken as 100), it is 108-111.

The sensitiveness to impact is slightly lower than that of TNT. According to Wohler and Wenzelberg [25], an impact energy of 12.1 kgm/cm^2 is necessary to produce 50% explosion. Thus compared with picric acid (100) its relative sensitiveness is 109, i.e. to bring about an explosion, the impact energy has to be higher by 9% than that necessary to explode picric acid.

PREPARATION OF SYM-TRINITROBENZENE

Direct nitration of *m*- dinitrobenzene. Hepp [30] who first used this method in 1887, reported that he was able to nitrate only two thirds of the dinitrobenzene used, in spite of using anhydrous nitric acid and fuming sulphuric acid.

De Bruyn [16] in 1894 could not obtain a yield higher than 50%, by reacting 500 g anhydrous nitric acid and 1000 g of fuming sulphuric acid with 60 g of *m*- dinitrobenzene, in spite of carrying out the process for 5 days (1 day at 80-100°C and the next 4 days at 110°C).

Trinitrobenzene has three good qualities as an explosive: high stability, great explosive power, and a low sensitiveness to impact and friction. There were good reasons for seeking more economic production methods. These investigations were particularly intensive during World War I.

Radcliffe and Pollitt [45a] found that on nitrating *m*- dinitrobenzene with a mixture of anhydrous nitric acid and 60% oleum at 110-120°C for 6½ hr, a 71% yield could be obtained, and that by using 20% oleum a 56% yield was obtained. According to Drumond [46], a yield amounting to only 29% theoretically can be obtained as a result of nitration with a mixture of nitric acid and 20% oleum at 130°C for 3 hr.

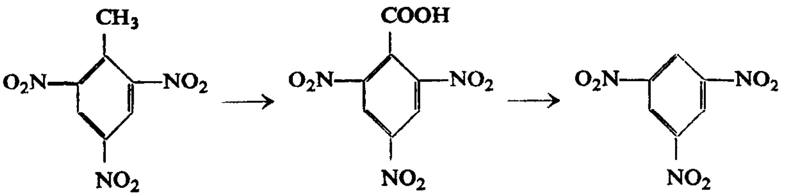
The results of Hepp, Lobry de Bruyn and Desvergnes have been confirmed by T. Urbanski and Simon [46a].

Moreover, Radcliffe and Pollitt found, that under certain conditions, the nitration of *m*- dinitrobenzene yielded a product melting at 61°C which was not the 1,2,4-isomer but, as they assumed, an "isomorphic modification of sym-trinitrobenzene".

However, this view was shown to be wrong. Gibson [47] cast a certain doubt on their statement and later T. Urbanski and Simon [46a] proved that the product melting at 61°C formed in the nitration of *m*- dinitrobenzene is simply a mixture of *m*- dinitrobenzene (35-50%) and sym-trinitrobenzene.

R. Robinson [67] reported that G. Müller nitrated *m*- dinitrobenzene to sym-trinitrobenzene by using cold anhydrous mixtures of nitric and perchloric acids.

Preparation from a- trinitrotoluene. In 1893 a patent was granted to the Chemische Fabrik Griesheim [47a] for the manufacture of sym-trinitrobenzene from trinitrotoluene. The method was based on the fact observed by Tiemann [48] and by Claus and Becker [49], that trinitrotoluene can be oxidized with nitric acid to trinitrobenzoic acid, the latter being readily decarboxylated to form sym-trinitrobenzene:



(13)

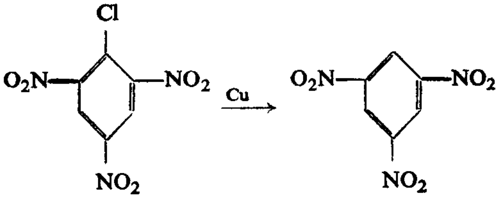
In the Griesheim method the oxidation of trinitrotoluene is accomplished by means of chromic acid in the presence of sulphuric acid, a temperature 40-50°C being maintained. By diluting the solution with water, trinitrobenzoic acid is precipitated. Boiling the acid in water results in the evolution of CO_2 and the formation of trinitrobenzene.

The Griesheim method is generally used for the laboratory preparation of sym-trinitrobenzene. However, it is too expensive to be applied in industry. Trinitrobenzene prepared in this way is much more costly than trinitrotoluene, whereas the gain in explosive power obtained is relatively small.

A less expensive method which Gamer and Abernethy [50] attribute to Koehler, consists in the oxidation of trinitrotoluene with 90-92% nitric acid in the presence of 93% sulphuric acid at 190°C. However, it requires very prolonged heating-about 40 hr. The method has not been adopted because of the considerable risk of explosion. Indeed, an explosion occurred in a factory at St. Chamas when experiments on a semi-industrial scale were carried out.

It should be mentioned that sym-trinitrobenzene is formed as a by-product of the nitration of toluene to trinitrotoluene (p. 338).

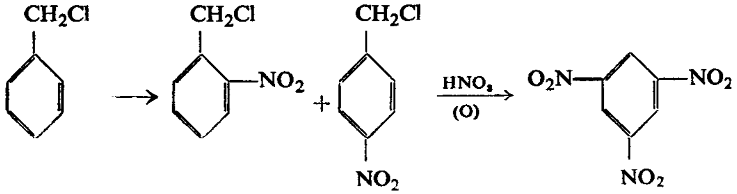
Preparation from picryl chloride. According to Ullmann and Bielecki [51] and also J. Meyer [52], trinitrobenzene may. be obtained by removing the chlorine atom from picryl chloride in the presence of copper:



(14)

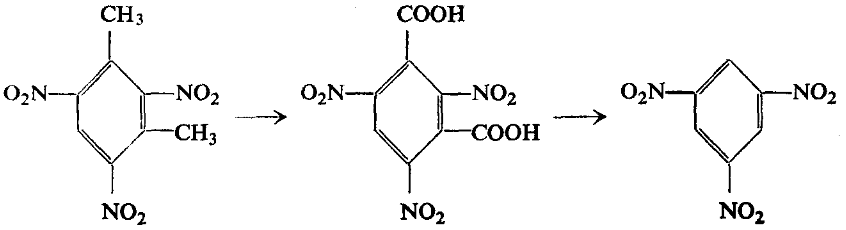
The reaction is carried out in about 85% alcohol solution at boiling point. Difficulties in obtaining picryl chloride are a drawback for applying the method industrially.

Preparation from benzyl chloride. This method has been proposed by Bronchard [53]. It consists in the nitration and oxidation of benzyl chloride:



(15)

Preparation from *m*- xylene. Giua [15] suggested sym-trinitrobenzene might be prepared by the nitration of *m*- xylene to the trinitro derivative, followed by oxidation and decarboxylation:

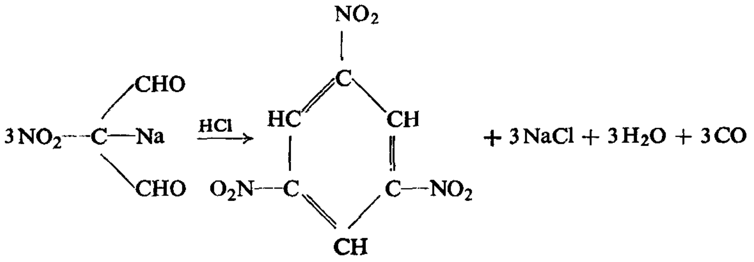


(16)

The method is rarely used, for pure *m*- xylene is not easily available in industry.

Other preparatory reactions. sym-Trinitrobenzene is also formed as a result of the prolonged treatment of benzene with nitrogen dioxide in a closed vessel (Wieland [54]).

The preparation of sym-trinitrobenzene by cyclization of nitromalonic aldehyde (Hill and Torray [55]):

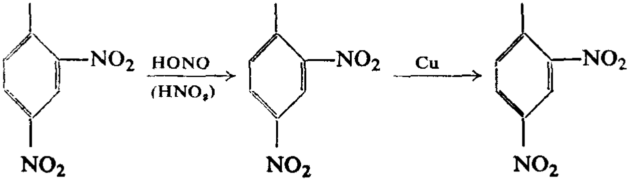


(17)

is of theoretical importance only.

PREPARATION OF UNSYMMETRICAL ISOMERS OF TRINITROBENZENE

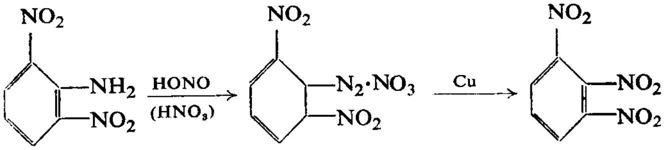
1,2,4-Trinitrobenzene may be obtained only in moderate yield by nitration of *o*- or *p*- dinitrobenzene. A product of high purity may be obtained from 2,4-dinitroaniline (Korner and Contardi [56]):



(18)

This isomer dissolves less easily in alcohol or ether than sym-trinitrobenzene. The nitro group in position 1 can readily be substituted by a hydroxyl or amino group.

1,2,3-Trinitrobenzene cannot be obtained by the nitration of *o*- dinitrobenzene. Kamer and Contardi have prepared this isomer from 2,6-dinitroaniline:

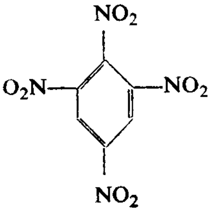


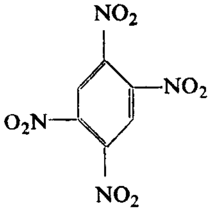
(19)

The nitro group in position 2 can readily be substituted by a hydroxyl or amine group.

TETRANITROBENZENES

Two isomers of tetranitrobenzene are known : 1,2,4,6-tetranitrobenzene and 1,2,4,5-tetranitrobenzene:

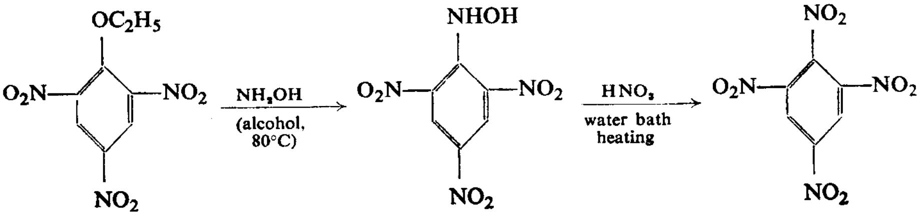




Their melting points arc 129-130°C and 188°C respectively.

1,2,4,6-Tetranitrohenzene. It was Borsche [57] who first prepared 1,2,4,6-tetranitrobenzene in 1923, by treating picrylhydroxylamine with anhydrous nitric acid.

According to Borsche, the reaction steps are as follows:

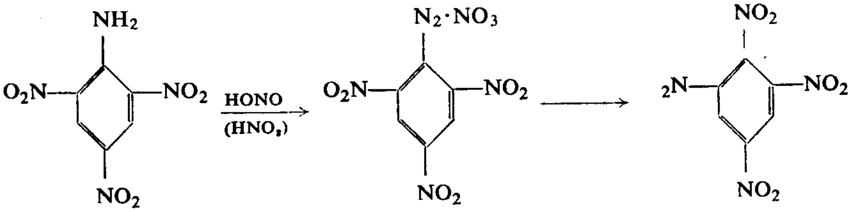


m. p. 125-126°C

(20)

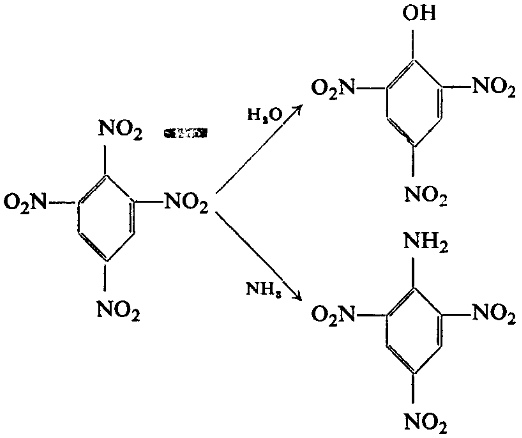
Picrylhydroxylamine is oxidized in a yield of about 60% of theory.

Holleman [58] obtained tetranitrobenzene in another way, starting from picramide:



(21)

Tetranitrobenzene is a crystalline substance, melting at 129-130°C. In the presence of moisture it is readily decomposed to form picric acid. When boiled with water it is fully converted to picric acid. It reacts with ammonia even at room temperature, forming picramide:



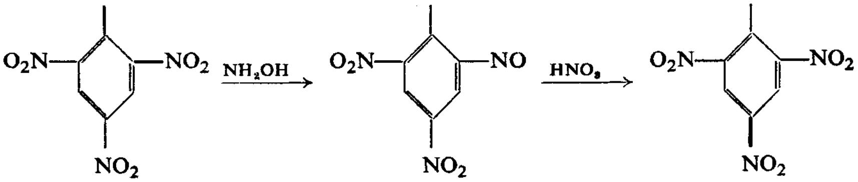
(22)

Holleman gave the following data on the explosive properties of tetranitrobenzene: sensitiveness to impact - explosion caused by a 2 kg weight falling from the height of 25 cm; expansion in the lead block = 447 cm^3.

According to other data, relative sensitiveness to impact is 67 (compared with picric acid = 100), and relative lead block test expansion amounts to 143 (picric acid = 100).

Brzozowski [59] gave additional data on the explosive properties of tetranitrobenzene. He determined the detonation rate of tetranitrobenzene, at a density of 0.7 g/cm^3 to be 5375 m/sec. At the same density, the detonation rate of trinitrobenzene is 3990 m/sec, and that of dinitrobenzene is 1795 m/sec.

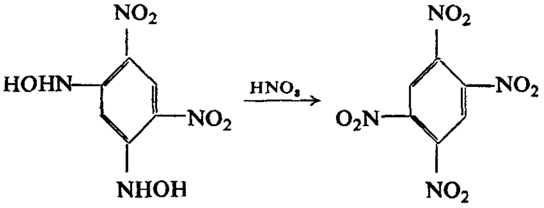
(The preparation of tetranitrobenzene was first mentioned in the literature by Nietzki and Dictschy [60] in 1900. The authors described the preparation of the new compound by the following reactions:



(23)

The product obtained melted at 116°C. However, the results have not been confirmed by the investigations of other workers. For example, Will [61] boiled 1,2-dinitroso-4,6-dinitrobenzene with nitric acid for 3 hr, but failed to observe any change in the compound. This is probably due to furoxane structure of *o*- dinitroso groups (p. 603).

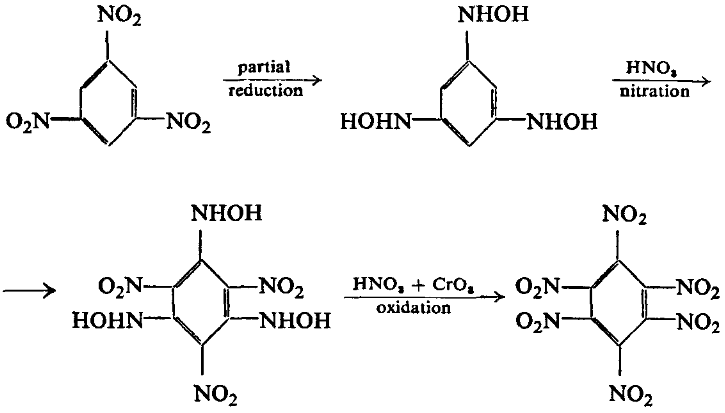
1,2,4,5-Tetranitrobenzene. This compound forms bright yellow crystals. It was prepared by Borsche and Feske [62] by the action of concentrated nitric acid on 1,3-dinitro-4,6-dihydroxylaminobenzene :



(24)

HEXANITROBENZENE

During World War II a method of synthesis of hexanitrobenzene was suggested in Germany, and the product was supposed to be manufactured on a semi-industrial scale according to the following scheme:



(25)

No details of this method are available.

Hexanitrobenzene is not stable enough for practical application, as it decomposes in the presence of moisture to form trinitrophloroglucinol.

THERMOCHEMICAL PROPERTIES OF NITRO DERIVATIVES OF BENZENE

The values of the heats of formation of benzene derivatives, given below, have been calculated from the corresponding heats of combustion (Table 44, Fig. 50).

On the basis of the above values, Garner and Abernethy [50] have calculated the corresponding heats of nitration (Table 45, Fig. 50). They have also determined the heats of crystallization, viz., for nitrobenzene they found a value of 2.78 kcal/mole, and for *m*- dinitrobenzene, 4.87 kcal/mole.

TABLE 44

HEATS OF COMBUSTION AND HEATS OF FORMATION OF BENZENE NITRO DERIVATIVES ACCORDING TO SEVERAL AUTHORS (1) -(5)

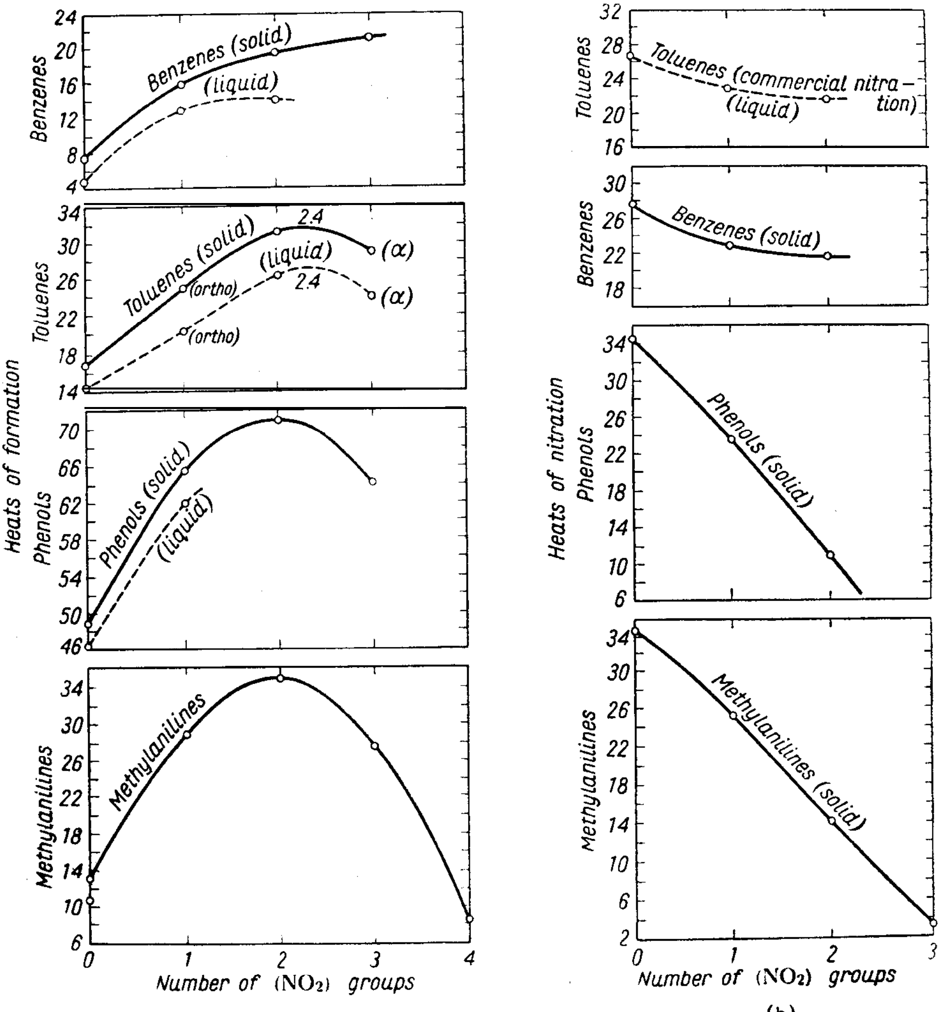
Nitro derivative of benzene	Heat of combustion (at constant volume), kcal/mole	Heat of formation (for amorphous carbon), kcal/mole
Nitrobenzene	739.9(1)	+13.1(1)
		+ 3.9(4)
		+ 6.0(5)
o- Dinitrobenzene	702.6(1)	+16.0(l)
m- Dinitrobenzene	699.4(1)	+19.2(t)
		+24.2(2)
		+ 8.6(4)
p- Dinitrobenzene	692.5(1)	+26.1(1)
sym-Trinitrobenzene	655.6(1)	+21.1(1)
	666.1(1)	+25.8(2)
		+23.0(3)
1,2,4-Trinitrobenzene	675.9(1)	+10.8(1)

(1) Gamer and Abemethy [50].
(2) Kast [3a].
(3) Berthlot and Matignon [63].
(4) Swarts [64].
(5) Chem. Techn. Reichsanstalt [65].

TABLE 45

HEATS OF NITRATION OF BENZENE AND ITS NITRO DERIVATIVES

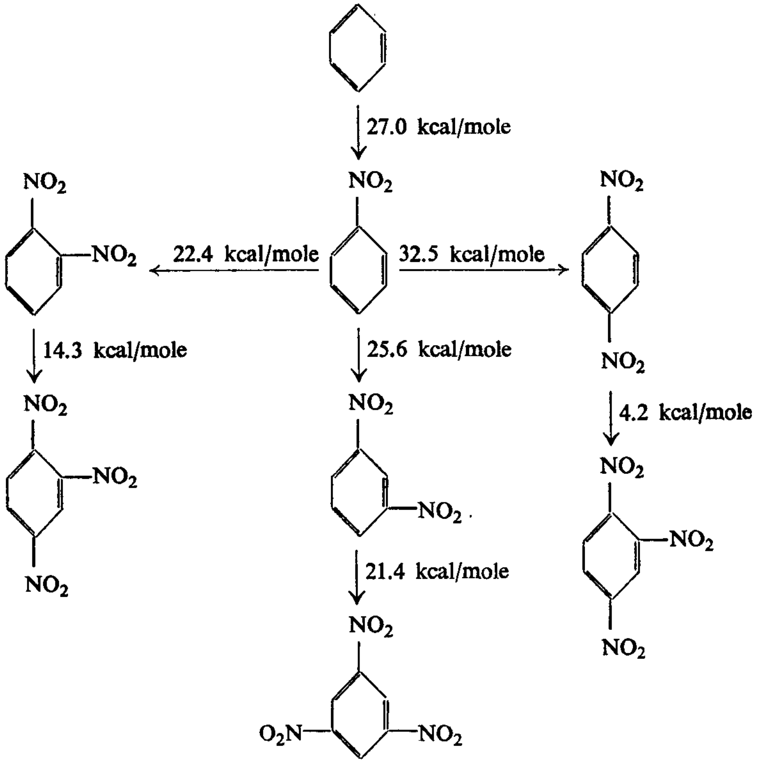
Starting product	Nitration product	Heat of reaction kcal/mole
Benzene	Nitrobenzene	+27.0
Nitrobenzene	*m*- Dinitrobenzene	+25.6
Nitrobenzene	*o*- Dinitrobenzene	+22.4
Nitrobenzene	*p*- Dinitrobenzene	+32.5
m- Dinitrobenzene	sym-Trinitrobenzene	+21.4
o- Dinitrobenzene	1,2,4-Trinitrobenzene	+14.3
p- Dinitrobenzene	1,2,4-Trinitrobenzene	+ 4.2



(a) (b)

FIG 50. Heats of formation of nitro derivatives of benzene and toluene (a) and heats of nitration of benzene and toluene (b) in kcal/mole. (Garner and Abernethy [50]).

On the basis of these data the following diagram of the thermochemistry of the nitration of benzene to trinitrobenzene may be presented:



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CHAPTER VIII

NITRO DERIVATIVES OF TOLUENE

ONE, two, or three nitro groups can be introduced by direct nitration of toluene. Tetranitrotoluene can be obtained only by indirect methods.

Of all nitro derivatives of toluene, trinitrotoluene is the most important as an explosive. It is by far the most often used high explosive among those derived from aromatic compounds. It is popular because it is simple and relatively safe to manufacture, and has high explosive power, and above all because its high chemical stability and low sensitiveness to impact and friction make it safe to handle. In addition, its toxicity is low and thus it compares favourably in this respect with the nitro derivatives of benzene.

NITRATION OF TOLUENE

Nitration of toluene has this specific feature: the presence of a methyl group greatly facilitates the nitration as compared with benzene. The reaction of introducing the first nitro group therefore proceeds very quickly. In addition to this. the methyl group is readily oxidized. Mononitration results in the oxidation of the ring and the formation of cresols (as in the case of benzene, which is oxidized to phenol). The oxidation reactions proceed especially readily under drastic conditions which introduce several nitro groups at a high temperature.

Sometimes, for example, if the nitration mixture is poor in nitric acid, tar formation may take place readily. It may also occur if an insufficient amount of the nitration mixture (calculated on HNO_3) has been used for the nitration. For this reason it is preferable to use mixtures richer in HNO_3, and to use a distinct excess of the nitrating mixture. On the other hand, both these factors (high content of HNO_3, and excess of nitrating mixture) favour oxidation processes in practice; therefore, limits are applied, i.e. nitrating mixtures should not be too rich in HNO_3, and a very slight excess (e.g. 1-2%) of it should be used.

Kostevich and Sapozhnikov [1] have carried out extensive studies on the nitration of toluene to mononitrotoluene, using nitrating mixtures of various compositions and determining the composition of mixtures leading to dinitrotoluene. All the reactions were carried out under similar conditions. The results are given in a diagram which shows the influence of the composition of the nitrating mixtures on the product obtained (Fig. 51).

As Gorst [2] points out, it is advisable to relate the nitration results to the composition of the nitrating mixture at the moment when the organic substance has ceased being nitrated. Gorst presented the corresponding results in a diagram (Fig. 52).

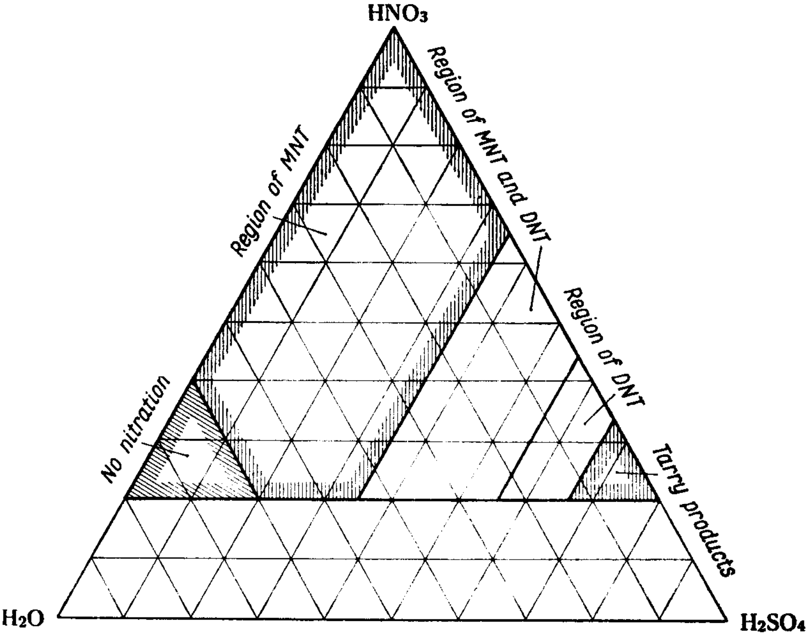


FIG. 51. Nitration of toluene with HNO_3-H_2SO_4-H_2O mixtures (Kostevich and Sapozhnikov [1]).

There is an important feature of nitrating toluene to nitrotoluenes, namely the very low solubility of toluene and nitrotoluenes in nitrating mixtures. Therefore the nitration proceeds in a two phase system and the rate of nitration depends greatly on dispersion which in turn depends on keeping the two phases efficiently stirred. Attention has previously been drawn to the importance of stirring on the yield of nitrotoluene (Fig. 25, p. 153).

Orlova [2a] gives a similar but fuller figure depicting the change of yield of nitrotoluene against the rate of stirring (Fig. 53). This relationship was established when toluene was nitrated for 30 min with an acid mixture: 11% HNO_3, 64% H_2SO_4, 25% H_2O (Φ = 69%) with a nitrating acid/toluene ratio of 3, at 30°C.

The ratio r = nitrating acid/toluene is also of importance and should be as high as economic considerations permit. The ratio r is given in Fig. 54. Here toluene was nitrated for 50 min with an acid mixture: 27% HNO_3, 55% H_2SO_3, 18% H_2O (Φ = 68%) at 30°C.

The distribution coefficient of HNO_3 between the toluene and acid layers is 0.066 at 5°C and the concentration of sulphuric acid 70% H_2SO_3. At lower acid concentrations it is practically zero. This means that on heterogeneous nitration nitric acid passes into the organic layer only in small quantities. Therefore there is practically no nitration in this layer.

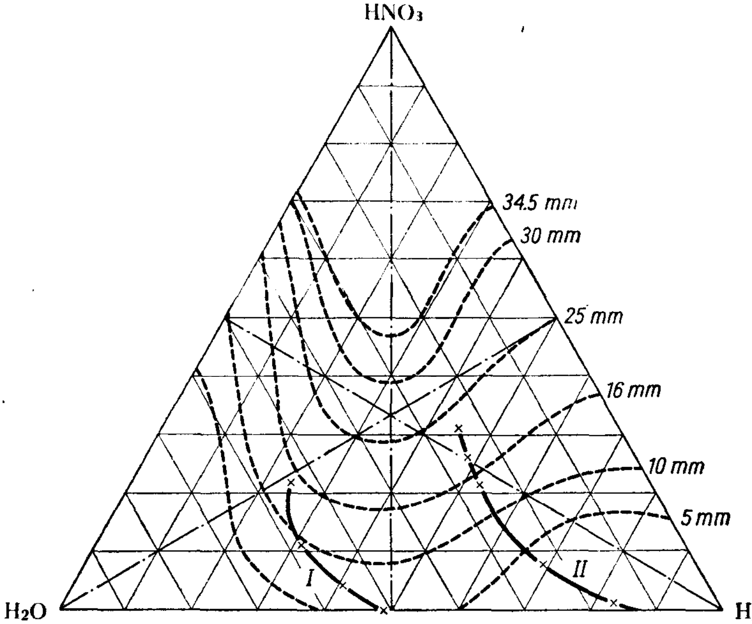


FIG. 52. Nitration of toluene with HNO_3-H_2SO_4-H_2O mixture, at temperature, of di- and trinitration 65° and 80°C respectively. Area between I and II - dinitration, to the right of II - trinitration (Gorst [2]).

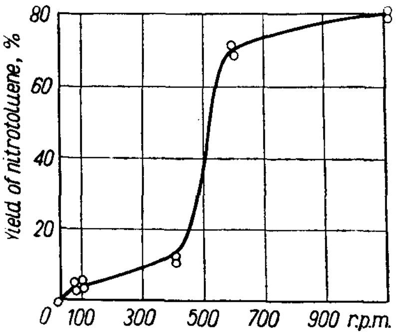


FIG. 53. Influence of the rate of stirring on the rate of nitration of toluene (Orlova [2a]).

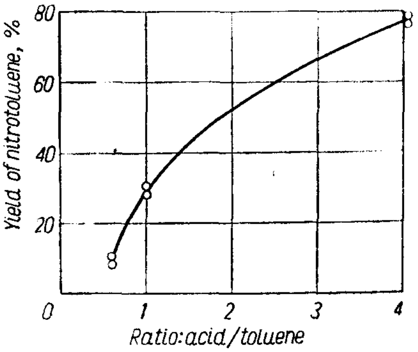


FIG. 54. Change of yield of MNT with the ratio acid/toluene (Orlova [2a]).

The reaction most probably occurs on the surface dividing the two reacting layers. The rate of nitration is therefore determined by the concentration of reactants on the surface. This in turn is determined by the rate of diffusion of two phases.

The rate of nitration is plotted against temperature of nitration in Fig. 55 (nitration mixture with Φ = 70.9%, r = 7.9, time 30 min) and the rate of nitration against the factor Φ, - in Fig. 56. Here two curves are given: one for a homogeneous system (nitrating mixture of low H_2SO_4 and HNO_3 content) and another one for a heterogeneous system (the usual nitrating mixture with a high H_2SO_4 content). The change in the rate of nitration with Φ is particularly significant in the homogeneous system.

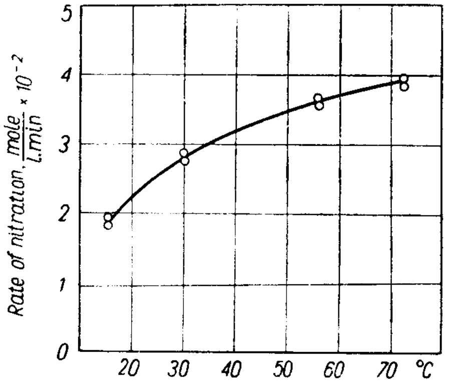


FIG. 55. change of the rate of nitration of toluene with temperature (Orlova [2a]).

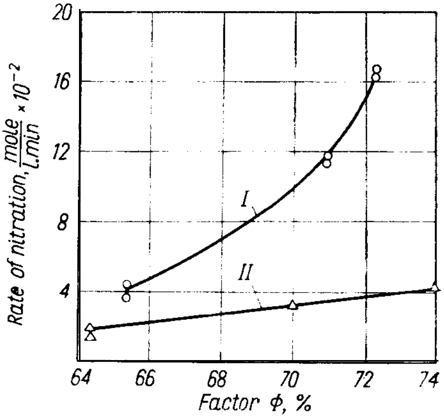
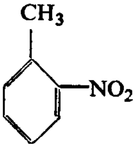
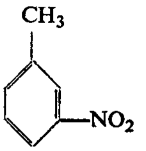


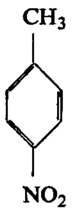
FIG. 56. Influence of the factor @ (nitrating activity) on the rate of nitration of toluene: I - in a homogeneous system, II - in a heterogeneous system (Orlova [2a]).

MONONITROTOLUENES

Three isomers of mononitrotoluene, *ortho-, meta-, and para-,* are known.







PHYSICAL PROPERTIES

The ortho-isomer can exist in the α -form, melting at -10.5°C, and in the β -form, melting at -4.1°C. The melting point of the meta-isomer is 16°C, and that of the *para-* isomer 52°C. The boiling points of the *ortho-, meta-,* and *para-* isomers are 222, 230 and 238°C respectively.

All three isomers are pale yellow substances, with the smell characteristic of mononitro compounds. They are soluble in most organic solvents. The solubility of technical MNT in sulphuric acid is shown in Table 46. Due to the presence of a methyl group, the isomers are much less toxic than nitrobenzene (p. 260).

TABLE 46

SOLUBILITY OF TECHNICAL MNT (MIXTURE OF ISOMERS) IN SULPHURIC ACID (GORST [2])

Concentration of sulphuric acid % H_2SO_4	Solubility	
	at 20°C	at 50°C
50	0.04	0.08
75	0.50	0.81
80	1.56	2.09
83	2.73	12.28
88	19.50	20.14
90	33.20	33.90

THERMOCHEMICAL PROPERTIES

Garner and Abernethy [3] give the following thermochemical data for the isomers of mononitrotoluene :

TABLE 47

HEATS OF COMBUSTION AND HEATS OFFORMATION OF MONONITROTOLUENE ISOMERS

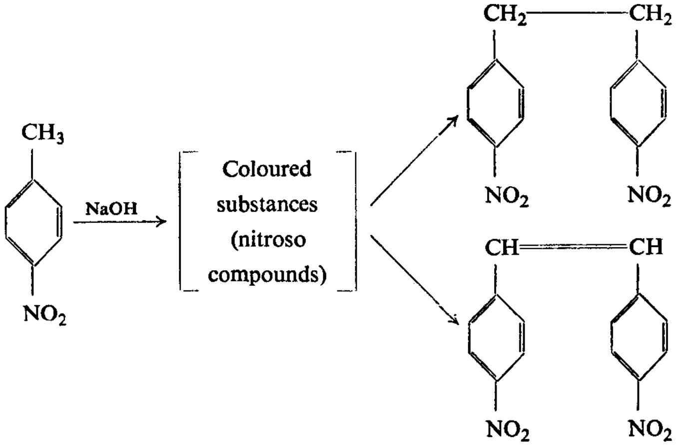
Isomer	Heat of combustion (at constant volume) kcal/mole	Heat of formation kcal/mole
o- Nitrotoluene (liquid)	897.0	+ 2.0
m- Nitrotoluene	892.9	+ 6.1
p- Nitrotoluene	888.6	+10.4

From these data Gamer and Abemethy have calculated the heats of nitration of toluene (Fig. 50 p. 261):

ortho nitration	+25.3 kcal/mole
meta nitration	+29.4 kcal/mole
para nitration	+33.7 kcal/mole

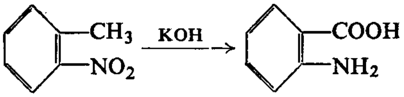
CHEMICAL PROPERTIES

Nitrotoluene is unaffected by acids but oxidized by strong alkalis (e.g. NaOH), dibenzyl and stilbene derivatives being formed (Bender and Schultz [4], Fischer and Hepp [5]). Intensely coloured substances appear transiently, to which the nitroso structure is ascribed (Fischer and Hepp [5], Green and Crossland [6]). They are easily oxidized by atmospheric oxygen to give nitro derivatives of dibenzyl and stilbene:



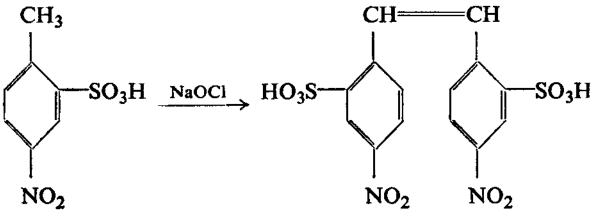
(1)

On melting with anhydrous KOH the oxidation of the methyl group takes place. with simultaneous reduction of the nitro group:



(2)

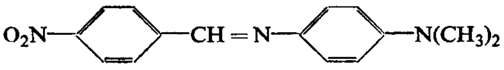
By treating a sulpho derivative of *p*- nitrotoluene with NaOCl the corresponding nitrostilbenesulphonic acid is obtained:



(3)

This is a valuable intermediate in the manufacture of direct dyes.

The methyl group in nitrotoluene is activated by the nitro group and can react, for example, with *p*- nitrosodimethylaniline to form an anil:



TOXICITY

Nitrotoluenes are considered to be toxic substances, though their toxicity is considerably lower than that of nitrobenzene. It has been suggested that this should be ascribed to the ease with which nitrotoluene is oxidized in the human body to nitrobenzoic acid, which is only slightly toxic.

PREPARATION OF MONONITROTOLUENES

In the nitration of toluene all three isomers are formed, the *o-* isomer being the predominant product. The proportion of isomers formed depends to some extent on the nitration temperature.

It was Pictet [7] who first observed, in 1893, that when nitrating toluene with a mixture of nitric and sulphuric acids at -5°C, relatively more *p-* isomer could be obtained than at 0°C.

Hollernan and Arend [8] observed the following relationship between the composition of the product of mononitration of toluene and the temperature (Table 48).

TABLE 48

RELATIONSHIP BETWEEN THE COMPOSITION OF THE MONONITRATION PRODUCT OF TOLUENE AND THE TEMPERATURE

Temperature °C	Composition of the product		
	o- isomer content, %	*p-* isomer	*m-* isomer
-30	55.6	41.7	2.7
0	56.0	40.9	3.1
+30	56.9	39.9	3.2
+60	57.5	38.5	4.0

W. W. Jones and Russel [9] determined experimentally the rate of nitration of toluene at 0°C and 30°C. Then they calculated the relative values of the A coefficient in the well known Arrhenius formula applying the conclusions of Bradfield and B. Jones (p. 65) derived from the formula:

$$A_o=2.90\ A_m$$
$$A_o=2.70\ A_m$$

From this they calculated the compositions of the products obtained by mononitration of toluene at -30°C and +60°C, as well as the differences in the activation energies :

$$E_m-E_o=917\ \text{cal/mole/degree}$$
$$E_m-E_p=1103\ \text{cal/mole/degree}$$

From these data the following rule can be derived: a lower nitration temperature causes an increase of the *p-* nitrotoluene content in the product at the cost of the *o-* and *m-* isomers.

Orlova [2a] gave similar figures:

at 30°C the proportion of *m-* nitrotoluene was 4.6%
at 55°C , ’ ’ ’ ’ 5.3%
at 70°C , ’ ’ ’ ’ 7.5%

The composition of the nitrating mixture also has an influence on the composition of mononitrotoluene. The proportion of *m-* nitrotoluene is reduced by an increase of the factor Φ. Figure 57 gives the proportion of *m*- nitrotoluene when acids with 10% HNO_3 and various concentrations of H_2SO_4 were used at 55°C for a period of 100 min. The factor varied from 46% to 82.7%.

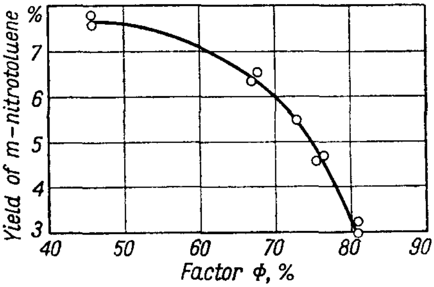
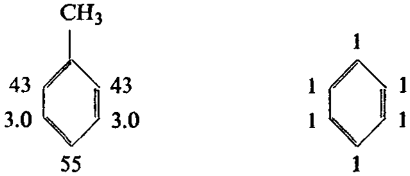


FIG. 57. Influence of the factor Φ (nitrating activity) on the yield of *m*- nitrotoluene (Orlova [2a]).

According to Ingold [9a], the relative rate of nitration on each nuclear position of toluene can be illustrated by the diagram where the rate of attack on one nuclear position of benzene has been made the unit:



R. M. Roberts, Browder, and Kobe [10] carried out a number of experiments using isotope dilution analysis to determine the proportion of *m*- nitrotoluene formed in the course of nitration of toluene.

They nitrated radioactive toluene-l-^{14}C with a mixture of nitric and sulphuric acid at 0°, 30°, 45° and 60°C. After nitration the whole was diluted, with water and steam distilled. Thus mononitro-products were separated from unnitrated toluene and dinitro products. The weighted sample of isomeric mononitrotoluene was diluted with a known quantity of non-radioactive *m*- nitrotoluene and the mixture was distilled through an efficient micro-fractionating column in order to recover a pure sample of *m*- nitrotoluene. The *m*- nitrotoluene was oxidized by dichromate-sulphuric acid mixture to *m*- nitrobenzoic acid and this material was radio-assayed. The proportion of *m*- nitrotoluene in the mixed nitrotoluenes was calculated from the formula

$$\%\ m\text{- nitrotoluene} = \frac{100x}{y(a/b-1)}$$

where

x is the weight of *m*- nitrotoluene diluent,

y is the weight of mixed nitrotoluenes diluted,

a is the molar radioactivity of the toluene-1-^{14}C nitrated,

b is the molar radioactivity of the *m*- nitrobenzoic acid.

The results from nitration at four different temperatures are given in Table 49.

TABLE 49

Temperature °C	Yield of mixed nitrotoluenes	% of *m*- nitrotoluene in mixed nitrotoluene
0	100	2.08
30	92	3.44
45	84	4.18
60		4.70

Noelting and Forel [11] found that the content of *p*- nitrotoluene increased gradually with increase in the HNO_3 content of the nitrating acid. Thus, when nitrating toluene with a mixture of nitric and sulphuric acids, the authors obtained 60% of the *p*- isomer but if nitric acid alone was used, 66% of *p*- nitrotoluene was obtained.

The effect of temperature and of the composition of the nitrating mixture on the quantity of *m*- nitrotoluene formed has been the subject of numerous studies. The results are shown in Table 50.

The order of introducing the reagents may also affect the composition of the nitration product. For example, if the toluene is added to the acid, then the first portions of toluene come into contact with a large excess of acid, and the nitration process may proceed beyond mononitration resulting in a mixture of di- and mononitrotoluene. If the amount of HNO_3 used has been calculated accurately, the last portions of toluene may be left unnitrated and the resultant product may not be uniform. If, on the contrary, the acid is added to the toluene, an excess of acid cannot occur, since each portion added reacts with the toluene very quickly.

TABLE 50

INFLUENCE OF TEMPERATURE AND COMPOSITION OF NITRATING MIXTURES ON *m*- NITROTOLUENE FORMATION

Nitration temperature °C	*m*- Nitrotoluene content, %					
	(1)	(2a)	(2b)	(2c)	(3)	(4)
-30	3.5	-	-	-	-	2.97
0	3.9	2.5	4.5	3.3	3.7	5.68
20	-	4.3	4.5	3.9	-	-
30	4.4	-	-	-	4.4	4.39
40	-	-	4.2	--	-	-
50			4.3			-
60	5.1	-	-	-	-	4.90

(1) Hollemart, Vermeulen, de Mooy [12].

(2) Gibson. Duckham, Fairbairn [13]: (a) -nitration with 94% nitric acid; (b) - nitration with a mixture: HNO_3-23.8%. H_2SO_4-58.7%. H_2O-17.5%; (c)-nitration with a mixture: HNO_3-13.7%. H_2SO_4-64.4%. H_2O--21.9%.

(3) Ingold. Lapwotth, Rothstein and Ward [14] -nitration in acetic anhydride and nitromethane.

(4) W. W. Jones and Ruse1 [9] -nitration with a mixture: HNO_3-5.35%, HNO_2-1.75%. H_2SO_4-71.4%. H_2O-21.5%.

For TNT manufacture the presence of *m*- nitrotoluene in mononitrotoluene is naturally undesirable, as it is a source of unsymmetrical trinitrotoluenes.

Therefore, it would be preferable to apply a nitration method in which the *m*- isomer would not be formed at all, or only in an insignificant quantity. But as Table 50 indicates, this is impossible to achieve by nitrating with a mixture of nitric and sulphuric acids.

The fact that in the nitration of toluene with a solution of nitric acid in acetic anhydride, a mixture of 88% of *o*- and 12% of *p*- nitrotoluene, i.e. a mixture free from *m*- nitrotoluene, can been obtained, has been mentioned in the literature only once (Pictet and Khotinsky [15]).

T. Urbanski and his co-workers [16] recently confirmed this observation and reported the following nitration conditions:

composition of the nitrating mixture	68% of acetic anhydride 32% of nitric acid
excess of nitrating mixture (calculated on HNO_3)	10%
temperature of nitration	10°C
nitration period	2 hr

The mixture of *o*- and *p*- nitrotoluene they obtained was free from the *m*- isomer. The authors used it for further nitration, and found that the resulting trinitrotoluene was of much higher purity than that produced from mononitrotoluene according to the conventional industrial method.

An interesting method of reducing the proportion of *m*- nitrotoluene was developed by Orlova [2a]. It consists in adding sodium nitrite to the nitrating mixture. The results of these experiments are given in Table 51.

The nitration was carried out using acid with 10% HNO_3, for 100 min at 55°C.

TABLE 51

% $NaNO_2$	0	1.5	3.0	4.5	5.9	8.6	11.0
Proportion of *m*- nitrotoluene	5.4	4.3	4.1	3.5	2.8	2.1	2.6
Setting point of TNT, °C	78.0	78.6	78.75	78.75	78.93	78.2	77.9

Recently Kobe and Lakemeyer [17] drew attention to the fact that nitrating mixtures used for mononitration of toluene prepared spent acid from trinitration contain 14-17 wt. % of nitrosylsulphuric acid. They investigated the influence of nitrosylsulphuric acid, $SO_2(OH)ONO$, on the rate of mononitration of toluene. The rate at 35°C is at a maximum at ca. 4.0 mole % of nitrosylsulphuric acid.

More dilute nitric acid, when used for nitration, favours side reactions, primarily oxidation reactions, yielding benzoic acid. According to Konovalov [18], if a 70% nitric acid (sp. gr. 1.42) is used for the nitration of toluene, nothing but benzoic acid is formed.

According to the same author, nitrating with a more dilute nitric acid (e.g. 32%, sp. gr. 1.32) at 105°C leads to the formation of phenylnitromethane, i.e. nitration takes place in the side chain.

When nitrating toluene with nitrogen dioxide in the liquid or gaseous phase, nitrotoluene along with phenylnitromethane is obtained. As Topchiyev [19] reported. the following yields expressed as per cent theoretical, were obtained, using a large excess of N_2O_4 (200 g for 40 g of toluene) (Table 52):

TABLE 52

At temperature °C	Phenylnitromethane %	Nitrotoluene %	Unreacted toluene %
14-15	9	46.2	**40**
105-110	5	17	3

INDUSTRIAL METHODS OF NITRATION OF TOLUENE

Various methods of preparing nitrotoluenes for subsequent nitration to TNT are described below (pp. 348, 357) where methods of manufacturing TNT are discussed.

Here only those methods are reviewed which are used industrially for preparing the pure isomers : *o*-, ***m*-,** and *p*- nitrotoluene.

In industrial practice nitrating mixtures of the composition: 28-62% HNO_3, 56-21% H_2SO_4, 5-20% H_2O are used for the nitration of toluene.

Usually more of the mixture is used for nitration than theory demands, e.g. a 1-5% excess is applied so that the ratio of HNO_3 used to HNO_3 calculated varies from 1.01 to 1.05. An excess of the nitrating mixture not only favours complete nitration, but also inhibits the formation of undefined, dark coloured tarry by-products, which are readily formed if an insufficient amount of nitrating acid is used. Toluene may be added to the acid or vice versa.

The latter operation (adding acid to toluene) favours the formation of tarry products (see p. 266) but at the same time the formation of higher nitrated products is avoided, as the toluene is never in contact with an excess of acid.

A temperature within the range 25° to 40°C is maintained during mixing. Then it is raised to 60°C and maintained thus for 30 min to 1 hr. After cooling the reaction mass to 25-30°C, nitrotoluene is separated from the waste acid in a separator, the nitrotoluene being the upper layer.

A commonly used method of obtaining TNT is the direct nitrating of a mixture of the three isomers of nitrotoluene. Details are given later (Chapter IX) in the description of the manufacture of DNT and TNT. The purification of TNT from unsymmetrical derivatives of *m*- nitrotoluene consists as a rule in the sulphitation of di- or, more often, tri-nitrotoluenes or in crystallization of the trinitro-products.

However, in factories producing dye intermediates, the isomers of nitrotoluene are separated individually, as all three are raw materials for the manufacture of the corresponding toluidines and tolidines, which are valuable dyestuffs intermediates.

Recently, as the disposal of large volumes of toxic waste waters from the purification of TNT by sulphitation has. become a problem (p. 390), new ways are being sought for the manufacture of TNT free from the unsymmetrical isomers. Apart from the possibility, mentioned above, of the utilization of nitrotoluene obtained by nitrating toluene with a mixture of acetic anhydride and nitric acid, factories TNT are now tending to separate nitrotoluene isomers by methods similar to those applied in the manufacture of dyestuffs intermediates.

This separation may be accomplished in two ways:

(1) By fractional distillation (under reduced pressure, if possible).

(2) By freezing. When the mixture has been cooled to about -12°C, *p*- nitrotoluene crystallizes out, while the *o*- and *m*- isomers remain liquid. Further cooling results in the crystallization of *o*- nitrotoluene, while the *m*- isomer remains liquid, forming an eutectic with the *o*- isomer.

The Griesheim (I. G. Farbenindustrie) method, described below, may be cited as an example of an industrial method of preparing and separating nitrotoluenes.

3000 1. of toluene are run into a nitrator of 12 m^3 capacity. Mixed acid of composition :

HNO_3	28-32%
H_2SO_4	52-56%
H_2O	20-12%

is added in over a period of 8 hr at a temperature of 25°C. The amount of acid is 99% of the theoretical, calculated on the quantity of HNO_3 required. After adding all the mixed acid, the temperature is raised to 35-40°C and the nitrator contents are stirred for 2 hr. A sample taken from the nitrator should have a density of 1.155-1.160 g/cm^3.

The stirrer is then stopped and the contents allowed to settle for 2 hr. The waste acid (the lower layer) containing less than 0.2% HNO_3(sp. gr. = 1.60-1.61) is transferred to a storage vessel.

The oil is run into a washing tank where it is mixed with 100 1. of a 10% NaOH solution. The aqueous alkaline solution becomes dark red owing to the presence of sodium salts of mono- and di-nitrocresols.

The aqueous layer is separated and the oil washed with water until alkali free when tested with phenolphthalein. The oil is steamed to remove un-nitrated toluene and aliphatic compounds. Distillation is continued until the oil coming over sinks in water. The distillate is collected and fractionated once or twice a year. It contains ca. 20% of nitrotoluenes.

The steamed oil is dried in a drier of 25 m^3 capacity under reduced pressure (40 mm Hg) until a sample dissolves completely in an equal volume of 95% sulphuric acid.

To obtain 100 kg of nitrotoluene require

toluene	69 kg
mixed acid	150 kg
sodium hydroxide solution (10%)	2.2 kg
electricity	22 kWh
steam	930 kg

The washed and dried crude product should have a setting point not lower than 15.1%.

At Griesheim a continuous method of nitrating toluene to nitrotoluenes was also used. The nitration unit consisted of two nitrators connected by their bottom outlets, fed with mixed acid of the same composition as in the batch process.

The temperature in the two nitrators was:

I	25°C
II	45°C

The product and spent acid overflowed into a lead-lined separating tank. The nitration product contained l-2% of dinitrotoluene.

SEPARATION OF ISOMERS

The composition of the mononitrotoluenes prepared at Griesheim is:

62-63%	*ortho*
33-34%	*para*
3-4%	*meta*

Distillation of crude nitrotoluene. The still kettle is of 60 m^3 capacity, heated with 18.5 atm steam. The column has 40 plates, 8 m height, 2 m diameter.

55,000 1. of the crude, steam distilled and dried nitrotoluene are sucked into the still while heating up. Distillation begins under reduced pressure (15 mm Hg on the receiver and 120 mm Hg in the kettle) at a still temperature of 160°C. First runnings (ca. 200 1.) have a setting point lower than -10°C and contain nitrobenzene. As soon as the setting point reaches -10°C the second fraction (mainly *o*- nitrotoluene) is collected at a still base temperature of 180°C. The bulk of this faction has a setting point of -9.2°C.

When the contents of the still have a setting point of 40°C, the column is emptied into the base and distillation is continued without the column, at the still base temperature 185°C. This third fraction (mainly p-nitrotoluene) has a setting point of 40°C. The residue is tar.

Further purification is carried out by crystallization.

Crystallization of *p*- nitrotoluene. 8000 1. of crude molten *p*- nitrotoluene are charged into a tubular crystallizer, cooled to 39-40°C and this temperature is maintained for 24 hr. Then the whole is cooled to 18°C for 24 hr and the crystallizer is opened. The mother liquor is collected and the crystalline contents heated slowly to 50°C. The oil that was drawn off is collected separately and when it reaches a setting point of 49°C, the pure p-nitrotoluene (s.p. 51°C) remaining in the crystallizer is melted out, dried and flaked. The mother liquor is distilled, and the oil collected during the heating up process is put back into the crystallizer.

Distillation of the mother liquor. 10,000 kg of *p*- nitrotoluene mother liquor are sucked into a still of 10 m^3 capacity with a column of 40 plates, of 8 m height and 1 m diameter. Distillation conditions are the same as in the distillation of crude nitrotoluene.

The first fraction (ca. 1500 kg) consists of crude *o*- nitrotoluene (70-80% *o*- and 20-30% *m*- isomer). The distillate has a setting point of ca. - 15°C. It drops to -20°C and at this temperature the collection of a second fraction (ca. 4000 kg) starts. The setting point continues to fall to ca. -30°C and then rises to +5°C. The distillate contains *ca*. 50% *meta*-, the rest being mainly *ortho*- isomer.

When the setting point of still contents reaches 40°C the third fraction is distilled off without the column. This is crude *p*- nitrotoluene (4500 kg). It is purified by crystallization as above.

Pure *m*- nitrotoluene is isolated by further distillation.

Continuous vacuum distillation of mononitrotoluene

The following modem continuous distillation unit is described by Vorontsov [20].

A neutralized, washed and dried crude mixture of nitrotoluenes passes from container (2) into the rectifying column (4), where *o*- nitrotoluene is distilled off. The column is 12 m high and 0.6 m diameter and is provided with boiler (3) still-head (5) and condenser (6). Before entering the column, the crude material passes through the lower part of the still-head, the expansion vessel (20) and a flowmeter which regulates the rate of supply of the liquid.

Steam supplied for heating the column (through a coil) has a pressure of 18-20 atm. It is fed through the boiler (3) and regulating valve (22). A constant level in the boiler is maintained by means of regulator (25). The vapours are partially condensed in the still-head (5), cooled by water flowing from (1). The same water is used to cool the condensers of both columns. The flow of water is regulated by means of valves (29) and (27).

The condensed distillate (pure *o*- nitrotoluene) flows partly back to the column but mostly down through (19) and the pump (14) transfers it into a storage tank. The vapours passing from the still-head (also o-nitrotoluene) are condensed in (6). From here they pass through (18) and pump (13) into a storage tank. If the condensed distillate is not of sufficient purity, it is sent back to the container (2) and subjected to a second distillation.

A mixture of *m*- and *p*- nitrotoluene which leaves the lower part of the column passes through the pump (15) into a second column (8). A part of it returns to column (4) (to avoid a fall of the level there in it). If, due to any disturbance of the process, the product flowing from the lower part of the column contains *o*- nitrotoluene, it is fed to (2) through pump (15) and rectified again.

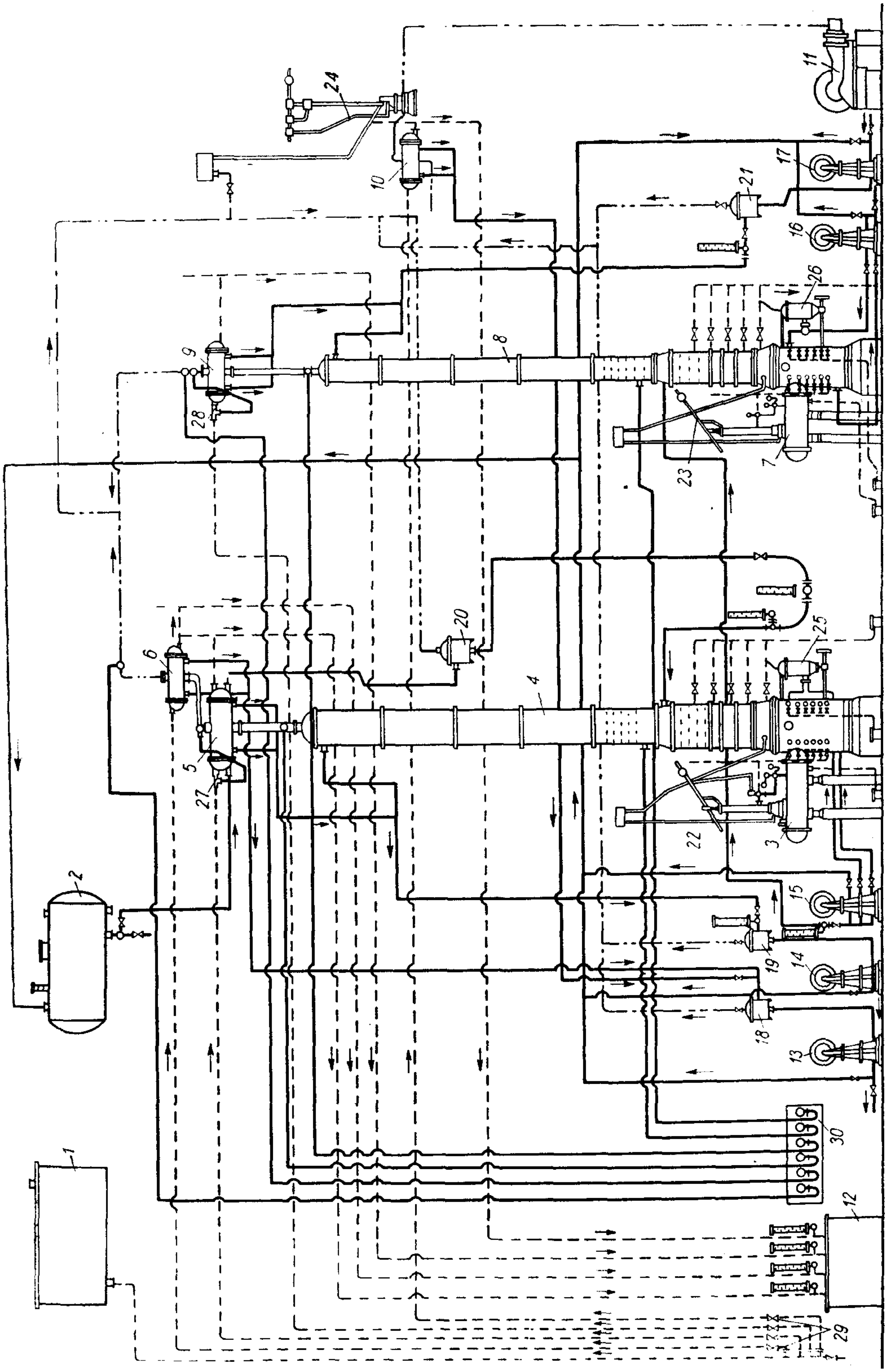


FIG. 58. Continuous distillation of nitrotoluene (Vorontsov 20])

Column (8) is 12 m high and 0.35 m in diameter. Here *m*- nitrotoluene is distilled off. *p*- Isomer flows to the lower part of the column. The column is heated through valve (23) and boiler (7) by means of a coil. The vapours leaving the column are condensed in (9) and cooled with water passing through (28).

Most of the condensed vapour returns to the column, and the rest flows down through (21) via a flowmeter and the pump (17) to a storage tank. Samples are taken through the valves near the pump and the setting point of the product is determined.

p- Nitrotoluene which falls into the lower part of the second column is transferred through the pump (16) to a crystallizer. Some of the *p*- nitrotoluene returns through (26) to the column if the level in the column is too low. Thermometers (30) serve to control the process.

TABLE 53

SPECIFICATION FOR *O*- NITROTOLUENE (AFTER U.S.S.R. DATA, GORST [2])

	I grade	II grade
Appearance	Clear oily liquid of a light yellow to light brown colour	
Boiling range not less than 90 vol. % at 760 mm Hg pressure should distil between	218-223°C	217-223.5°C
Dinitrotoluene	none	
Hydrocarbons	below 0.1%	below 0.1%
p- Nitrotoluene	below 1%	below 2%
Moisture	below 0.1%	below 0.1%

TABLE 54

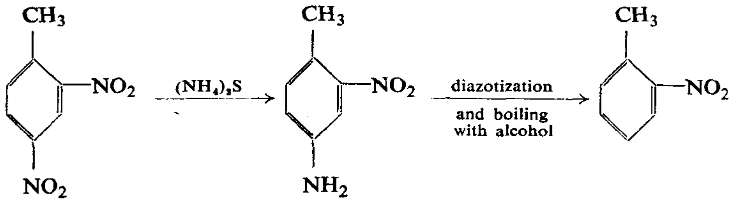
SPECIFICATION FOR P-NITROTOLUENE (AFTER U.S.S.R. DATA, GORST [2])

	I grade	II grade
Appearance	light grey to light yellow crystals	
Freezing point, not below	50°C	49°C
Dinitrotoluene	none	
Hydrocarbons	none	
Moisture	below 1%	
Toluene insoluble substances	below 0.1%	

Distillation in both columns occurs in the upper parts under a reduced pressure of 10 mm Hg. The vacuum pipe is connected with condensers (6) and (9) and expansion vessels (18) (19) (20) (21) and with the regulatingvalve (24). The vapours which penetrate into the vacuum pipe, are condensed in condenser (10) and flow down through (18). All pipes for *m*- and *p*- nitrotoluene should be insulated to avoid solidification of the products.

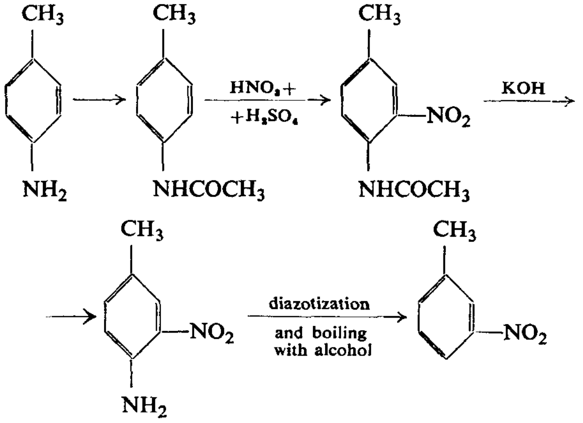
Preparation of pure isomers. Since the isolation of high purity *o*- and *m*- isomers from a mixture obtained by direct nitration is rather difficult, the very pure substances have been obtained by indirect methods.

o- Nitrotoluene was obtained by Beilstein and Kuhlberg [21] from 2,4-dinitrotoluene :



(4)

m- Nitrotoluene has also been obtained from *p-* toluidine by the same workers:

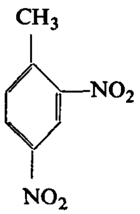


(5)

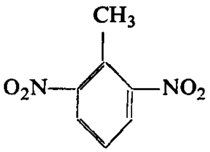
The fairly pure *p-* isomer may be isolated from a mixture of nitrotoluenes by freezing and repeated crystallization.

DINITROTOLUENES

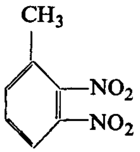
Six isomeric dinitro derivatives of toluene are known:



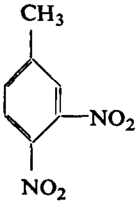
2,4- m.p. 71°C



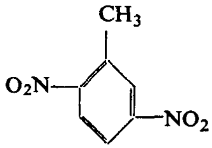
2,6- m.p. 65.5°C



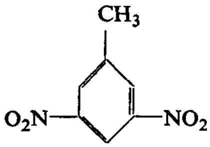
2,3- m.p. 63°C



3,4- m.p. 60°C



3,6-(or 2,5-) m.p. 52.5°C



3,5- m.p. 91°C

PHYSICAL PROPERTIES

All the isomers are pale yellow, crystalline products. The composition of the eutectic formed by 2,4-dinitrotoluene with α– trinitrotoluene is given in Table 66 (p. 295).

The solubility of technical DNT (the mixture of isomers) in sulphuric acid was given by Orlova [2a] (Table 55).

TABLE 55

SOLUBILITY OF TECHNICAL DNT IN SULPHURIC ACID

Concentration % H_2SO_4	Solubility: g of DNT in 100 g of the acid at temperatures °C					
	20	40	50	70	100	120
80.0	1.2	-	2.5	3.8		
83.6	-	3.6	4.7	6.3	6.4	6.5
88.7	6.1	10.0	12.8			17.4
90.0	8.5	-	16.8	20.0	-	-
93.0	-	26.4	33.8	58.3	82.4	66.6
99.8	-	72.6	14.4	1121	1360	-

THERMOCHEMICAL PROPERTIES

According to Bichel [22] the heat of formation of 2,4-dinitrotoluene is 7.7 kcal/mole; Koehler [23] has reported it to be 5.9 kcal/mole.

Garner and Abernethy [3] give the following values for the heats of combustion and heats of formation of the isomers (see also Fig. 50, p. 261).

The same authors have calculated the heat of nitration of mono- to di-nitrotoluene.

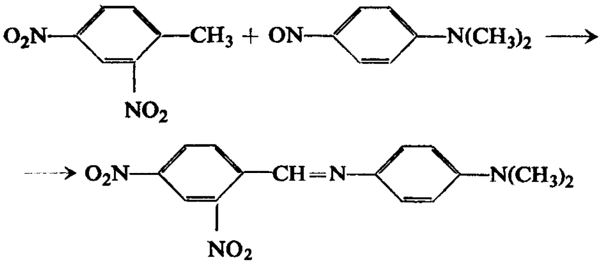
TABLB 56

HEATS OF COMBUSTION AND HEATS OF FORMATION OF THE DINITROTOLUENE ISOMERS

Dinitrotoluene isomer	Heat of combustion (at constant volume) k&/mole	Heat of formation kcal/mole
2,4-Dinitrotoluene	853.7	+31.3
2,6-Dinitrotoluene	855.2	+29.6
2.3-Dinitrotoluene	860.5	+24.3
2,5-Dinitrotoluene	856.1	+28.7
3,4-Dinitrotoluene	860.8	+24.0
3,5-Dinitrotoluene	853.9	+30.9

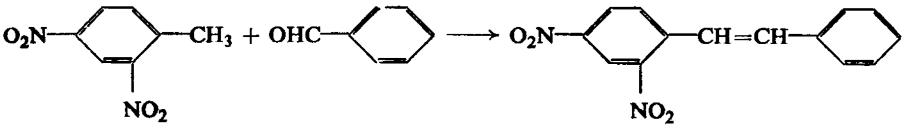
CHEMICAL PROPERTIES

The methyl group in dinitrotoluenes is particularly reactive due to the presence of two nitro groups. Thus it readily undergoes such reactions as for example with *p*- nitrosodimethylaniline to form an anil:



(6)

or with benzaldehyde, in the presence of piperidine, to form a stilbene derivative:



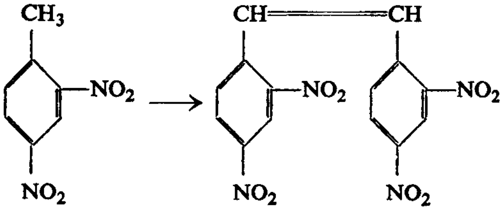
(7)

TABLE 51

HEAT OF NITRATION OF MONO- TO DINITROTOLUENE (CF. FIG. 50)

Starting product	Nitration product	Reaction heat kcal/mole
o- Nitrotoluene	2.4-Dinitrotoluene	+29.7
o- Nitrotoluene	2,6-Dinitrotoluene	+28.2
p- Nitrotoluene	2,4-Dinitrotoluene	+21.3
m- Nitrotoluene	2,3-Dinitrotoluene	+18.8
m- Nitrotoluene	3,4-Dinitrotoluene	+18.5
m- Nitrotoluene	3,6-Dinitrotoluene	+23.2
m- Nitrotoluene	3,5-Dinitrotoluene	+25.4

Under the influence of alkalis it forms a stilbene derivative, especially easily in the presence of oxidizing agents (air oxygen, NaOCl):



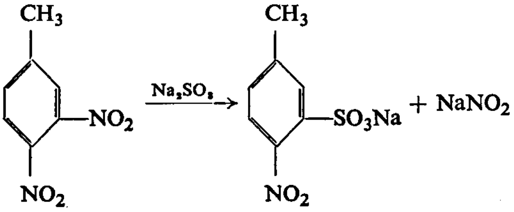
(8)

The ease of these reactions can be explained in terms of the hyperconjugation of toluene accentuated by the influence of the nitro groups.

With lead in the presence of dilute nitric acid, 2,4-dinitrotoluene forms inflammable organo-metallic products (for further details see p. 306, Kovache and Thibon’s work).

An acetone solution of 2,4-dinitrotoluene treated with a 10 per cent solution of KOH gives a blue colour (the Janovsky reaction), unlike the 2,6-isomer, which gives no colour at all.

Dinitrotoluenes derived from *m*- nitrotoluene react with sodium sulphite to form sodium salts of nitrosulphonic acid, e.g.:



(9)

The reaction occurs with more difficulty than the corresponding one with the unsymmetrical trinitrotoluenes and requires a higher temperature or more concentrated solutions of sodium sulphite. The reaction of “sulphitation” of dinitrotoluene may be used in practice for removing m-nitrotoluene derivatives from mixtures of dinitro-isomers. Thus the sulphitation of trinitrotoluene becomes unnecessary.

Dinitrotoluenes are able to form molecular compounds with condensed ring aromatic hydrocarbons and also with amines. According to Kremann [24], 3,5-dinitrotoluene is the most ready to form such compounds, while the others can be ranged according to their decreasing ability to do so in the following order: 2,4-, 2,6-, 3,4-.

Here is a list of some of the molecular compounds obtained by Kremann:

	Dinitrotoluene isomer	Molecular proportion	m. p., °C
with: naphthalene	2.4-	1:1	59
naphthalene	3,5-	1:1	63.2
acenaphthene	2,4-	1:1	61
acenaphthene	3,5-	1:1	94
aniline	3,5-	1:1	46.5
p- toluidine	3,5-	1:1	non uniform
β -naphthylamine	3,5-	1:1	53
α -naphthylamine	2,4-	1:1	107.8
α -naphthylamine	3,5-	1:1	62

Aniline, *p*- toluidine and β -naphthylamine do not combine with 2,4-dinitrotoluene.

TOXICITY

Dinitrotoluene is regarded as a poisonous substance, but in a less degree than dinitrobenzene. If has been suggested that poisoning by dinitrotoluene should be ascribed to the impurities present in it, mostly dinitrobenzene.

PREPARATION OF DINITROTOLUENES

The principal reaction products in the nitration of toluene are the isomers: 2,4- formed from *o*- and *p*- nitrotoluenes, and 2,6- formed from *o*- nitrotoluene. From *m*- nitrotoluene the 2.3-, 3,4- and 3,6-isomers are formed. The possibility of the formation of the 3,5-isomer in the direct nitration of *m*- nitrotoluene has not been definitely proved.

Dinitrotoluene (2,4-) was first obtained by Beilstein and Kuhlberg [21] in 1870. However, it may be that "dinitrobenzene", m.p. 71°C obtained in 1841 by St. Claire Deville [25] by the nitration of "nitrobenzene" prepared from light oil, was in fact dinitrotoluene. As Rosensriel [26] found in 1872 *p*- nitrotoluene yields only one product of dinitration, viz. the 2,4-isomer, while *o*- nitrotoluene gives in addition another isomer, the structure of which he did not determine.

The first indication of the existence of the other dinitrotoluene isomers can be found in the Limpricht's work [27]. He was able to isolate from the nitration products the 3,6-isomer, besides the 2,4- and 2,6-isomers. In 1903 Zaloziecki [28] nitrated the aromatic fraction of Galicia oil and isolated the 2,4- and 3,6-nitrotoluenes.

Beilstein and Kuhlberg nitrated the *m*- nitrotoluene in 1873 and obtained the 3,4-isomer.

The data were confirmed by Häussermann and Grell [29] in 1894. They stated that besides the isomers already mentioned, the 3,5-isomer was also isolated. Several authors questioned the presence of the latter isomer in the nitration products. For example, Sirks [30] reporttd that nitration of *m*- nitrotoluene resulted in the formation of the 3,4-, 2,3-, and 3,6-isomers, but not the 3,5-isomer.

Gibson, Duckham and Fairbairn [13] have carried out more detailed studies, in which they established that the following proportions of isomers are formed in the nitration of various mononitrotoluenes (Table 58):

TABLE 58

NITRATION OF NITROTOLUENE ISOMERS

Substance being nitrated	Dinitrotoluene isomers, content %				
	2,4-	2,6-	3,4-	2,3-	3.6-
o- Nitrotoluene	67	33	-		-
p- Nitrotoluene	100	-	-	-	-
m- Nitrotoluene	-	-	55	25	20

De Beule [31] carried out the most extensive study of nitration of *m*- nitrotoluene. He found the product was composed of 54.6% of 3,4-dinitrotoluene, 30.6% of 2,3-dinitrotoluene, 13.0% of 2,5-dinitrotoluene, and 1.8% of 2,5-dinitrotoluene. Thus he confirmed the formation of 3,5-isomer.

The crude dinitrotoluene consists (according to de Beule) of the following isomers :

2.4-dinitrotoluene	76.1%
2,6-dinitrotoluene	19.8%
3,4-dinitrotoluene	2.25%
2,3-dinitrotoluene	1.23%
2,5-dinitrotoluene	0.54%
3,5-dinitrotoluene	0.08%

Recently Kobe, Skinner and Prindle [32] reported their extensive studies on the nitration of *o*- and *p*- nitrotoluenes to dinitrotoluene. They concluded that the most favourable parameters of the nitration of *o*- and *p*- nitrotoluenes differed somewhat from each other. Thus the concentration of mixtures for nitrating *o*- nitrotoluene might vary within a wider range, especially with regard to the quantity of sulphuric acid. Also, lower temperatures may be applied for the nitration of *o*- nitrotoluene.

According to these authors, the following conditions are the most favourable in the nitration of 200 g of nitrotoluenes:

	o- Nitrotoluene	*p*- Nitrotoluene
Nitric acid weight	theoretical	theoretical
Sulphuric acid weight	250-350 g	350 g
Sulphuric acid concentration	90%	90%
Temperature	50°C	65°C
Reaction time	15-20 min	15-20 min.
Yield	100%	98%

Figures 59, 60 and 61 show the influence of temperature and concentration of sulphuric acid on the yield of dinitrotoluene using *o*- and *p*- nitrotoluene as starting materials.

Gorst and Trufanova [32a] stated that the nitration of *p*- nitrotoluene proceeds with a noticeable rate at 70°C when the nitrating mixture has the factor Φ = 72%. Increase of Φ to 79.84% increases the rate of the reaction five times (Table 59 and Fig. 62).

TABLE 59

Φ, %	71.83	74.07	75.92	77.77	79.84
Rate, $\frac{\text{mole}}{\text{1. min}} \times 10^{-2}$	16.3	42.9	60.6	74.4	85.0
Quantity of nitrated mononitrotoluenes, %	17.8	46.5	65.1	78.7	88.8

Increased rate of stirring also produces an increase in the rate of nitration. Orlova [32a] gives a diagram (Fig. 63) related to the nitration of *p*- nitrotoluene with nitrating mixture containing 4% HNO_3, 74% H_2SO_4 and 23% H_2O at 70°C.

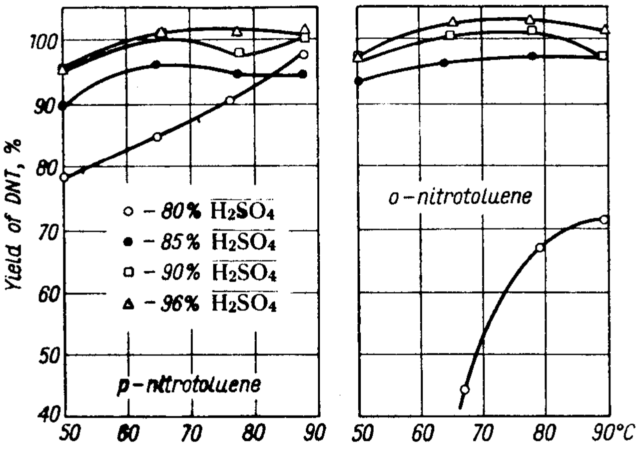


FIG. 59. Influence of temperature on the yield of DNT. Nitration of *o*- and *p*- nitrotoluenes in nitrating mixtures with various concentrations of sulphuric acid (Kobe. Skier and Prindle ([32]).

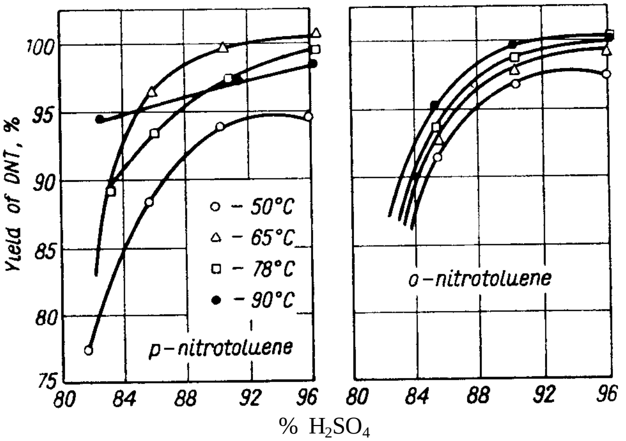


FIG. 60. Influence of the concentration of sulphuric acid on the yield of DNT. Nitration of *o*- and *p*- nitrotoluenes (Kobe, Skinner and Prindle ([32]).

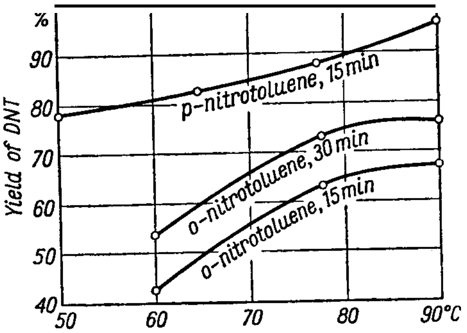


FIG. 61. influence of temperature and time on the yield of DNT. Nitration of *o*- and *p*- nitrotoluenes (Kobe, Skinner and Prindle ([32]).

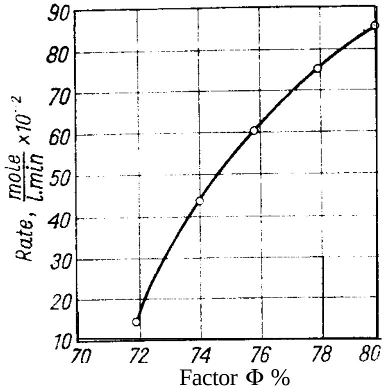


FIG. 62. Influence of the factor Φ (nitrating activity) on the rate of nitration of *p*- nitrotoluene at 70°C (Gorst and Trufanova [32a]).

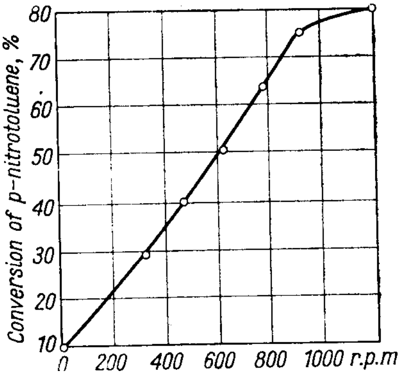


FIG. 63. Influence of the intensity of stirring on the rate of nitration of *p*- nitrotoluene (Orlova ([2a]).

INDUSTRIAL METHODS OF PREPARATION OF DINITROTOLUENE

In industrial practice, mononitrotoluene is nitrated with a mixture of composition ranging:

HNO_3 28-34% H_2SO_4 60-64% H_2O 5-8%

The manufacture of dinitrotoluene at the Griesheim factory (I. G. Farbenindustrie), described below, may serve as an example.

4000 kg of *o*- and *p*- nitrotoluene (the latter should be melted) is run into the nitrator at a temperature of 25°C and 55°C respectively. Then 5500 kg of mixed acid of composition :

HNO_3 33.5% H_2SO_4 60.7% H_2O 5.8%

are run in, so that the temperature in the case of *p*- nitrotoluene follows the curve (Fig. 64).

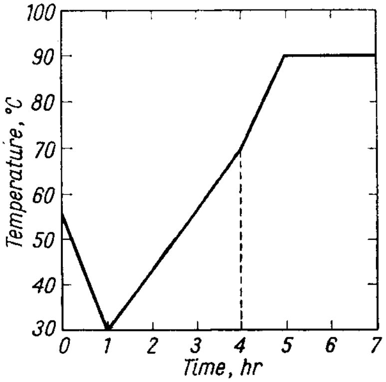


FIG 64. Temperature change during the nitration of *p*- nitrotoluene (BIOS 1144).

When all the acid has been added over a period of 4 hr, heat is applied to raise the temperature to 90°C which is held for a further 2 hr. A test sample is steam distilled and no smell of nitrotoluene should be present in the distillate.

If mononitrotoluene is detected, a further 50 kg of mixed acid is added and heating is continued at 90°C for a further half an hour. The contents of the nitrator are diluted with 350-400 1. of water to give a waste acid of 73% H_2SO_4 containing ca. 0.1% HNO_2.

After settling, the waste acid is run into the washing tank (a lead-lined vessel of 12 m^3 capacity) where the acid from three or four previous nitrations is collected and washed with sufficient crude nitrotoluene and *o*- nitrotoluene to form one batch for nitration to dinitrotoluene. After settling, the washed waste acid is collected in the acid storage tank. The nitrotoluene is pumped or blown to the nitrator.

In the washing tank, a stainless steel vessel of 12 m^3 capacity, dinitrotoluene is washed with 4000 1. hot water and the wash water is blown to drain. 4000 1. of hot water are then run in and while stirring, sufficient solid NaOH is added to obtain a neutral reaction. The wash liquor is discarded and the product is washed with water to remove excess NaOH.

The molten dinitrotoluene is run into the vacuum dryer, and heated at 120°C at a pressure of 15 mm Hg for 5 hr. It is tested for moisture by heating a small amount in a test-tube and looked for condensation on the side of the tube. The material is made up into solid blocks or flakes (flaking as for TNT, p. 379).

Dinitrotoluene, prepared by nitrating *p*- nitrotoluene, and free from *m*- nitrotoluene, should not melt below 64.5°C. It should contain not less than 96% of 2,4-dinitrotoluene.

The specification, according to U.S.S.R. data (Gorst [2]) given below (Table 60) is for commercial dinitrotoluene, i.e. for the product prepared from a mixture of nitrotoluenes.

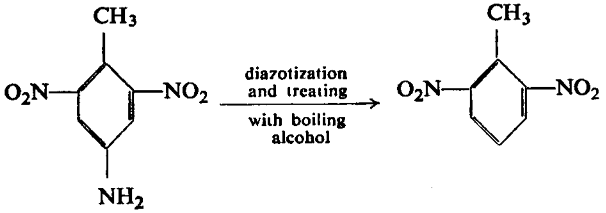
TABLE 60

SPECIFICATION FOR COMMERCIAL DINITROTOLUENE

Appearance	crystalline yellow product, free from visible impurities
Moisture content	below 1.5%
Mononitrotoluene con tent	below 1.0%
Benzene insoluble substances	below 0.1%
Ash	below 0.1%
Sand in the ash	not more than 0.05%
Acidity	not more than 0.005% as H_2SO_4
Melting point of the dry product	not below 50°C and not higher than 55°C
Product used for nitration to TNT	below 76°C

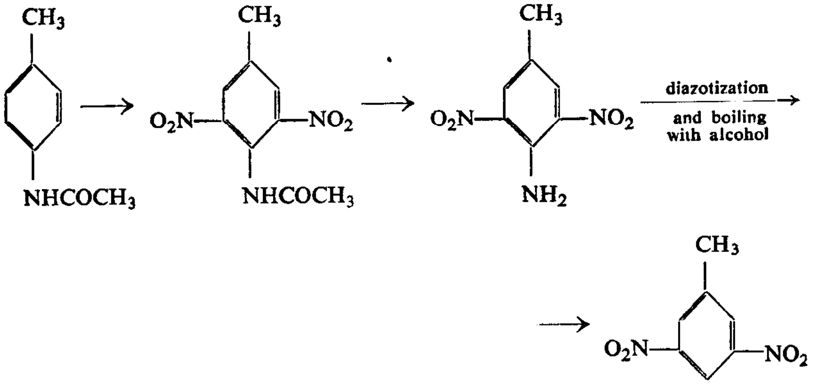
PREPARATION OF PURE ISOMERS

Pure 2,4-dinitrotoluene may be obtained by the direct nitration of *p*- nitrotoluene. 2,6-Dinitrotoluene of high purity may be obtained from 2,6-dinitrotoluidine:



(10)

3,5-Dinitrotoluene, difficult to obtain by direct nitration, may be prepared in the following way:



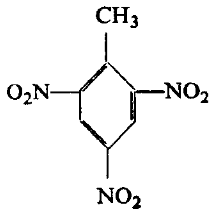
(11)

3,6 (or 2,5-)-Dinitrotoluene was obtained by Page and Heasman [33] by the oxidation of 5-nitro-o-toluidine with Caro's acid.

All other isomers are prepared by nitration of *m*- nitrotoluene, followed by fractional crystallization of the product.

α– TRINITROTOLUENE (TNT)

The commercial product for military purposes consists of α– trinitrotoluene (2,4,6-isomer) of high purity.



In the explosives industry it is known under various names: Tolite (France); Tri, Trotyl, Tutol, Trinol. Füllpulver 1902 - abbreviation Fp02 (Germany); Tritolo (Italy); Trotyl and TNT (Poland); Trillit, Tolita (Spain); TNT (United Kingdom and U. S. A.); Tol, Trotil, TNT (U. S. S. R.).

Trinitrotoluene was first mentioned in 1863. It was obtained by Wilbrand [34], who treated toluene with a mixture of nitric and sulphuric acids at a temperature "close to boiling point”. Later Beilstein and Kuhlberg [21], in a paper published in 1870, which describes the most extensive work on the nitration of aromatic hydrocarbons carried out in the last century, gave details of the nitration of *o*-, *m*-, and *p*- toluencs to trinitro derivatives. Besides α– trinitrotoluene they also isolated the γ– isomer.

The β– and γ– isomers were obtained by Hepp [35] in 1882. The constitution of the α -isomer was determined by Claus and Becker [36] in 1883, and that of the β– and γ by Will [37] in 1914 (see also pp. 311 and 336, 337).

PHYSICAL PROPERTIES

α– Trinitrotoluene crystallizes in the form of small columns or needles.

According to Artini [38], α– trinitrotoluene forms monoclinic crystals, of the prismatic class, with the axial ratio ***a:b:c*** = 1.64047:1:0.61936.

Melting point and purity. The melting point of α– trinitrotoluene has been determined by several workers as 80.6°C, 80.65°C, 80.8-80.85°C, 80.66°C. The value of 80.65°C is generally accepted, and usually determined as setting point.

Three grades of commercial TNT are usually prepared, the main difference between them consisting in their purity and hence in the melting point. The standards for TNT, accepted in several countries, differ somewhat.

Polish standards of 1930 cover the requirements for the following grades of TNT:

I. m.p. 80.3°C
II. m.p. 80.0°C
III. m.p. 76.0°C

U.S.S.R. standards (Gorst [2]) specify the following grades of TNT:

I. military TNT	m.p. 80.2°C
II. TNT for the manufacture of ammonites:	
(a) sulphited (for permissible explosives)	m.p. 80.0°C
(b) washed only	m.p. 77.5°C
III. waste TNT	m.p. 75.0°C

In Great Britain, during World War I the following minimum melting points of TNT were specified:

I. m.p. 80.0°C
II. m.p. 79.5°C
III. m.p. 76.0°C

In the U. S. A. two grades of TNT have been introduced on the market:

I. m.p. 80.2°C
IL m.p. 76.0°C

According to Gorst [2], the U. S. S. R. requirements to crystallized TNT are as follows.

(1) Light yellow crystalline powder without any visible foreign inclusion. Should pass through the 3 mm size sieve.
(2) Setting temperature not below 80.2°C

(3) Water and volatile matters-no more than 0.075%.
(4) Acidity (as H_2SO_4) - no more than 0.01%.
(5) Substances insoluble in benzene - no more than 0.15%.
(6) Content of ash - no more than 0.1%.
(7) Content of oily products - lower than in the standard substance.

The low melting point of α– trinitrotoluene is due mainly to the presence of trinitrotoluene isomers, and to a lesser degree, to the presence of other impurities, such as trinitrobenzene, trinitrocresol, dinitrotoluene.

Since the trinitrotoluene isomers are formed as a result of the nitration of *m*- nitrotoluene, W. W. Jones and Russel [9] undertook the task of determining to what extent the presence of *m*- nitrotoluene in mononitrotoluene lowers the melting point of α– nitrotoluene. The authors nitrated mixtures of *m*- and *p*- nitrotoluenes (Table 61).

TABLE 61

RELATIONSHIP BETWEEN LOWERING THE MELTING POINT OF TNT AND THE CONTENT OF *m*- NITROTOLUENE IN MONONITROTOLUENE

m- Nitrotoluene content, % / Melting point °C	0	2.11	3.22	4.58	5.75
Found experimentally	80.78	79.87	79.26	78.70	78.13
Calculated from formula (12)	80.80	79.82	79.30	78.67	78.13

Pure 2,4-dinitrotoluene was also nitrated for comparison and, as a result trinitrotoluene melting at 80.80°C was obtained.

Jones and Russel propose the following empirical formula for the calculation of the melting point of TNT, depending on the *m*- nitrotoluene content in mononitrotoluene:

$$\text{m. p.} = 80.80-0.465c \qquad (12)$$

where c is the percentage of *m*- nitrotoluene.

Solubility. *a*- Trinitrotoluene is rather insoluble in water. It dissolves in concentrated sulphuric or nitric acids and is precipitated from the solutions on adding water.

The solubility data for α– trinitrotoluene in sulphuric acid of various concentrations are tabulated in Table 62 (Belenkii [39]).

TNT dissolves with difficulty in nitrating mixtures. Its solubility may however be fairly high when the content of HNO_3 in the nitrating mixture falls to a few per cent, as in waste acid.

Solubility data for α– trinitrotoluene in various mixtures at 20°, 50° and 70°C are shown in Table 63.

The solubility of α– trinitrotoluene in nitric acid is high even when the acid is relatively dilute (Table 64). This property is sometimes used in industry to crystallize TNT.

α– Trinitrotoluene dissolves readily in organic solvents, such as acetone, benzene, and toluene. The corresponding data, after Taylor and Rinkenbach [40], are presented in Table 65.

TABLE 62

SOLUBILITY OF a- TRINITROTOLUENE IN SULPHURIC ACID (IN %)

Concentration H_2SO_4, % / Temperature °C	70	75	80	85	90	95	100
0	-.	0.3	0.4	0.6	2.0	3.5	13.0
10	-	0.3	0.45	0.75	2.2	4.0	13.5
20		0.3	0.50	0.85	2.5	4.8	15.0
25	.-	0.32	0.55	0.95	2.6	5.2	15.5
30	--	0.35	0.60	1.0	2.7	6.0	16.5
40	0.2	0.4	0.65	1.3	3.0	7.0	18.0
50	0.2	0.45	0.70	1.7	3.5	8.5	21.0
60	0.22	0.50	1.0	2.3	5.2	11.0	24.8
70	0.35	0.7	1.6	3.3	7.0	13.5	29.0
80	0.6	1.3	2.4	4.8	10.0	18.0	26.5

TABLE 63

SOLUBILITY OF α– TRINITROTOLUENE IN ACID MIXTURES

Composition of the mixture, %				Solubility, %	
H_2SO_4	HNO_3	H_2O	20°C	at 50°C	at 70°C
60	0	40	0.20	0.52	0.70
80	0	20	0.59	1.25	2.07
90	0	10	2.55	4.70	7.63
60	1	39	0.22	0.41	0.62
80	1	19	0.55	1.08	1.68
90	1	9	1.85	4.35	7.49
60	5	35	0.25	0.55	1.23
80	5	15	0.73	1.48	1.85
90	5	5	1.76	4.49	7.53

100 parts of carbon disulphide dissolve 0.4 parts of α– trinitrotoluene at 15°C and 2.7 parts at 46°C.

α– Trinitrotoluene forms eutectics with higher nitrated aromatic compounds and with nitric esters. Some of them have a considerable practical importance such as the mixtures of α– trinitrotoluene with cyclonite, pentaerythritol tetranitrate, tetryl etc. (Vol. IV).

TABLE 64

SOLUBILITY OF α– TRINITROTOLUENE IN NITRIC ACID (ACCORDING TO ORLOVA [2a])

Concentration % HNO_3	Temperature °C	Solubility in g of α– trinitrotoluene in 100 g of nitric acid
78.2	48	100
	53	150
	56	200
	59	250
	61	300
80.4	44	100
	50	150
	54	200
	56	250
82.5	38	100
	46	150
	50	200
	54	250
	56	300
84.7	33	100
	41	150
	46	200
	54	300
91.8	26	150
	34	200
	45	300
	55	500
97	34	235
	47	376
	52	458
	57	650
	61	830

TABLE 65

SOLUBILITY OF α– TRINITROTOLUENE (g/100 g SOLVENT)

Temperature	Water	CCl_4	Benzene	Toluene	Acetone	Ethanol 95%	$CHCl_3$	Ether
0	**0.0100**	**0.20**	**13**	**28**	**57**	**0.65**	**6**	**1.73**
5	**0.0105**	**0.25**	**24**	**32**	**66**	**0.75**	**8.5**	**2.08**
10	**0.0110**	**0.40**	**36**	**38**	**78**	**0.85**	**11**	**2.45**
15	**0.0120**	**0.50**	**50**	**45**	**92**	**1.07**	**15**	**2.85**

Table 65 (continued)

Temperature, °C	Water	CCl_4	Benzene	Toluene	Acetone	Ethanol 95%	$CHCl_3$	Ether
20	0.0130	0.65	67	55	109	1.23	19	3.29
25	0.0150	0.82	88	67	132	1.48	25	3.80
30	0.0175	1.01	113	84	156	1.80	32.5	4.56
35	0.0225	1.32	144	104	187	2.27	45	-
40	0.0285	1.75	180	130	228	2.92	66	
45	0.0360	2.37	225	163	279	3.70	101	
50	0.0475	3.23	284	208	346	4.61	150	—
55	0.0570	4.55	361	272	449	6.08	218	
60	0.0675	6.90	478	367	600	8.30	302	
65	0.0775	11.40	665	525	843	11.40	442	-
70	0.0875	17.35	1024	826	1350	15.15		
75	0.0975	24.35	2028	1685	2678	19.50		
80	0.1075	-	-.	-	-	-	-	—
85	0.1175	-	-	-	-	_	-	
90	0.1275	-	-	-	-	-.	-	
95	0.1375	-	-	-		-	-	-
100	0.1475	-	-	-	-	-	-	-

TABLE 66

EUTECTICS WITH *a*- TRINITROTOLUENE

The second component	Weight % of TNT	m.p., °C	Author
Cyclonite	97.5	78.6	T. Urbanski and Rabek-Gawroriska [41]
m- Dinitrobenzene	54.5	51	Hrynakowski and Kapuscinski [42]
1,8-Dinitronaphthalene	82	73.4	Khaibashev and Gromova [43]
2,4-Dinitrotoluene	50	45.6	Bell and Herty [44]
	46	45	Langenscheidt [45]
	48	45.8	Hrynakowski and KapuScitMi [421
	41.4	46.3	Burkhardt [150]
Hexyl	88	78.2	Giua [46]
Nitrobenzene	7	2.0	Hammick, Andrews and Hampson [47]
Nitroglycerine	17.6	7.0	Tamburrini [48]
	15	6.4	Lehmstedt 1491
	17.1	6.3	Hackel [50]
o- Nitrotoluene	16	-15.6	Bell, Gordon, Spry and White [51]
	19.5	-9.7	
p- Nitrotoluene	42	34	Bell and Herty [44]
Pentaerythritol tetranitratc	87	76.1	T. Urbanski [52]
Picric acid	65	59.8	Taylor and Rinkenbach [40]
	66	55	Giua [46]
	68	59	Hrynakowski and Kapu&ciiki [42]
	66.4	63.3	Burkhardt [151]
Tetryl	57.9	58.3	Jefremov and Tikhomirova [53]
Trinitro-m-cresol	43.3	41.3	Jefremov [54]
Trinitro-m-xylene	92	75	Bell and Sawyer [55]; Jefremov and Tikhomirova [53]

Some of the eutectic compositions are given in Table 66.

A number of tertnery eutectics containing α– trinitrotoluene have also heen examined, e.g. *a*- trinitrotoluene, 2,4-dinitrotoluene, *p*- nitrotoluene, m. p. 16.7°C (Bell and Herty [44]); α– trinitrotoluene, *p*- nitrotoluene, *o*- nitrotoluene, m. p. -19.5°C (Bell and Spry [56]) ; α– trinitrotoluene, β– trinitrotoluene, γ– trinitrotoluene, m. p. 44.4°C (Gibson, Duckham and Fairbairn [13]) ; α– trinitrotoluene, 2,4-dinitrotoluene, *m*- dinitrobenzene, m.p. 29°C (Hrynakowski and Kapuscinski [42]).

Hygroscopicity. α– Trinitrotoluene is practically non-hygroscopic. At room temperature, when exposed to air, saturated with water, it absorbs only 0.05% of water.

Specific gravity and density of loading. The specific gravity of solid α– trinitro toluene is 1.654-1.663 according to various authors, while that of the molten product is 1.467 at 82°C. The density of TNT, compressed under pressures varying from 1450 to 4350 kg/cm^2, is 1.54-1.62 g/cm^3 (Kast [57] 1907).

According to Dautriche [58], depending on the pressure applied, the following average density of loading can be obtained:

pressure, kg/cm^2	Mean density, g/cm^3
215	1.320
685	1.456
1375	1.558
2000	1.584
2750	1.599
3435	1.602
4125	1.610

The apparent weight of crystalline α– trinitrotoluene is 0.9.

If molten trinitrotoluene solidifies under pressure, a high specific gravity amounting to 1.62 may be obtained at a low pressure of about 5 kg/cm^2. Zanardi [59] obtained the following values :

Pressure, kg/cm^2	Mean density, g/cm^3
1	1.54
2	1.58
3	1.60
4	1.616
5	1.620

According to Kast [57] (1921), the specific gravity of α– trinitrotoluene, when allowed to solidify slowly after being melted is 1.57. When rapidly cooled with stirring, a product is obtained having a specific gravity of 1.59-1.61.

Plastic properties of TNT. In 1945 Jefremov and Khaibashev [60] found that at a temperature of 50°C and above, TNT exhibits the properties of a plastic material, as under pressure (e.g. 31.6 kg/mm^2) at 50°C it flows off through the holes in the vessel. At a temperature ranging from 0°C to 35°C TNT behaves as typical brittle material. At a temperature of 35-40°C (or at 45-47°C with TNT of high purity) a transition from the brittle to the plastic state can be observed.

Jefremov and Khaibashev [60] have also investigated melts of TNT with other nitro compounds. They observed deep minima on the isotherms of plastic flow of mixtures of TNT and picric acid, trinitroxylene or 1,8-dinitronaphthalene. corresponding to eutectic mixtures. Unlike those the corresponding curves for mixtures of TNT and 2,4-dinitrotoluene, *m-* dinitrobenzene, and tetryl, showed an additive character.

Crystallization. Very often it is necessary to obtain explosives (TNT among them) in readily precipitated form. Cave, Krotinger and McCaleb [61] developed a general method of crystallization which consists essentially in introducing the hot solution of a substance into cold diluting liquid or solid carbon dioxide.

Thus when a solution of α– trinitrotoluene in methanol is introduced into water, small and uniform crystals which are readily "pourable" are formed. Less uniform crystals of needle like form are obtained by pouring a methanol solution of α– trinitrotoluene into solid carbon dioxide. The results are given in Table 67.

TABLE 67

Methanol solution of TNT is poured into	Average dimensions of the crystals, μ	Limits of dimensions of the crystals, μ	Ratio of axes length/width
solid CO_2	29	3.5430	9.6
water	25	6-60	3.0

The rate of crystallization of TNT has been studied by Pelchowicz and Bergmann [62]. They found it decreased when various compounds were added, forming homogeneous melts with TNT, for example certain aromatic compounds, among others picric acid.

The elucidation of the influence of admixtures on the linear rate of crystallization of TNT has been the subject of more detailed studies by Gey, Dalbey and Van Dolah [63]. They found that some compounds, as for example 2,4,6-trinitrostilbene and a number of its derivatives (e.g. 3-nitro-, 4-nitro-2-chloro-, 2-methoxy-, 4-hydroxy-, 4-methoxy-), caused a very sharp fall of the rate of crystallization of TNT. For example, the addition of 1 mole % of 2,4,6-trinitrostilbene to TNT reduced its linear rate of crystallization at 74°C almost nine times: from 2.5 cm/min (pure TNT) to 0.29 cm/min.

Other compounds such as 2,4-dinitrotoluene, 2,4,6-trinitro-m-xylene, 2,4,5-trinitrotoluene, hexogen, only slightly decreased the rate of crystallization (e.g. the addition of 1 mole % of 2,4-dinitrotoluene and hexogen caused a decrease in rate of crystallization of TNT at 74°C from 2.5 cm/min to 1.89 and 1.78 cm/min respectively).

Boiling point and vapour pressures. Giua [64] reported in 1919 that trinitrotoluene may be boiled. According to this author, it can be distilled off at 210-212°C, under a reduced pressure of 10-12 mm Hg without any visible decomposition.

Belayev and Yuzefovich [65] found the boiling point of TNT at 2 mm Hg pressure to be 190°C and at 50 mm Hg 245-250°C; these values are consistent with those quoted above.

The authors have determined the boiling point of trinitrotoluene at normal pressure by extrapolation and found it to be 300±10°C. The direct determination of the boiling point, is of course impossible, since it is near to the initiation temperature of the substance.

A. J. B. Robertson [66] reported 345°C as the condensation temperature of trinitrotoluene vapours at 760 mm Hg, and 232°C at 30 mm Hg. Considering that the experimental conditions were difficult, it should be accepted that the results of all three workers are consistent. The value of 530°C, earlier determined by Menzies [67] by extrapolation of the results of vapour pressures measurements and heats of evaporation, is less probable.

Vapour pressures of trinitrotoluene have been determined by several authors. The first measurements were carried out by Verola [68] between 1911 and 1912. He found a value of 25 mm Hg at 183°C and soon after attaining this temperature decomposition began. The evolution of gases causes the pressure to rise rapidly. The rate was as high as 20 mm Hg/min.

Menzies [67], A. J. B. Robertson [66] and G. Edwards [69] have also carried out investigations on the vapour pressures of α– trinitrotoluene.

Edwards reported the following vapour pressures:

Temperature, °C	Pressure, cm Hg
60.1	5.43×10^{-5}
78.5	6.44×10^{-4}
80.2	7.16×10^{-4}
82.4	7.96×10^{-4}
99.5	4.07×10^{-3}
110.6	8.26×10^{-3}
131.1	3.48×10^{-2}
141.4	6.21×10^{-2}

Absorptivity. α– Trinitrotoluene is relatively strongly adsorbed on chromatographic columns and can be separated in this way from nitro derivatives of toluene with a lower number of nitro groups. Various columns have been suggested filled with basic adsorbents, but these were liable to produce a deep change in the trinitro compounds (Halfter [70], Ovenston [71]). A considerable improvement was reported by Kemula and his co-workers [72], using his chromate-polarographic method. Here the chromatographic column was filled with pulverized rubber swollen with n-heptane (immobile phase), the mobile phase being 0.2 M KI in a 50/50 methanol-water solution of the nitro compounds.

When the column was fed with a mixture of mono-, di- and tri-nitrotoluenes, *p*- nitrotoluene was eluted first, dinltrotoluene followed, and the last substance eluted was α– trinitrotoluene.

THERMOCHEMICAL PROPERTIES

Specific heat. C. A. Taylor and Rinkenbach [40] give the following values for α– trinitrotoluene at temperatures, ranging from 0°C to the melting point of the compound :

Temperature, °C	Specific heat, Cal/g °C
0	0.309
20	0.328
40	0.345
60	0.361
80	0.374

The *thermal conductivity,* λ, of α– trinitrotoluene is 0.00043 at 25° (Prentiss [73]).

Heat of crystallization and heat of evaporation. According to Tammann [74], the heat of crystallization of α– trinitrotoluene is 4.88 Cal/mole, and according to Edwards [69] is 5.6 Cal/mole. The heat of evaporation of α– trinitrotoluene, as found by Edwards [69], equals 22.7 Cal/mole. According to A. J. B. Robertson [66], it is 17.5 Cal/mole.

Heat of combustion and heat of formation. The heat of combustion of α– trinitrotoluene is 822.5 Cal/mole (Garner and Abernethy [3]). The value relates to constant volume and includes a correction that allows for the nitric acid formed in the calorimetric bomb.

From the measured heat of combustion, the heat of formation of α– trinitrotoluene has been calculated as +29.1 kcal/mole (assuming amorphous carbon), or +128.2 kcal/kg. Assuming the diamond form for carbon, Abemethy and Gamer [3] found a lower heat of formation, viz. +10.2 kcal/mole (Fig. 50. p. 261).

Other authors give the following values for the heat of formation of α– trinitrotoluene :

+ 16.0 kcal/mole (Kast [54])
+ 7.7 kcal/mole (Bichel [22])
+ 5.9 kcal/mole (Koehler [23])

For calculating the thermal effects of the processes in which α– trinitrotoluene takes part the values given by Gamer and Abernethy, or by Kast are generally used.

Heat of nitration. The heat of conversion of dinitrotoluene to trinitrotoluene, calculated from the heats of formation of the reactants and of the reaction products is:

+ 17.5 kcal/mole (starting product 1,2,4-dinitrotoluene) (Fig. 50)
+ 19.0 kcal/mole (starting product 1,2,6-dinitrotoluene)

Heat of explosion is discussed later (under explosive properties p. 318).

CHEMICAL PROPERTIES

Reactions with acids and alkalis

Like other aromatic nitro compounds, trinitrotoluene is resistant to the action of acids. Only concentrated nitric acid at a temperature over 110°C can oxidize it to 2,4,6-trinitrobenzoic acid, and at 200°C trinitrobenzene is formed, as a result of decarboxylation (p. 254).

However, trinitrotoluene reacts with alkalis, yielding organo-metallic products. The readiness of trinitrotoluene to react with alkalis has suggested the idea that it is an acid. This problem was studied by Farmer [75] in 1901. He applied a method, based on determining the partition coefficient K for trinitrotoluene between two liquid phases: water and benzene or water and ligroin phase, with addition of sodium hydroxide to the water phase.

While for picric acid a value $K = 0.164$ had been found by this method (Rothmund and Drucker [76]), for trinitrotoluene Farmer found $K = 2.0 \text{ x } 10^{-14}$, which means that trinitrotoluene is an acid 1013 times weaker than picric acid. In effect it has virtually no acidic properties.

Similarly Brand and his co-workers [77] inferred from the results of spectrophotometric studies that 2,4,6-trinitrotoluene, in a solution of 100% sulphuric acid, was not ionized, and could undergo partial ionization only in very concentrated oleum. These investigations are discussed more fully on p. 219.

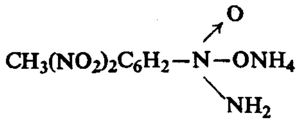
On the other hand, attention should be drawn to the cryometric investigations of nitro compounds, already referred to (p. 218), which made Hantzsch express the view that the nitro group may confer a basic character to the compound. He gave only *p*- nitrotoluene as an example. Gillespie [78] has suggested that 2,4,6-trinitrotoluene in sulphuric acid solution also behaves as a base.

Wyatt and Brayford [79] have tried to explain the inconsistency of the spectrographic and cryometric results. On the basis of their cryometric measurements on solutions of 2,4,6-trinitrotoluene, 1,3,5-trinitrobenzene and picric acid in sulphuric acid in the presence of compounds interferring with the dissociation of the solvent, they finally concluded, on the basis of the spectrophotometric measurements, that polynitro compounds should be regarded as non-electrolytes.

Alkalis, when reacted with trinitrotoluene, very easily effect a considerable change in the substance, yielding red or brown coloured addition products containing metal. Inorganic acids separate from these products an organic substance, which is no longer trinitrotoluene. Numerous investigations carried out to elucidate the structure of this substance have given no definite answer as yet.

Several workers investigating trinitrotoluene many years ago took an interest in the nature of these substances (e.g. Wilbrand [34] in 1863; Hepp [35] in 1882).

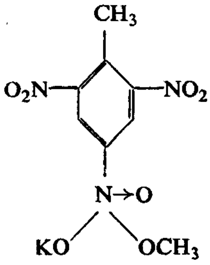
Korezynski [80] was one of the first who investigated the reaction quantitatively. In 1908 he introduced dry ammonia to various nitro compounds, including trinitrotoluene and trinitrobenzene. When the reaction was carried out at a low temperature (-10°C), he found that one molecule of trinitrotoluene absorbs two of ammonia to form a complex to which the author ascribed the following formula:



$$CH_3(NO_2)_2C_6H_2-\underset{\searrow NH_2}{\overset{\nearrow O}{N}}-ONH_4$$

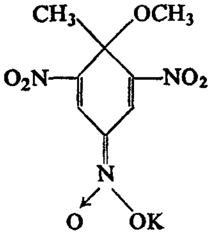
(cf. Faar, Bard and Wheland [160]).

Hantzsch and Kissel [81] by treating trinitrotoluene with potassium alcoholate (e.g. methylate) obtained an addition product to which they ascribed the structure given earlier by Angeli [82] for the product obtained from trinitrobenzene and CH_3OK (I).



I

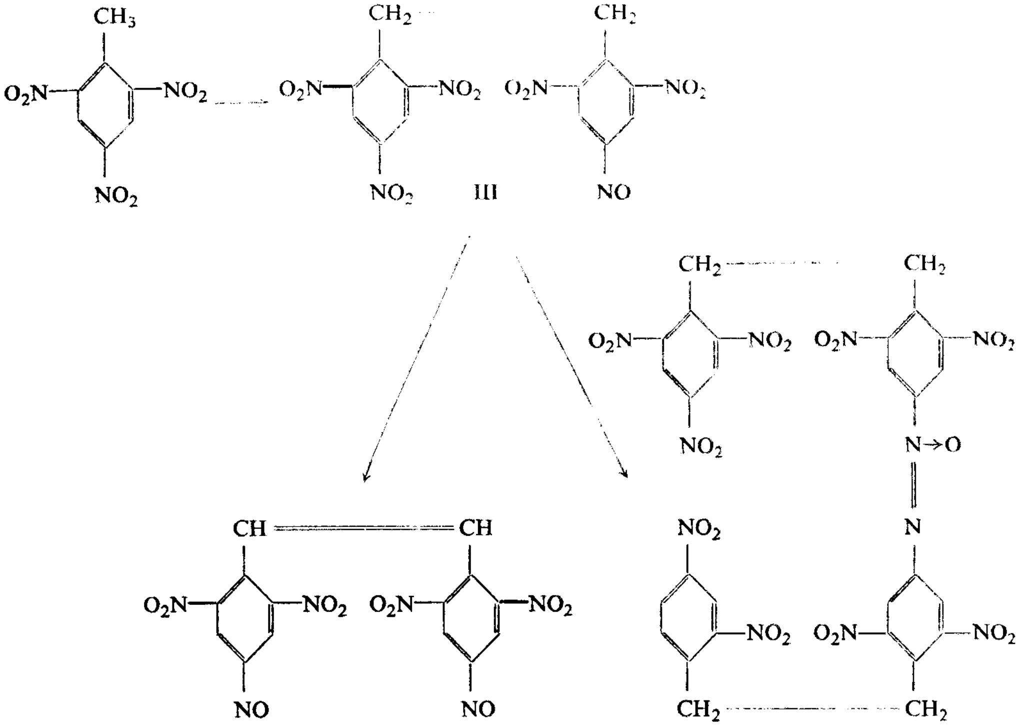
In accordance with Meisenheimer's work [83, 84] (p. 202), however, the structure should be presented by the formula II (using the more modem annotation).



II

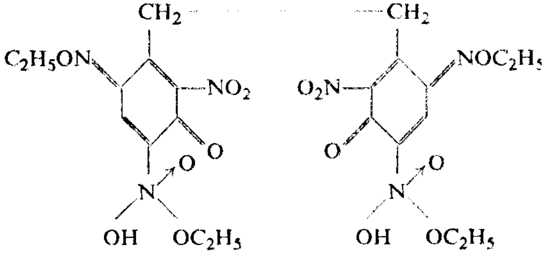
Further studies (Hantzsch and Picton [85]) showed, that inorganic acids, e.g. sulphuric, decompose these salts, with the evolution of nitrogen oxides. Products of a drastic transformation of trinitrotoluene are precipitated simultaneously, among them stilbene derivatives, products of oxidation of the methyl group.

Copisarow [86] tried to express the changes which trinitrotoluene undergoes under the action of alcoholates or alkali metal hydroxides by the following scheme, in which he postulated the formation of nitro-nitroso derivatives of dibenzyl (III), and stilbene (IV), followed by the formation of an azoxy compound (V), which might be transformed into more complex azoxy compounds:



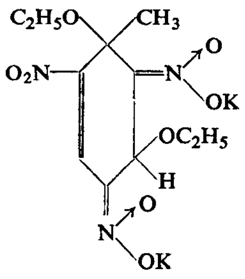
III

Giua and Reggiani [87] reacted sodium alcoholate with trinitrotoluene in acetone solution and obtained several addition products, containing various proportions of alcoholate (l-3 molecules of C_2H_5ONa for 1 molecule of trinitrotoluene). By treating the products with an inorganic acid, they obtained yellow, amorphous compounds, which they regarded as mixture of several substances, which were dibenzyl delivatives. e.g.:

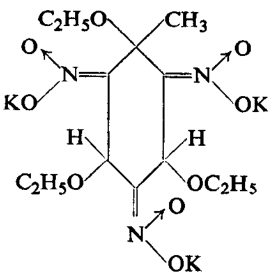


VI

Stefanovich [88], on the basis of Meisenheimer’s formulae, ascribes the formulae VII and VIII to the addition products of α– trinitrotoluene with two or three molecules of potassium alcoholate respectively.



VII



VIII

He has stated that a maximum of three molecules of an alcoholate can be added to α– trinitrotoluene, the number being equal to the number of nitro groups.

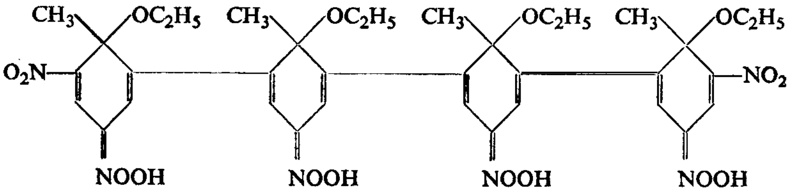
T. Urbanski and Pawlowski [89] investigated the salts formed on treating trimtrotoluene in acetone-alcohol solution with sodium alcoholate and also with an alcoholic solution of $Ba(OH)_2$. Various addition products were obtained, according to the proportion of the alcoholate or hydroxide, e.g.:

from $CH_3.C_6H_2(NO_2)_3 + C_2H_5OBa_{1/2}$ to $CH_3.C_6H_2(NO_2)_3 + 3C_2H_5OBa_{1/2}$

On acidification of these salts with sulphuric acid a pale yellow product was precipitated with simultaneous evolution of nitrogen oxides.

The pale yellow precipitate, "T acid", dissolves in acetone, but it is insoluble in most organic solvents, thus differing from TNT. It has an acid character and is able to form salts.

T. Urbanski [90] assumes that it has the structure of the diphenyl-diphenylene compound (IX) :



IX

The explosive properties of the compound TX differ considerably from those Of trinitrotoluene. Its explosive power is much lower than that of trinitrotoluene, which may be explained by the smaller number of the nitro groups present. Both "T acid" itself, and also its salts, are much more sensitive to mechanical and thermal stimuli than trinitrotoluene.

T. Urbaliski and Pawlowski [89] obtained the following characteristic values:

“T acid” ignites, when heated to	210°C	after	4	see
	225°C	,,	0.5	,,
Sodium salt of “T acid” at	185°C	,,	4	,,
	200°C	„	0.5	„
Copper salt of “T acid” at	210°C	,,	4	,,
	225°C	„	0.8	„
Ferric salt of “T acid” at	220°C	„	4.5	„
	235°C	„	0.6	„
Zinc salt of “T acid” at	230°C	,,	3.5	,,
	245°C	„	0.8	„

“T acid”, when contacted with a flame, ignites instantaneously like dry nitrocellulose. Salts of “T acid” ignite just as readily. Its sensitivity to impact is also very high, being of the same order as tetryl.

According to Bowden [91], the initiation temperature of the product of prolonged treatment of TNT with moist ammonia (for 66 hr) is merely 67°C. This observation has not been confirmed by other authors, who found the initiation temperature of the product to be about 250°C, i.e. of the same order as that of TNT (290°C) within the limits of experimental error. Even if not all authors agree with Bowden’s low figure for the temperature of initiation of the products obtained by reacting trinitrotoluene with alkalis, it has been stated repeatedly that these products are much more sensitive to heat, impact and friction than trinitrotoluene itself. Their high sensitiveness is of greatest practical importance, and is a warning that great care should be taken to avoid bringing TNT into contact with alkalis, especially in the presence of organic solvents such as alcohol, acetone etc.

There is evidence that the reaction product of trinitrotoluene with potassium alcoholate, which explodes when heated to 130-150°C, may even ignite spontaneously at room temperature.

According to Dupre [92], the ignition temperature of trinitrotoluene is considerably lowered by the addition of various substances, e.g. sulphur, phosphorus, aniline black. When potassium hydroxide is added at 160°C, trinitrotoluene ignites or explodes immediately. A mixture of powdered trinitrotoluene and powdered potassium hydroxide ignites when heated to 80°C. A mixture with sodium hydroxide behaves similarly although the reaction is less vigorous, On rapid heating, ignition occurs at a temperature of 80°C but on slow heating the mixture does not explode; even at 200°C - only gradual decomposition takes place.

When a piece of potassium hydroxide is put into molten trinitrotoluene at 100°C, it becomes coated with a film that prevents it from reacting further. But on addition of a drop of alcohol, which dissolves both trinitrotoluene and potassium hydroxide, the mixture ignites at once.

Reaction with inorganic substances

A. J. B. Robertson [66] investigated the influence of various substances on the rate of thermal decomposition of trinitrotoluene. He measured the diminution of the induction period (i.e. the period of time elapsing between the application of heat to the sample and the moment of explosion), brought about by the addition of foreign matter to trinitrotoluene (Table 68).

TABLE 68

INFLUENCE OF ADMIXTURES ON THE INDUCTION PERIOD OF THERMAL DECOMPOSITION OF α– TRINITROTOLUENE

Admixture	Temperature °C	Diminution of the induction period, t, by sec
1.9% of Fe_2O_3	297	3.9
11% of ferro-a-nitroso-*p*- naphthol complex	276	45
9% of diphenylamine	287	14

The induction period for pure trinitrotoluene at 275°C is 12 min and at 328°C-50 sec.

As T. Urbanski and Pillich [93] found, the addition of sulphur to TNT causes the initiation temperature to fall. This can be seen from the following data:

Sulphur content, %	Initiation temperature, °C
Pure TNT	333
5	304
10	294
20	284
30	275

The explosion caused by heating TNT to which 5-10% of sulphur has been added is more violent than the explosion of pure TNT.

Investigations on the influence of metals on TNT are of special importance. Extensive studies on the effect of lead, aluminium and iron on TNT in the presence of nitric acid were carried out by Kovache and Thibon [94] as early as in 1918. These investigators found, that when heating TNT with chips of lead, aluminium or iron in the presence of nitric acid diluted with water to a concentration of about 13% of HNO_3, a product was formed which contained a considerable proportion of the metal, and which was insoluble in toluene, inflammable and sensitive to friction and impact. The products of the reactions of TNT with lead and iron were particularly sensitive. They also could be ignited when heated with nitric acid or with mixtures of nitric and sulphuric acids.

The constitution of these products has not been determined. It is possible that they arc mixtures of complex compounds of various composition. The lead content in the product obtained in the reaction with lead provides evidence of variable composition. The lead content varies from 23.5 to 64.5% Pb, depending on the mode of their preparation.

On reacting TNT with metals in the presence of mixtures of nitric and sulphuric acids diluted with water similar products were obtained, although the presence of sulphuric acid inhibited their formation to some extent. These products can be formed in production while TNT is being washed free of acid by water, for when most of the sulphuric acid has been removed, the remaining nitric acid is strongly absorbed by molten TNT.

According to the Kovache and Thibon, these metal compounds may be formed in several lead or iron parts of the plant and are a potential cause of accidents.

Kovache and Thibon also found that similar inflammable metal products were formed by lower nitrated toluene derivatives, e.g. *p*- nitrotoluene and 2,4-dinitrotoluene, and also by trinitrobenzene. Nitrobenzene and trinitroxylene did not react in this way.

It seems certain that the products discussed have fairly complex structures, being the result of a partial reduction of a nitro group (or groups) by the metal in an acid medium, followed by oxidation by nitric acid. The oxidation leads to ill-defined inflammable products of high molecular weight.

Effect of heat

Trinitrotoluene is very resistant to heat. Extensive investigations of this property of TNT have been carried out by Kast [54] and Verola [68], both of whom obtained consistent results.

According to Verola, heating TNT at 130°C for 100 hr does not bring about any decomposition. Kast, when heating trinitrotoluene at 150°C for 4 hr, found no gases evolved from its decomposition. According to Verola, a distinct evolution of gaseous decomposition products starts at 160°C.

Kast established that at a temperature of 240°C, trinitrotoluene ignites in 0.5 hr. At 270°C marked exothermic decomposition takes place. Temperatures from 295-330°C are the true ignition temperatures of TNT (Verola found 281-286°C). According to Micewicz and Majkowski [95], the ignition temperature of TNT is 312-318°C.

Verola has also examined the effect of prolonged heating on the melting point of TNT. Heating at 145-150°C gave the following results:

	m. p., °C
Before the experiment	80.75
After 18 hr heating	80.66
After 42 ,, ,,	80.55
After 80 ,, ,,	80.25
After 127 ,, ,,	80.20
After 158 ,, ,,	80.13
After 177 ,, ,,	79.90

In another set of experiments Verola obtained:

	m.p. °C
After heating for nearly 290 min at 180°C	78
After heating for nearly 180 min at 201°C	17
After heating for nearly 45 min at 217.5°C	59

TNT is difficult to ignite. When heated directly in a flame it melts, and ignites only when brought to a high temperature (about 300°C). For this reason the view has been accepted that TNT is safe to handle at high temperatures and in the presence of a flame.

However, the fact should be taken into account that molten TNT is more sensitive to impact than in the crystalline state (p. 320, Table 75, Fig. 74). Moreover, if large quantities of TNT ignite, combustion might proceed very vigorously, and even cause detonation.

Experiments carried out after the accident described on p. 393 have shown that a lighted cigarette, thrown onto a sack containing about 50 kg of TNT, is able to cause the TNT to detonate.

Effect of light

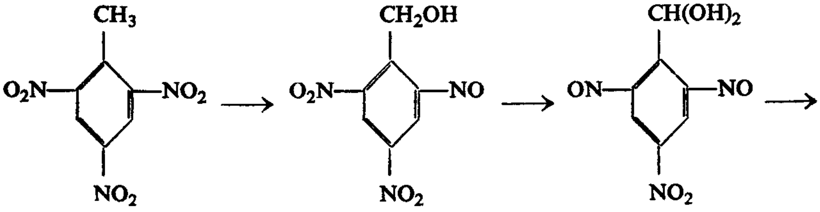
It has long been known that trinitrotoluene undergoes far-reaching changes under the influence of sunlight. Dark coloured products are formed, the structure of which is not yet fully understood.

In 1907 Kast [57] found that the melting point of trinitrotoluene fell from 80.0°C to 795°C after irradiation for a fortnight.

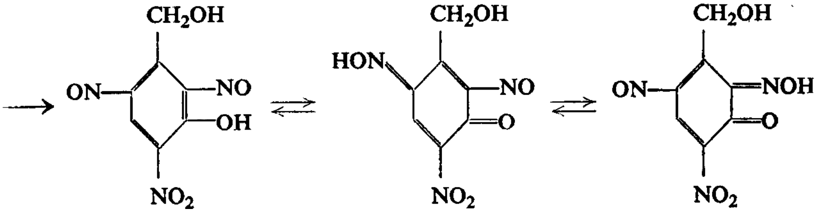
Molinari and Giua's investigations [96] showed that the melting point of trinitrotoluene which has been exposed to sunlight for 3 months in the open fell from 80°C to 74°C. When, however, trinitrotoluene was irradiated in absence of air in vacuum, hardly any changes in colour and melting point were observed.

According to Oddo [97] and Lodati [98], under the influence of radiation trinitrotoluene partly loses nitrogen and is transformed into a compound of acidic character.

Schultz and Ganguly [99] suggest that trinitrotoluene undergoes a number of isomerization processes, consisting in transferring the oxygen of a nitro group to the methyl group (as in Ciamician and Silber's reaction). The nitro compound XIII reacts like quinone oxide (XIVa and XIVb):



XI XII



XIII XlVa XIVb

The authors isolated the intermediate product XI but the products XII and XIII are hypothetical.

Naoum [100] found that trinitrotoluene, when exposed to light, yields a product of the formula $C_{14}H_8O_{10}N_5$, insoluble in benzene or water, and exceptionally sensitive to impact. In addition, a water-soluble red dye is formed.

Krauz and Turek's suggestion [101] that on exposure to sunlight mainly picric and trinitrobenzoic acids are formed has not been confirmed by other authors (Wichert and Donat [102]).

The fact that trinitrotoluene undergoes marked changes when exposed to sunlight indicates the necessity of shielding it against radiation. All the windows in TNT factory buildings should be protected against the sunlight (e.g. painted blue).

Reaction with sodium sulphite

α– Trinitrotoluene reacts only very slowly with aqueous solutions of sodium sulphite, thus differring from its unsymmetrical isomers which can react very rapidly (p. 332). The trend of the reaction of α– trinitrotoluene may also be different. α– Trinitrotoluene reacts with dilute (5%) solutions of sodium sulphite at room temperature to yield red coloured addition products. According to Muraour [103]. at room temperature

a 3% solution of sodium sulphite dissolves 0.3% α– trinitrotoluene
a 6% ., ,, ,,, ,. 0.6%
a 12% ,, ,,, ,, ,, 2.3% .,

α– Trinitrotoluene can be recovered from the solutions by acidifying it or simply by dilution with water.

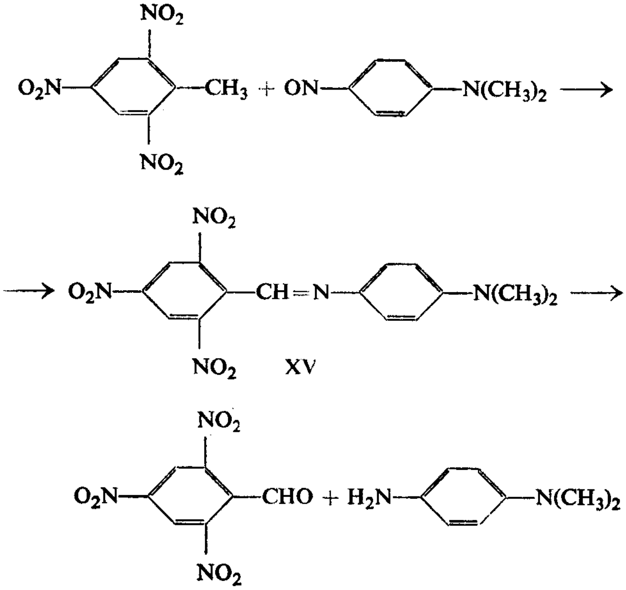
At higher temperatures, however, the α– trinitrotoluene undergoes a more drastic transformation. This is the result of both the action of Na_2SO_3 and of the high pH of the solutions: one NO_2 group is substituted by an SO_3Na group. Thus the reaction proceeds in essentially the same way as in the case of the unsymmetrical isomers.

$$CH_3C_6H_2(NO_2)_3 + Na_2SO_3 \rightarrow CH_3C_6H_2(NO_2)_2SO_3Na + NaNO_2$$

For more details see also pp. 332-335.

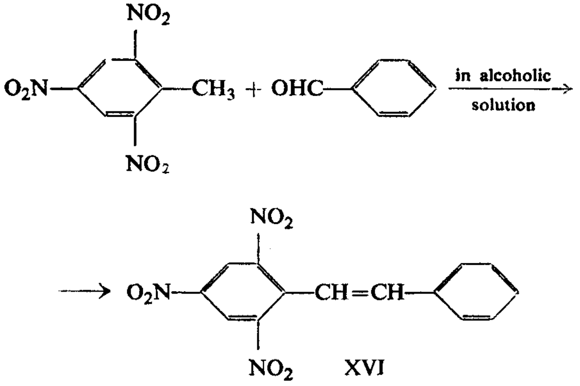
Other reactions

The methyl group in trinitrotoluene becomes strongly activated by the nitro groups present. This could be ascribed to the hyperconjugation of toluene (p. 200) strongly reinforced by the induction effect of three nitro groups. This is why trinitrotoluene readily reacts with *p*- nitrosodimethylaniline in the presence of hydroxides to form an anil (XV), which then hydrolyses to trinitrobenzaldehyde:



(13)

Trinitrotoluene reacts in a similar way with benzaldehyde in an alkaline medium to form a stilbene derivative:



(14)

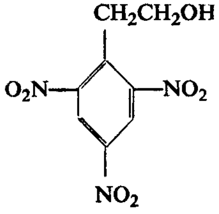
The reaction is strongly exothermic. For example, a mixture of trinitrotoluene and benzaldehyde, in the absence of a solvent, reacts when a few drops of piperidine are added. The reaction is so violent that the mixture may ignite. The methyl group of trinitrotoluene reacts with other aldehydes in a similar way. For this reason trinitrotoluene should be protected against the action of aldehydes, especially in alkaline media. Aldehydes may be formed under the influence of acids on wood. Hence, wooden vats which were formerly used for washing TNT are hardly used. now.

According to Heinke [104], trinitrotoluene reacts with diazomethane, three molecules of the latter losing their nitrogen atoms and combining with a molecule of trinitrotoluene as methylene groups, the fourth molecule of diazomethane being directly attached to the same molecule of trinitrotoluene:

$$C_6H_3N_3O_6 + 4CH_2N_2 \rightarrow C_{10}H_{11}N_5O_6 + 3N_2 \quad (15)$$

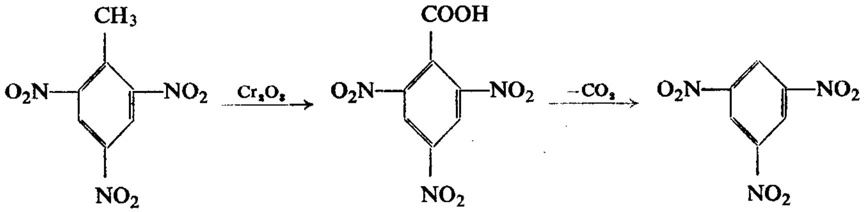
The constitution of the product has been determined by de Boer [161].

The reactivity of the methyl group in trinitrotoluene is also evident in the reaction with formaldehyde, a molecule of the latter being attached to form a trinitro derivative of phenylethyl alcohol (XVII) [162]:



XVII

The methyl group is readily oxidizable, giving rise to trinitrobenzoic acid which, because of the accumulation of nitro groups, is unstable and in turn loses its CO_2 to form trinitrobenzene:



Addition products

Trinitrotoluene, like other highly nitrated aromatic hydrocarbons, easily forms addition products with polycyclic hydrocarbons and amines. The addition products formed by α– trinitrotoluene have been extensively studied by Hepp [35] and Kremann [104a,104b]. Some of the products are listed below (Table 69).

α– Trinitrotoluene also forms addition compounds (1 : 1) with α– nitronaphthalene m. p. 64.7 (melts with simultaneous dissociation) (Wogrinz and Vári [105]; Taylor and Rinkenbach [40]; Frolova [106]).

The β– and γ– isomers of trinitrotoluene also form molecular compounds (1 : 1) with naphthalene, acenaphthene, fluorene, phenanthrene and anthracene (Jefremov and Bogush [107]; Jefremov and Frolova [107a]).

According to T. Urbaliski [log], α– trinitrotoluene forms with erythritol tetranitrate an unstable addition compound, (4 : l), melting at about 65°C.

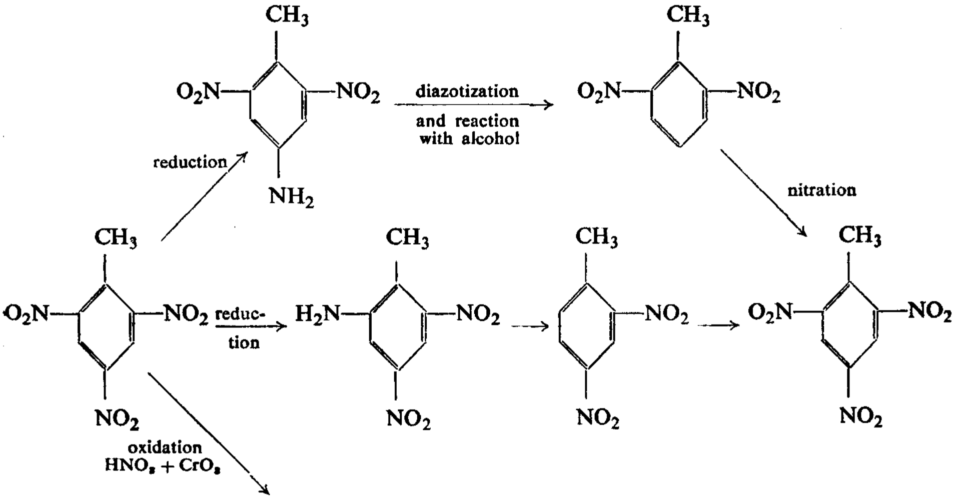
The composition of various eutectics of α– trinitrotoluene were given on p. 295.

TABLE 69

Hydrocarbon or amine, etc.	Molecular proportion α– trinitrotoluene/second component	Melting point °C	Form
anthracene	1:1	102.5	brown-yellow needles
acenaphthene	1:1	112.0	
phenanthrene	1:1	87.5	
fluorene	1:1	85.0	
naphthalene	1:1	96.5	straw yellow needles
aniline	1:1	83-84	red needles
dimethylaniline	1:1	-	violet needles
diphenylamine	2:3	31.0	red needles
carbazoie	1:1	~ 140.0	yellow needles
α– naphthylamine	1:1	141.5	dark red needles
&naphthylamine	1:1	113.5	light red needles
benzyl-/?-naphthyhunine	1:1	106.5	purple needles
dibenzyl-&naphthylamine	1:1	108.0	brick red needles
o-toluidine	1:1	53-55	light red needles
m-toluidine	1:1	62-63	light red needles
benzaldehyde phenyl-hydrazone	2:1	84	dark red needles

ELUCIDATION OF THE CONSTITUTION OF α– TRINITROTOLUENE

The constitution of α– trinitrotoluene has been established on the basis of the following reactions [36]



see eqn. (16) p. 310.

KINETICS OF THE NITRATION OF DINITROTOLUENE TO TRINITROTOLUENE

From the results of their studies on the kinetics of the nitration of 2,4-dinitrotoluene to 2,4,6-trinitrotoluene Bennett and his co-workers [109, 110] inferred that the reaction is of the third order, represented as follows:

$$DNT + NO_2^+ + HSO_4^- \rightarrow TNT + H_2SO_4 \qquad (17)$$

$$DNT + NO_2^+ + H_2SO_4 \rightarrow TNT + H_2SO_4 \qquad (18)$$

In the presence of oleum the reaction

$$DNT + NO_2^+ + HS_2O_7^- \rightarrow TNT + H_2S_2O_7 \qquad (19)$$

may also take place.

The rate of the nitration reaction in the presence of sulphuric acid can be represented by :

$$\frac{d[TNT]}{dt} = k[DNT][NO_2^+][HSO_4^-] + k'[DNT][NO_2^+][H_2SO_4] \qquad (20)$$

The constants ***k*** and ***k’*** are independent of the medium and of the concentration of sulphuric acid. If Q denotes the proportion of nitric acid dissociated into NO_2^+ ions, then :

$$[NO_2^+] = Q\,[HNO_3] \qquad (21)$$

From this the following equation for the rate of nitration can be derived:

$$\frac{d[TNT]}{dt} = \{k[HSO4^-] + k'[H_2SO_4]\}[DNT][HNO_3]Q \qquad (22)$$

At a constant concentration of sulphuric acid the nitration rate can be represented by a second order reaction equation:

$$\frac{d[TNT]}{dt} = k_2[HNO_3][DNT] \qquad (23)$$

where k_2 is the rate constant of a second order reaction.

From equation (22) Bennett and his co-workers derived the following general equation valid when oleum is used:

$$\frac{d[TNT]}{dt} = k\ [HSO_4^-] + k'[H_2SO_4] + k''[HS_2O_7^-][DNT][HNO_3]Q \qquad (24)$$

Values of ***k, k’*** and ***k”*** for concentrations of sulphuric acid ranging from 87.4% H_2SO_4 to oleum containing 29.1% SO_3, at temperatures from 60°C to 120°C, have been determined experimentally.

The experiments are in agreement with the equations derived. In particular, the equations show that an increase in the reaction rate due to decreasing the concentration of sulphuric acid from 100 to 92% may be explained by the fact that the concentration of HSO_4^- ions increases considerably, whereas the concentration of NO_2^+ ion decreases only slightly. Decreasing the concentration of sulphuric acid below 92% H_2SO_4 causes the NO_2^+ concentration to fall more rapidly than the HSO_4^- concentration increases, thus decreasing the reaction rate.

To check their theory, Bennett and his co-workers added $KHSO_4$ to the nitrating mixture. As they expected, at concentrations of acid over 92% the reaction rate increased. According to the theory, this was the result of increasing the concentration of HSO_4^- ions. However, at concentrations below 92% of H_2SO_4, adding $KHSO_4$ caused the reaction rate to fall, as increasing the concentration of the HSO_4^- ions resulted in a decrease in the concentration of NO_2^+ ions (Fig. 65).

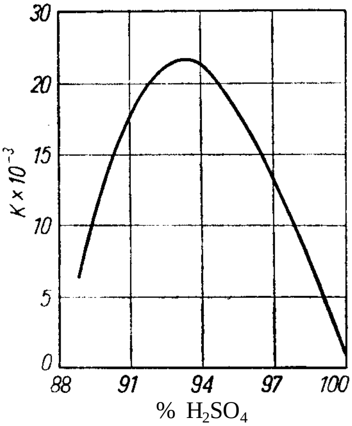


FIG. 65. Influence of the concentration of sulphuric acid on the rate of nitration of DNT in a heterogeneous medium (nitrating mixtures with a low content of HNO_3, Bennett et al. [110])

As pointed out earlier (p. 36) the concentration of the proton acceptor (HSO_4^- in our instance) is not the only factor determining the rate of nitration.

If the concentration of HSO_4^- appears to have a considerable influence on the rate of reaction this may be due to the fact that in concentrated nitrating mixtures (over 92% H_2SO_4) a high concentration of HSO_4^- is accompanied by 8 high concentration of NO_2^+.

However, the equations of Bennett are useful for calculating the rate of nitration of dinitrotoluene to trinitrotoluene.

Orlova [110a] repeated the experiments of Bennett et al., studying the kinetics of nitration of dinitrotoluene in nitrating mixtures rich in nitric acid that dissolve dinitrotoluene, i.e. in homogeneous conditions. For 0.7 mole of dinitrotoluene, 3.8 mole of HNO_3 in 12 mole of H_2SO_4 were used. The concentration of sulphuric acid was changed from 87 to 100% H_2SO_4. The temperature was 90°C. Contrary to the results of Bennett, Orlova did not find any maximum of the rate of nitration (Fig. 66) which she attributes to the homogeneity of the reaction medium.

Orlova [2a] also studied the change in rate of nitration of dinitrotoluene under the action of stirring. The reaction was carried out with a nitrating mixture containing 16% HNO_3, 81% H_2SO_4; ratio nitrating mixture/dinitrotoluene = 1.5, temperature 90°C, time 40 min. Orlova found that above a certain rate of stirring no improvement of the yield was obtained (Fig. 67).

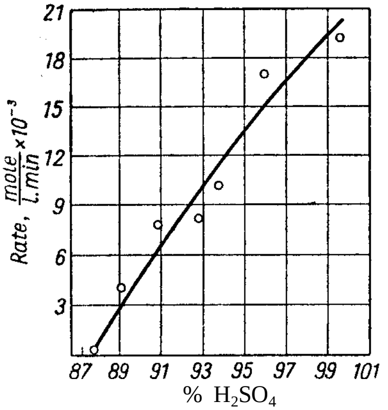


FIG. 66. Influence of the concentration of sulphuric acid on the rate of nitration in homogeneous conditions (nitrating mixtures with a high content of HNO_3, Orlova [2a]).

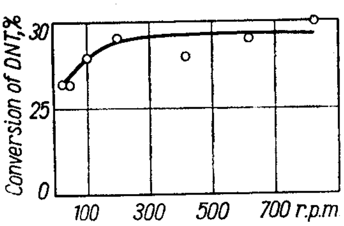


FIG. 67. Influence of the rate of stirring on the rate of nitration of DNT (Orlova [2a]).

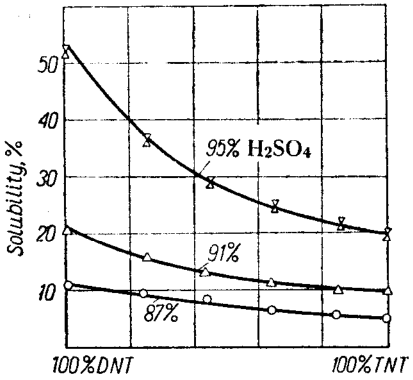


FIG. 68. Solubility of DNT and its molten mixtures with TNT in sulphuric acid of various concentrations (Orlova [2a]).

Another important factor governing the nitration of dinitrotoluene is the distribution of dinitrotoluene between the two phases: the organic phase consisting of trinitrotoluene (and dinitrotoluene) and the acid phase. The solubility of 2,4-dinitrotoluene in concentrated sulphuric acid is considerably diminished when 20-30% of trinitrotoluene is dissolved in the dinitrotoluene. Further addition of trinitrotoluene reduces the solubility to a lesser extent. This can be seen from Table 70 and Fig. 68.

The overall low solubility of nitro compounds in the acids causes the distribution coefficient of dinitrotoluene being very low (0.3-0.4). The distribution coefficient of dinitrotoluene when a 50 : 50 mixture of 2,4-dinitrotoluene and α– trinitrotoluene was treated with 90% sulphuric acid at different temperatures is given in Table 71 and Fig. 69. Figure 70 shows the influence of the concentration of sulphuric acid at 90°C.

TABLE 70

SOLUBILITY OF 2,4-DINITROTOLUENE AND α– TRINITROTOLUENE MIXTURES IN SULPHURIC ACID

Content of 2,4-dinitrotoluene in mixtures with α– trinitrotoluene	Solubility of the mixtures (in %) in sulphuric acid of different concentration		
%	87%	91%	95%
100	10.7	21.5	54.0
76	9.0	16.0	36.0
55	8.7	14.7	30.4
35	7.7	12.0	25.7
16.6	6.9	11.5	22.5
0	6.1	10.6	19.7

TABLE 71

COEFFICIENT OF DISTRIBUTION OF DINITROTOLUENE BETWEEN THE MINERAL AND ORGANIC LAYERS

Temperature, °C	70	80	85	90
Dissolved % of the mixture	16.8	17.9	19.3	19.0
composed of: DNT	13.8	12.9	12.1	8.9
TNT	3.0	5.0	7.2	10.1
Coefficient of distribution $R = \dfrac{\%\ \text{DNT in mineral layer}}{\%\ \text{DNT in organic layer}}$	0.32	0.29	0.26	0.18

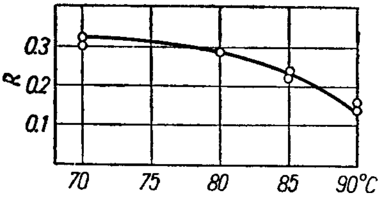


FIG. 69. Influence of the temperatur : on the distribution coefficient ***R*** of, DNT between the mineral and organi layers (Orlova [2a]).

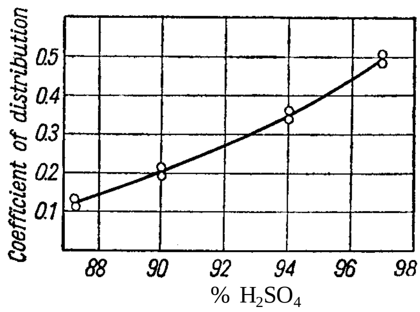


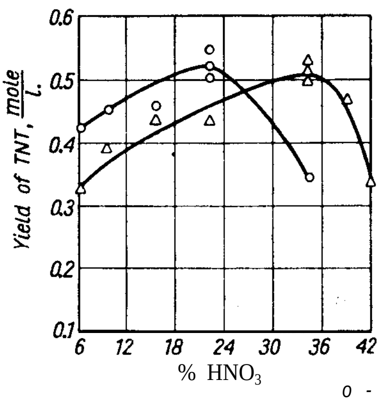
FIG. 70. Influence of the concentration of sulphuric acid on the distribution coefficient ***R*** of DNT between the mineral and organic layer (Orlova [2a]).

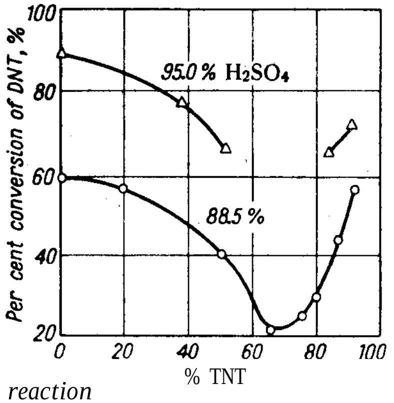
Another important feature in the nitration of dinitrotoluene is the coefficient of distribution of nitric acid between the mineral and organic layers. The data for sulphuric acid of 93% H_2SO_4 at 90°C are given in Table 72.

TABLE 72

INFLUENCE OF CONCENTRATION OF HNO_3 IN THE NITRATING MIXTURE ON THE RATE OF NITRATION OF DNT AND THE COEFFICIENT OF DISTRIBUTION OF HNO_3 BETWEEN THE MINERAL AND ORGANIC LAYERS

Concentration (in %) of HNO_3 in nitrating mixture	6.1	9.3	17.7	22.7	35.6	38.8	41.5
Yield of TNT (in mole/l.)							
in homogeneous system	0.420	0.455	0.510	0.535	0.375	-	-
in heterogeneous system	0.326	0.394	0.450	0.435	0.550	0.492	0.357
Coefficient of distribution of HNO_3 $\frac{\%\ HNO_3 \text{ in mineral layer}}{\%\ HNO_3 \text{ in organic layer}}$	1.24	1.20	**1.62**	0.84	0.99	0.91	1.05





o - homogeneous reaction
Δ -heterogeneous reaction

FIG. 71. Influence of the content of HNO_3 in nitrating mixtures on the rate of nitration of DNT to TNT (Orlova [2a]).

FIG. 72. Change of the rate of nitration of DNT in the presence of TNT (Orlova [2a]).

In both homogeneous and heterogeneous systems the rate of reaction increases and then falls with increasing concentration of nitric acid (Fig. 71). In heterogeneous systems the maximum corresponds to higher concentrations of HNO_3. The difference can be explained in terms of coefficient of distribution. Hence the concentration of HNO_3 in the mineral phase of the heterogeneous system reaches the value corresponding to the maximum rate of nitration when the total concentration is higher than in the homogeneous system.

This results from the rule already observed that nitration of aromatic compounds occurs mainly in the mineral acid phase.

When a large excess of nitric acid is used there is very little difference between the rate of nitration in heterogeneous and homogeneous systems. This is due to the larger excess of nitric acid present in the mineral acid phase.

Orlova has also investigated the influence on the rate of nitration of the presence of trinitrotoluene in dinitrotoluene. Table 73 gives the corresponding figures obtained in sulphuric acid of various concentrations at 100°C. The nitrating mixtures contained 10% HNO_3:

TABLE 73

YIELD OF TRINITROTOLUENE WHEN MIXTURES OF DINITROTOLUENE AND TRINITROTOLUENE ARE NITRATED

Content of TNT in the original mixture of DNT and TNT	% of dinitrotoluene nitrated within 30 min-- at concentration of sulphuric acid (in % H_2SO_4)					
%	87	91	95	98	101	104
0	7.8	21.0	22.0	-	–	-
24	7.1	19.5	22.0	-	-	-
45	2.0	18.2	22.0	-	-	-
64	0	17.5	27.5	-	-	-
84	0	26.0	48.3	74.0	75.0	78.4
92	-	-	47.0	81.1	82.7	83.9

Figure 72 shows the influence of trinitrotoluene on the rate of nitration of dinitrotoluene in heterogeneous systems at 90°C. It is interesting to note that the addition of 66-70% of trinitrotoluene to dinitrotoluene more than halves the rate of the nitration, Further increase in the content of trinitrotoluene promotes nitration of dinitrotoluene. When the content of trinitro compound reaches 91% the yield of trinitration is almost the same as that of the pure dinitrotoluene.

On the basis of her own experiments and those reported in the literature Orlova [2a] came to the conclusion that the mechanism of nitration of toluene to TNT in heterogeneous conditions can be depicted in the following terms.

Nitration of toluene to mononitrotoluene and of the latter to dinitrotoluene in heterogeneous conditions should be considered mainly a “surface” reaction. This is deduced from the fact that the rate of the reaction depends on the intensity of stirring. The reaction of nitration of dinitrotoluene to trinitrotoluene in heterogeneous system is not limited to the surface dividing the two phases. This is proved by the fact that the rate of nitration depends very little on the rate of stirring. The reactants - dinitrotoluene and nitric acid - are distributed between two phases according to their coefficients of distribution and to the ratio between the volumes of the two phases. The reaction occurs in both phases but the rate in the mineral acid phase is much higher than in the organic oil phase. In the latter it is relatively high only when the factor " Φ " is high.

This is because the organic oil phase contains only HNO_3 with practically no H_2SO_4. The rate of nitration of dinitrotoluene depends therefore largely on the solubility of dinitrotoluene in the acid layer.

To some extent the organic phase has a negative action on nitration. It is a good solvent of HNO_3 and considerably reduces the concentration of HNO_3 in the acid phase.

The secondary reaction of oxidation occurs in both the organic and mineral layers. It is likely that oxidation occurs strongly in the organic layer because of the presence of HNO_3 free from H_2SO_4.

The negative influence of the organic layer also consists in reducing the concentration of dinitrotoluene in the mineral acid phase. This occurs when the organic phase is composed mainly of molten trinitrotoluene. The distribution coefficient of dinitrotoluene between the two phases shifts the dinitrotoluene towards the organic layer. This particular negative action of the trinitrotoluene layer is less pronounced by the end of the nitration when very little dinitrotoluene is left unnitrated. To favour the reaction it is necessary to raise the temperature. Therefore the most favourable condition of heterogeneous nitration exists at the beginning of the reaction when the organic layer is composed only of dinitrotoluene. Therefore at this stage of the reaction it is possible to use less concentrated nitrating mixtures and a lower nitration temperature.

EXPLOSIVE PROPERTIES OF TNT

Decomposition of TNT during detonation, dependent on a number of factors. may be represented (Kast [57]) by the following equation:

$$16C_7H_5(NO_2)_3 = 20CO_2 + 47CO + CH_4 + H_2O + 2C_2H_2 + 2HCN + 14.5\ H_2 + 21.5\ N_2 + \\ + 3NH_4HCO + 29C$$

The heat of explosion of TNT is 950 kcal/kg, the volume of gases V_0 = 690 l/kg, the temperature t = 2820°C.

Schmidt gave [111] a number of the equations for TNT decomposition; calculated on 1000 g (4.4 moles) of trinitrotoluene. Here are two of them, for the extreme density of loadings d = 1.0 and 1.59 g/cm^3

(1) for A = 1.0 g/cm^3

$$4.4C_7H_5(NO_2)_3 = 2.84CO_2 + 17.0CO + 3.77H_2O + 2.49H_2 + 0.1C_mH_n + 0.1CH_4 + \\ + 2.85NH_3 + 0.47HCN + 0.2C_2N_2 + 4.75N_2 + 10C$$

The heat of explosion = 910 kcal/kg, the volume of gases V_0 = 773 l./kg, t = 3080°C.

(2) for $d = 1.59\ \mathrm{g/cm^3}$

$$4.4C_7H_5(NO_2)_3 = 5.47CO_2 + 9.39CO + 6.09H_2O + 1.63H_2 + 0.03C_mH_n + 0.42CH_4 + \\ + 1.5NH_3 + 0.32HCN + 0.3C_2N_2 + 5.39N_2 + 14.6C$$

The heat of explosion = 1085 kcal/kg, the volume of gases V_0 = 685 l./kg. I = 3630°C.

According to R. Robertson and Garner [112], the heat of explosion of TNT is 925 kcal/kg, and the volume of gases is 711 l./kg.

The sensitiveness of TNT to impact is very small, but because of the lack of a standard testing method, the data, reported by various authors, range within wide limits. Taking 100 for the sensitiveness of picric acid, values varying from 115 to 275 are quoted for TNT.

With increasing temperature the sensitiveness of TNT to impact increases like that of other explosives. This can be seen from Table 74, given by Rinkenbach [113].

TABLE 74

EFFECT OF TEMPERATURE ON THE SENSITIVENESS OF TNT TO IMPACT

Temperature °C	State of TNT	Height from which 2 kg weight must fall to cause explosion, cm
-40	solid	43
20	solid	36
80	liquid	18
90	liquid	7.5
105-110	liquid	5

Robertson [113a], however, reported that the sensitiveness of picric acid at 80°C is only 25% greater than that at 15°C. This may well be extended to other trinitro compounds, so it would be expected that the increase in sensitiveness of TNT with increasing temperature is less significant than that given by Rinkenbach.

T. Urbanski and Sikorska [141] recently determined sensitiveness to impact by means of the "piston apparatus" [115] (Fig. 73) as it gives uniform results at elevated temperature. The percentage of explosions were determined by striking the samples with a falling weight of 10 kg from heights of 25, 30 and 50 cm. The recoils were 4.5, 5 and 11 cm, and the calculated impact energies for a surface were 2.7, 3.1 and 5.0 $\mathrm{kgm/cm^2}$ respectively. The experiments were repeated 100 times at each height.

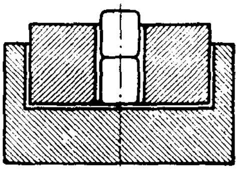


FIG 73. "Piston apparatus" of Kholevo-Andreyev [115] for determination of sensitiveness of explosives to impact.

The results are tabulated (Table 75) and presented in diagrammatic form (Fig. 74). There is a characteristic increase of the slope of the line of sensitiveness above the melting point of TNT. It is evident that the sensitiveness of molten TNT between 81°C and 100°C is well below that of tetryl at room temperature.

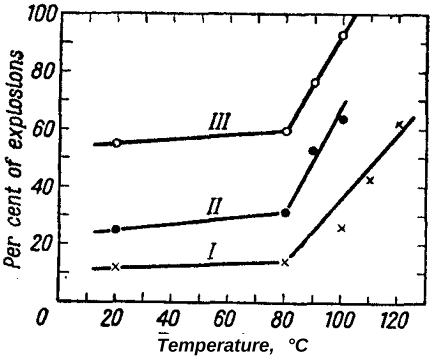


FIG. 74. Sensitiveness Of TNT to impact at various temperatures (T. Urbanski and Sikorska [114]).

TABLE 15

Substance	Temperature °C	Per cent of explosions at the height of		
		25 cm curve *I*	30cm curve *II*	50cm curve *III*
TNT	18	-	24	54
	20	11	-	-
	80	13	-	-
	81		31	59
	90	-	48	75
	100	25	63	89
	110	43	-	-
	120	62	-	-
Picric acid	18	-	50	75
Tetryl	18	48	81	94

The sensitiveness of TNT at 90°C is of the order of that of picric acid at room temperature.

In any case the handling of liquid TNT requires more safety measures than solid TNT, though the fact that detonation in molten TNT proceeds only with great difficulty reduces the danger. TNT becomes more sensitive when such solid substances as for example ammonium nitrate, are added to it (Vol. IV). Addition of sulphur also increases the sensitiveness to impact (T. Urbanski and Pillich [93]).

The sensitiveness of TNT to friction is also very low, but becomes higher when TNT is in the molten state.

TNT gives a lead block test figure of 260-310 cm^3, according to various authors, which is 94-98% of that given by picric acid. In a mortar it gives a value 90% of that for picric acid and its sand test value is 95% of that for picric acid.

The rate of detonation of TNT, as reported by various authors, is given in Table 76.

TABLE 76

RATE OF DETONATION OF TNT (m/sec)

Density of loading g/cm^2	according to Kast *[57]	according to Friedrich** [116]	according to Roth*** [117]	according to Cybulski**** [118]
0.25		2385	-	
0.56	-	3100	-	
0.83		4100	-	-
1.10		-	-	5250
1.21	-	4720	4720	
1.34	5940		-	-
1.40	-		5900	
1.45	6400		-	
1.50	6590		-	
1.52	-		7400	
1.60	6680		-	-
1.62	-	6990	-	6930

* For charges 21 mm in diameter. initiated by a 2 g detonator, in the open.

** In a metal pipe 10-15 mm in diameter.

*** Charges in bakelite pipes of 4.5-8.2 mm internal diameter.

**** In a steel pipe 31.7 mm in diameter.

Values ranging from 6900 to 7000 m/sec are usually accepted as the maximum rate of detonation of TNT.

Such outstanding advantages of TNT, its low sensitiveness to impact and friction, safe handling, considerable safety in storage (because of the low reactivity of the compound), relative safety in manufacture and relatively high explosive power, have made TNT the most widely used of all high explosives since the beginning of the twentieth century up to the present time.

As an explosive, TNT is used both compressed (in demolition charges) and in the cast form in shells and also in demolition charges. In the latter case detonators comprising compressed charges of TNT, tetryl, hexogen, or penthrite are used.

For large calibre armour-piercing shells, the sensitiveness of TNT alone is too high so it is usually diminished by adding a small quantity (1-2%) of desensitizing or "phlegmatizing" substances such as ozokerite, bee's wax or paraffin. The last is the least efficient because of its non-polar structure. Desensitized TNT was proved to be expedient during the great naval battle between the German and British fleets at Skagerrack in 1916. The British battleships *Indefatigable, Queen Mary, Invincible, Black Prince* and *Defence,* were sunk by the fire of the German fleet which was using desensitized TNT, whereas the British shells loaded with picric acid mostly exploded on impact and failed to penetrate the armour of the German warships, causing no damage.

TOXICITY OF α– TRINITROTOLUENE

There is a considerable diversity of opinion as to the toxicity of trinitrotoluene. In Germany the substance is considered to be completely or almost completely non-toxic, while in Great Britain it is regarded as a highly toxic material. The reason for these divergent views has not been fully explained.

In the opinion of Koelsch [119], Curshmann [120], Van Duin [121], and others, pure α– trinitrotoluene is non-toxic. They consider that impurities present in TNT, such as dinitrobenzene and tetranitromethane, are responsible for any toxic effects caused by TNT. According to Koelsch, idiosyncrasy manifested by poisoning symptoms, has heen met with.

As reported in German and French official literature, the manufacture and use of TNT has not been connected with any great difficulties from the viewpoint of industrial hygiene. Nevertheless, some data indicate that cases of poisoning by TNT, sometimes fatal, have happened. Thus, in the Darmstadt district in the period between 1915 and 1918, 443 cases of poisoning by nitro compounds (mainly TNT) were registered. Among them 13 were fatal (10 women and 3 men).

The wide demand for TNT during World War I compelled factories to hasten manufacture, sometimes with insufficient regard for industrial hygiene. In some countries (e.g. Great Britain, the U.S.A.) during the 1914-1918 war numerous illnesses or even deaths of people employed in TNT manufacture, filling shells etc., were registered:

Year	Number of cases	Fatalities
1916	181	52
1917	189	44
1918	34	10

The fall in the number of poisoning cases registered in 1918, was mostly the result of introducing stricter measures and appropriate safety regulations.

The Germans (e.g. Koelsch [119]) assert that the numerous cases of poisoning that occurred in Great Britain were caused mainly because benzene was present in the toluene used for nitration, thus giving rise to the formation of dinitrobenzene.

However, the results of the investigations carried out by British physicians do not agree with the German data. They show that chemically pure α– trinitrotoluene is as poisonous as the crude product. Finally, the view has been accepted in Great Britain that the small number of poisoning cases that occurred in Germany should be ascribed to the fact that TNT had been manufactured in Germany for many years before the World War I, so that the production processes (including safety regulations) had become well established, whereas in Great Britain TNT manufacture was something new and it was not until 1917 that the proper level of industrial hygiene was achieved in the factories and the appropriate regulations were framed.

In one of the ammunition factories in the United States, 17,000 poisoning cases, including 475 fatal cases, occurred during the first seven and a half months of World War I. They were supposed to be caused by TNT as this was a period of hasty production of ammunition. During the 20 months that followed, the number of poisoning cases fell to 7000, including 105 fatal cases.

Investigations by Legge [122] have demonstrated that the following toxic effects are produced by TNT:

(1) Irritation of the digestive tract (not differing from a similar effect produced by other agents).

(2) Methaemoglobinaemia (and the effects induced by oxygen deficiency): disturbed heart function, liver and kidney trouble and a dysfunction of the whole vascular system.

(3) A particularly harmful, effect on the liver tissues, causing severe jaundice, which in 25-30% of cases may end in death.

(4) Aplastic anaemia, manifesting itself by a fall of the number of red and white corpuscles, caused by the dysfunction of the bone marrow. Almost all of these cases end in death.

As Moore [123] believes, poisoning can occur when TNT is absorbed through the skin.

In 1918 a special medical committee in Great Britain published a statement on TNT poisoning. The committee believed that disturbances in the digestive tract are not decisive symptoms, and if caused by other factors may lead to wrong conclusions. Yellow stains on the skin, usually appearing when working with TNT, are not indubitable symptoms of poisoning. The presence of trinitrotoluene in the urine (Webster’s test [124]) should not be considered as a proof of poisoning. The real symptoms are :

(1) Paleness of face, a grey colour of lips, which disappears upon excitation. Sometimes the lips and the tongue may even be a violet colour.

(2) Stomach ache, characteristically localized.

(3) Constipation and flatulence.

If no jaundice has appeared, the treatment is simple, and the prognosis is good. The treatment should consist in:

(1) Isolation of the patient from contact with TNT and allowing plenty of fresh air.

(2) Staying in bed for one or two days.

(3) A special diet, consisting of milk, milk dishes, fruit and vegetables, and beverages such as tea and coffee.

Where jaundice occurs clinical treatment is necessary. The patient should be given milk, starting with small portions increasing to one liter daily.

Young people are far more liable to TNT poisoning than adults. For the first four working weeks some people exhibit a considerable resistance to poisoning, others fall ill within the fifth and the fifteenth week of work.

Here are the principal precautionary measures which should be strictly observed.

(1) The age of workers in TNT factories should not be below 18 years.

(2) All workers should be submitted to medical examination before starting work, and subsequently should be examined every week.

(3) Workers should be protected against dust, and as far as possible against skin contact with TNT. Working places should be adequately ventilated.

(4) Special working clothes put on in the changing room. They should fit tightly at the wrists, and neck, to prevent the penetration of dust. Hair should be covered with a cap or other form of protective head dress. This protective clothing should be washed every week.

(5) Personal cleanliness is imperative. All workers should wash before meals and before going home.

(6) Before starting work they should drink a pint or so of milk. Eating fresh vegetables should be recommended.

(7) Workers in TNT factories should be transferred periodically to other work, out of contact with TNT.

Norwood [124a] suggested using a special liquid soap to remove TNT from the skin. The liquid soap should contain 5-10% K_2SO_4 and 5-10% of a wetting agent.

There is no doubt that TNT is toxic to man. Experience gathered in the World War II has supplied statistical data which confirm this. Branslavljevic [125] gives the following data. Out of 66 workmen employed in a Yugoslavian factory in the section where ammunition was filled with TNT, 42 persons showed symptoms of poisoning such as cyanosis, pallor and jaundice.

Liver damage was confirmed in 19 workmen, another 19 suffered from anaemia, and in 5 a combination of both conditions was found.

Crawford [126] recorded 24 cases of aplastic anaemia in Great Britain, all of them the result of exposure to TNT during World War II.

Statistical data referring to the World War II reported for some thousand mild cases of poisoning by TNT in the U.S.A. apart from 379 more serious cases and 22 fatal ones. Eight men died of toxic hepatitis, 13 of aplastic anaemia and 1 of a combination of both (McConnell and Flinn [127]). The same authors reported that at a TNT dust concentration in the air amounting to 3 mg/m^3, distinct poisoning symptoms were observed. According to these authors, the maximum permissible concentration of TNT in the air is 1.5 mg/m^3.

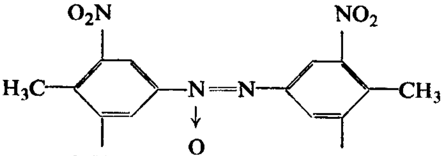
An important observation made by Larionovi [128] was that TNT, present in waste waters in a concentration of 25-80 mg/l., lowered the oxygen consumption of bacteria by 5-30% possibly because it inhibited their activity. In addition, TNT has been found toxic to some seaweeds and to fish.

According to Kratz [129], 1 mg of TNT in 1 l. of water kills fish. Seifert [130] reported that the lethal dose for fish was 2 mg of TNT in 1 1. of water, while a concentration of 0.15 mg TNT/l. might be lethal to plankton which form the principal nourishment for fish. For this reason the problem of decontamination of waste water from TNT manufacture is of primary importance (see further, p. 390).

METABOLISM OF TRINITROTOLUENE

Detailed studies on the metabolism of trinitrotoluene in the human body and in animals were carried out during World Wars I and II. They have since been published.

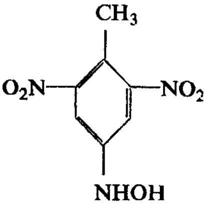
Voegtlin, Hooper and Johnson [131] reported that trinitrotoluene was reduced to dinitrotoluidine of an unknown structure, and to tetranitroazoxytoluene, the constitution of which was given later by Dale [132] :


I

This compound can be found in urine.

Extensive studies on the metabolism of α– trinitrotoluene in man and animals have been published by Channon, Mills and R. T. Williams [133]. The authors were able to prove that tetranitroazoxytoluene was not present in fresh urine, but was found as a product of an in vitro reaction between various products of metab olism.

The following amines and hydroxylamines were isolated from the urine of animals receiving TNT :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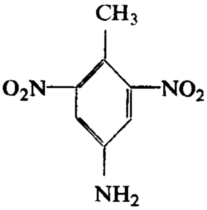
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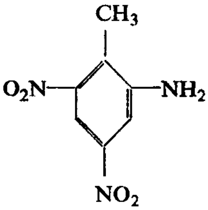
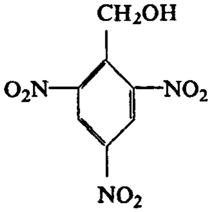
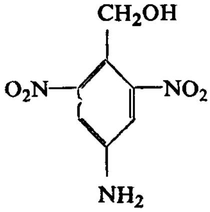

IV

The azoxy compound is presumably formed during the oxidation of product II. In addition, oxidation products and oxidation-reduction products are formed:



V



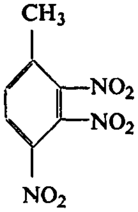
VI

Compound II is highly toxic. It results in the formation of methaemoglobin. The presence of trinitrotoluene in the human body leads to an enhancement of the formation of glucuronic acid, which reacts with the alcohols V and VI to form the corresponding esters.

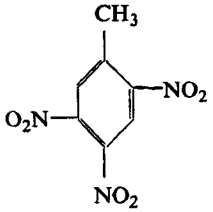
The formation of the amines III and IV has also been observed by Lamberg and Callaghan [134].

UNSYMMETRICAL ISOMERS OF TRINITROTOLUENE

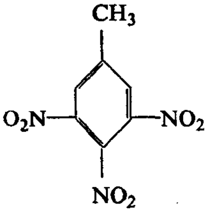
The following unsymmetrical trinitro derivatives of toluene are known:



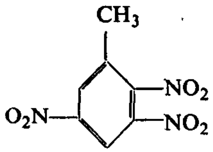
β
2,3,4-
m.p. 112°C



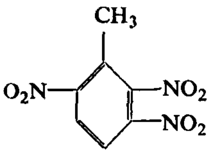
γ
2,4,5-(3,4,6-)
m.p. 104°C



δ
3,4,5-
m.p. 137°C



ε
2,3,5-
m.p. 97.5°C



η (ζ)
2,3,6- (2,5,6-)
m. p. 111°C

All isomers are formed by nitration of *m*- nitrotoluene. Hepp [35] isolated the β– and γ– isomers from the product of a severe nitration of *m*- nitrotoluene. Their structures have been determined by Will [37].

In a number of detailed investigations Marqueyrol, Koehler and Jovinet [135, 136, 137] and their colleagues found that the η– isomer is also formed during the nitration of *m*- nitrotoluene. Attempts to find the δ– and ε– somers in the products of nitration of *m*- nitrotoluene were originally unsuccessful. These compounds were obtained by an indirect method. Later de Beule [31] succeeded in obtaining all isomers by nitrating *m*- nitrotoluene. His results are summarized in the diagram (p. 328). The composition of crude TNT is according to de Beule: 95.1% of α– isomer, 1.36% of β–, 2.69% of γ–, 0.002% of δ–, 0.29% of η– and 0.009% of ε– isomer, and also unchanged 2,3-, 2,5- and 3,5-dinitrotoluenes in quantity of 0.33, 0.15 and 0.06% respectively.

The nitration of *m*- nitrotoluene was also studied by Brady and his co-workers [136-139] and by Drew [140].

PHYSICAL PROPERTIES

The physical properties of the unsymmetrical isomers of trinitrotoluene are similar to those of α– trinitrotoluene. They are crystalline substances of a pale yellow colour, soluble in most organic solvents, insoluble in water and non-hygroscopic.

THERMOCHEMICAL PROPERTIES

Heat of crystallization. Garner and Abemethy [3] found the following values for the heats of solidification of the β– and γ– isomers:

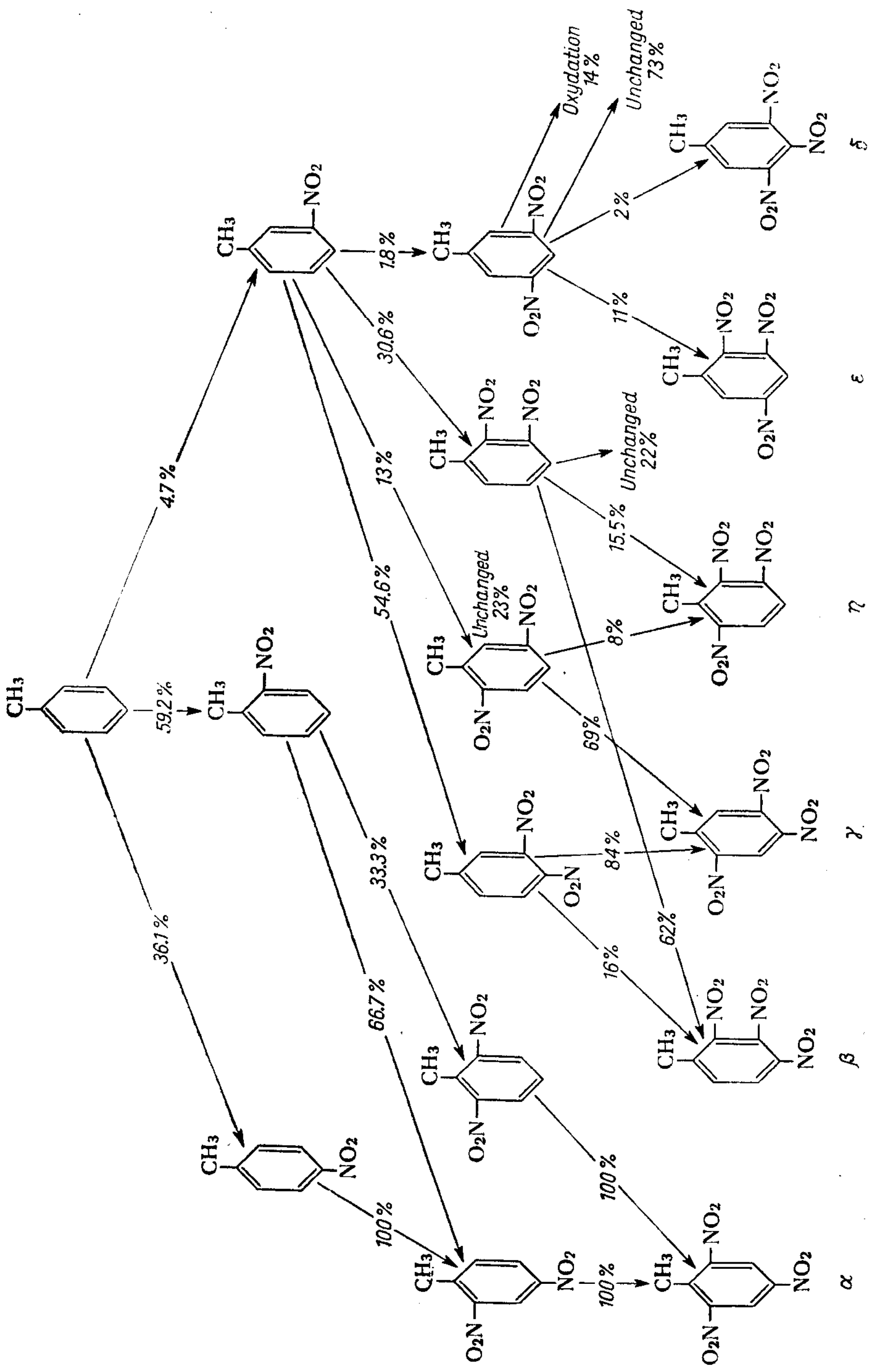
β– trinitrotoluene 5.0 kcal/mole
γ– trinitrotoluene 5.4 kcal/mole

Heat of combustion and heat of formation. The same authors give the following values for unsymmetrical trinitro derivatives of toluene (Table 77).

TABLE 71

HEATS OF COMBUSTION AND FORMATION OF UNSYMMETRICAL ISOMERS OF TRINITROTOLUENE

Isomer	Heat of combustion (at constant volume) with a correction for nitric acid kcal/mole	Heat of formation (for amorphous carbon), kcal/mole
β– trinitrotoluene	834.1	+16.9
γ– trinitrotoluene	827.4	+24.2
δ– trinitrotoluene	829.9	+21.7
ε– trinitrotoluene	825.6	+26.0
η– trinitrotoluene	827.1	+24.5



Isomers formed on nitration of toluene according to de Beule.

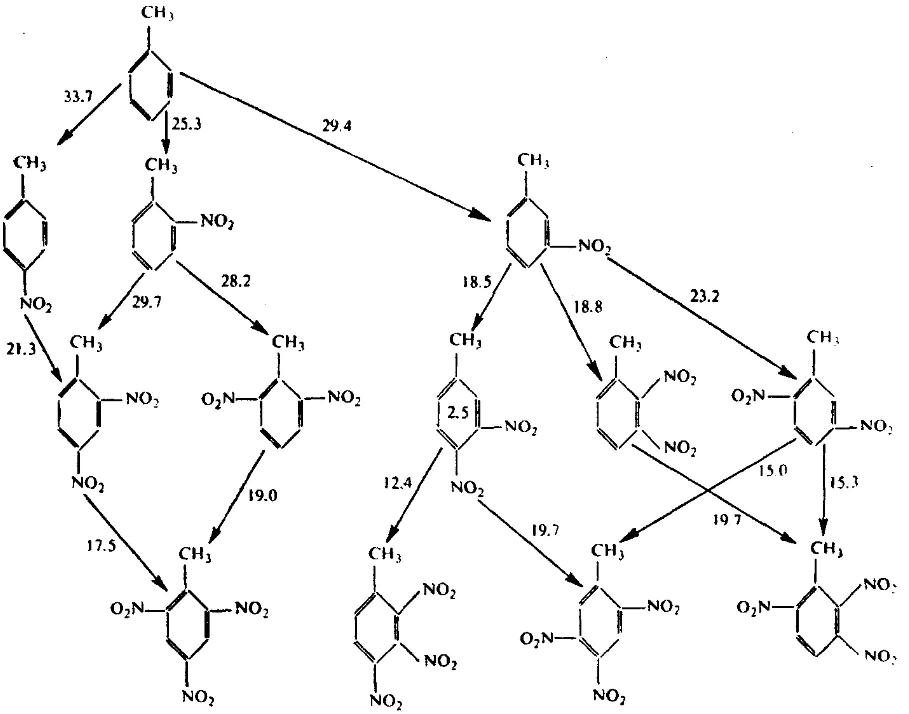
Heat of nitration. Heats of direct conversion of dinitrotoluenes to trinitrotoluenes are listed in Table 78 (after Gamer and Abemethy [3]).

TABLE 78

HEATS OF NITRATION OF DINITRO- TO TRINITRO-TOLUENE

Starting compound	Product	Heat, kcal/mole
3,4-Dinitrotoluene	2,3,4-trinitrotoluene	12.4
	2,4,5- (3,4,6) „	19.7
2,3 ,,	2,3,4- „	12.1
	2,3,6- „	19.7
2,5 ,,	2,4,5- (3,4,6-) „	15.0
3,6 ,,	2,3,6- „	15.3

SCHEME OF NITRATION OF TOLUENE*



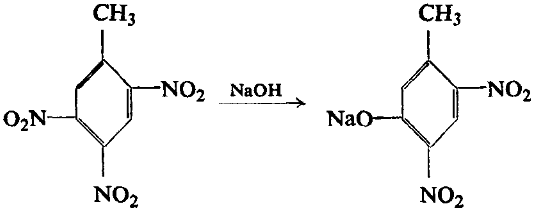
The figures accompanying the arrows indicate heats of reaction, in kcal/mole.

CHEMICAL PROPERTIES

The chemical properties of the unsymmetrical isomers of trinitrotoluene are in some respects similar to those of α– trinitrotoluene, e.g. they are not affected by acids. However, they differ from α– trinitrotoluene as their nitro group, located in the meta position to the CH_3 group, is rather mobile as it is in the *ortho* or *para* position to other nitro groups. Such mobile nitro groups are easily substituted. Here are the characteristic reactions, as shown by the most important γ– isomer.

Reactions with alkalis

The unsymmetrical isomers of trinitrotoluene readily react with aqueous solutions of sodium or potasium hydroxide, forming salts of dinitrocresol (Will [37]):

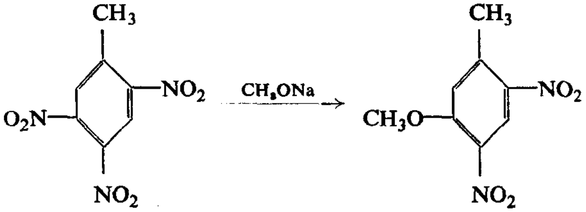


(25)

The reaction can take place at room temperature. The reaction with sodium carbonate at a temperature corresponding to the boiling point of alcohol, occurs in a similar way.

Brady [137] found that a concentrated solution of sodium acetate acted on unsymmetrical trinitrotoluene in a way similar to the action of weak alkalis, giving the corresponding dinitrocresols. Under such conditions less ill-defined amorphous products were obtained than in the reaction with strong alkalis, where they were formed in great quantities.

Under the influence of an alcoholic solution of sodium- or potassium methoxide or ethoxide one of the nitro groups may be replaced by the methoxy or ethoxy group :



(26)

Sodium hydroxide gives the following colour reactions with the unsymmetrical isomers of trinitrotoluene (Table 79).

TABLE 79

COLOUR REACTIONS OF THE UNSYMMETRICAL ISOMERS OF TRINITROTOLUNE WITH SODIUM HYDROXIDE

Isomer	Sodium hydroxide	
	in acetone solution	in alcohol-acetone solution
β	violet, bright	green, bright
γ	violet-greyish	blue with a violet tinge
η	light pink	red

Ammonia gives similar colour reactions.

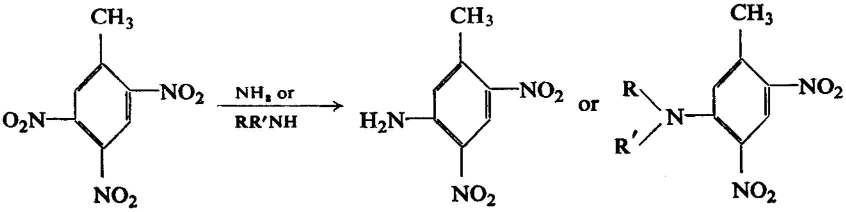
The unsymmetrical isomers of trinitrotoluene also give specific reactions with sodium carbonate and with lead oxide. The former also affects the ignition temperatures of the isomers. The corresponding data are tabulated below, in Table 80 (after Brunswig [141]).

TABLE 80

SPECIFIC REACTIONS OF THE UNSYMMETRICAL ISOMERS OF TRINITROTOLUENE WITH Na_2CO_3 AND PbO

Isomer	Reaction with boiling alcohol solutions		Ignition temperature, °C	
	Na_2CO_3	PbO	Pure isomer (0.29)	Compound (0.75 g) with some quantity of Na_2CO_3 (0.05 g)
α	forms brown salts (addition products)	no change	290	231
β	readily forms sodium dinitrocresolate	forms lead dinitk-cresolate	302	211
γ	,,	,,	291	194
δ	,,	,,	313	252
ε	some sodium dinitrocresolate is obtained, being formed very slowly	reacts only with great difficulty	332	249
η	sodium dinitrocresolate is formed	lead dinitrocresolate is formed	335	269

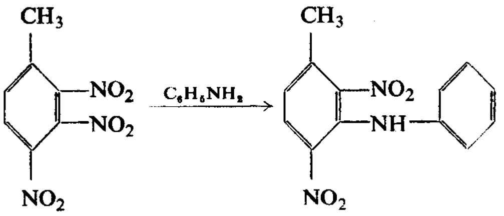
Reactions with ammonia or with amines lead to the formation of dinitrotoluidine or its N-substituted derivatives:



(27)

The reaction with ammonia in an alcoholic solution may proceed both in the hot and in the cold (Hepp [35]; Giua [46]). It may be utilized for the identification of amines (Brown and Campbell [142]). It has also been utilized for determining the structure of unsymmetrical isomers of trinitrotoluene (p. 336). The isomers react with hydrazine and phenylhydrazine in a similar way.

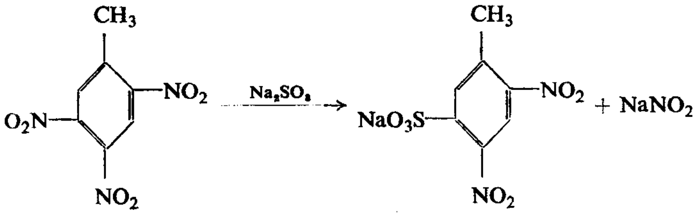
Brady, Hewetson and Klein [139] studied the action of aromatic amines on unsymmetrical trinitrotoluene. They obtained diphenylamine derivatives, e.g. :



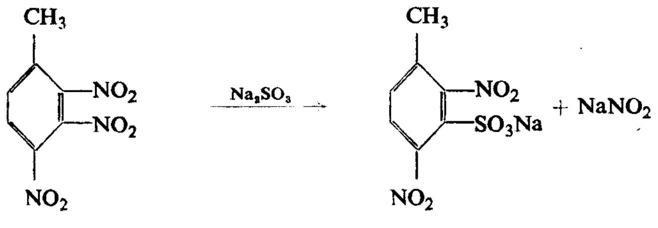
(28)

Reaction with sodium sulphite

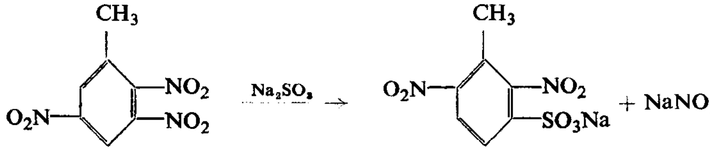
This reaction is of great practical importance, since it is the simplest and most frequently used way of removing the unsymmetrical isomers from crude TNT. The reaction involves the following transformations, taking place at room temperature:



(29a)



(29b)

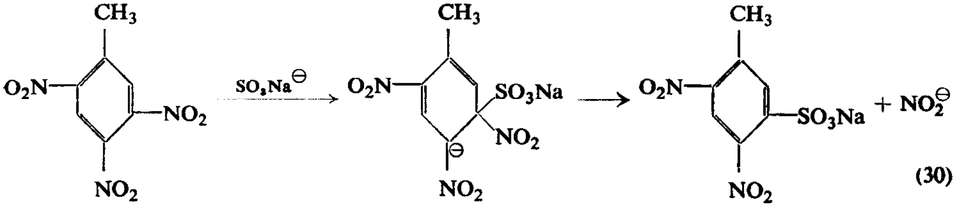


(29c)

The solution of sodium dinitrotoluenesulphonates formed is of a characteristic light red colour. The reaction is carried out using either a 2-3% solution at a temperature of 70-80°C or a 6-8% solution at room temperature to 30°C.

Brady, Hewetson and Klein [139] tried to elucidate the mechanism of the reaction of sulphitation of unsymmetrical trinitrotoluenes. They assumed the formation of an addition product of sodium sulphite and the nitro compound in the first stage.

This is a nucleophilic reaction, and its mechanism, according to the author of the present book, may possibly be represented as follows:



(30)

The reaction was first mentioned by Laubenheimer [143] when examining chloro-3,4-dinitrobenzene. However for a long time no notice was taken of the possibility of putting it into practice. It was only during World War I that the method was introduced in the U.S.A., and this happened quite accidentally. In the search for methods of removing unsymmetrical isomers from crude TNT, the reduction of trinitrotoluenes was studied. It was hoped that the nitro group in the meta position, being chemically more active, would be more easily reduced, and that the reduction product would be relatively soluble in water. Sodium polysulphide was used for the reduction. However, it was found that the product of the reaction was strongly contaminated with sulphur formed at the reaction. Among other reducing agents used, sodium sulphite was shown to be a very efficient one in removing unsymmetrical isomers, its action consisting, however, not in the reduction of the nitro group, but its replacement by a sulpho group.

As Muraour [103] found, the reaction of sodium sulphite was not confined to unsymmetrical trinitro derivatives of toluene. α– Trinitrotoluene also reacted with Na_2SO_3 to form dinitrotoluene sulphonic acid, the difference lying in the fact that the reaction proceeds much more slowly than with unsymmetrical isomers. A 3% solution of Na_2SO_3, acting for 1 hr, dissolves at room temperature about 1% of α– trinitrotoluene.

According to the British literature of World War I, the optimum temperature of sulphitation is 40-45°C. At higher temperatures α– trinitrotoluene reacts too vigorously, which results in a certain loss of the product. On the other hand, the action of sulphite on the unsymmetrical isomers at lower temperatures is too slow.

Since solutions of sodium sulphite are alkaline, which affects TNT unfavourably, a number of workers have developed other methods consisting in lowering the pH of the sodium sulphite solution by adding buffers.

Thus G. P. Davies [144] suggested the use of the Na_2SO_3 solution with such buffers as mono- and di-sodium phosphates or boric acid, which reduce the pH to 7.0-8.3.

In industrial practice, losses of crude TNT in the sulphitation process amount from 6 to 8%. Out of this 2%-3.5% is ascribed to the loss of α– trinitrotoluene and 3.5-4.5% to that of unsymmetrical isomers and other impurities, such as tetranitromethane (p. 339) and trinitrobenzene which is easily soluble in sodium sulphite, forming addition products.

Muraour observed the important fact that trinitro-m-xylene reacts with sodium sulphite only with great difficulty, while trinitromesitylene does not react with it at all. Tetranitromethane, which is a common impurity of TNT, reacts with sodium sulphite to yield a water-soluble salt of sulphonic acid (p. 339).

After sulphitation, the setting point of TNT rises on the average by 2.2°C (e.g. from 78.0°C to 80.2°C).

Barbiere [145] examined quantitatively the process of sulphitation of α–, β– and γ– trinitrotoluenes using a 6% solution of Na_2SO_3 at different temperatures (30-60°C) and in another series of experiments the influence of the concentration of sodium sulphite solution on the solubility of the isomeric trinitrotoluenes at 30°C. He also determined:

(a) the total solubility of α– trinitrotoluene (S_1) which includes both the formation of the soluble addition compound and sodium salts of nitrosulphonic acids;

(b) the "irreversible" or "real" or permanent solubility (S_2) which is caused only by formation of sodium salts of nitrosulphonic acids.

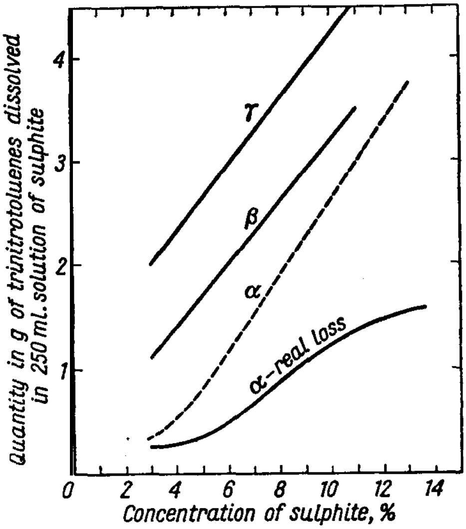


FIG. 75. Influence of the concentration of sodium sulphite solution on solubility of α–, , β– and γ– trinitrotoluene (Barbiére [146a]).

This was determined by diluting the solution to hydrolyse the addition compounds. Precipitation of recovered α– trinitrotoluene gives the "transient" solubility (S_3). By definition $S_2 = S_1 - S_3$.

Some of Barbiére's results are given in Fig. 75. Here both the total and real solubility of α– trinitrotoluene are shown.

D. Smolenski and Plucinski [146] made a thorough study of the sulphitation of *a*-, β– and γ– trinitrotoluenes. Some of their results are summarized diagrammatically in Fig. 76 which illustrates the influence of sulphitation temperature on total, permanent and transient solubility of a-trinitrotoluene in solutions of sodium sulphite of different concentrations. The trend of the curves is similar to that found earlier by Barbiére [145].

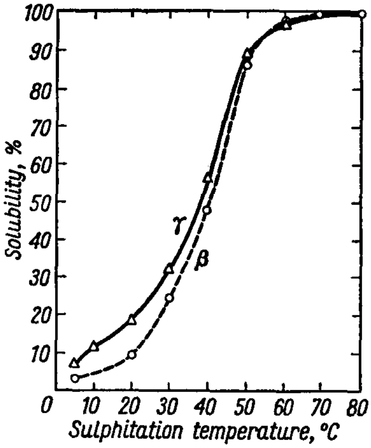


FIG. 76. Influence of the temperature of sulphitation on the solubility of α– trinitrotoluene at different concentrations of sodium sulphite (Smolenski and Plucinski [146]).

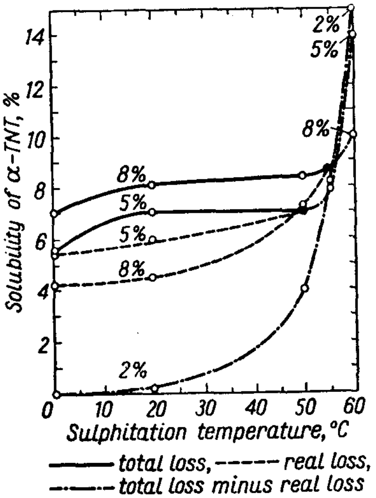


FIG. 77. Influence of the time of sulphitation on the solubility of a-trinitrotoluene at different temperatures and constant concentration (4%) of sodium sulphite (Smolenski and Plucinski [146]).

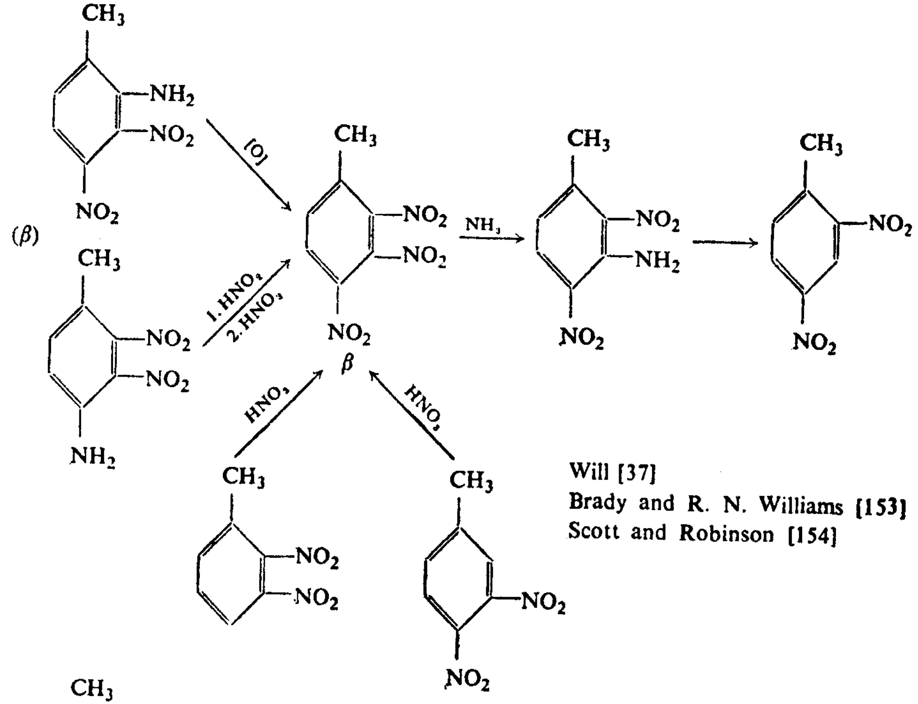
The influence of the time of sulphitation on the solubility of β– and γ– trinitrotoluene at different temperatures according to D. Smolenski and Plucinski [146] is given on the Fig. 77.

Effect of light

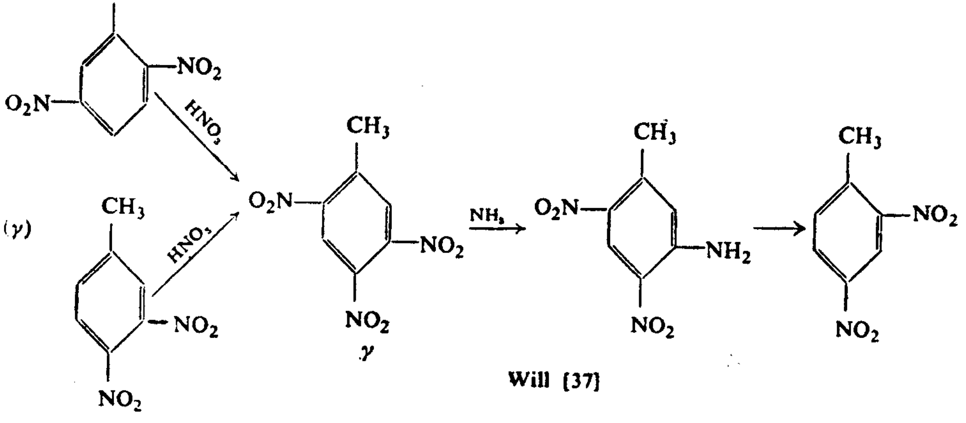
The unsymmetrical isomers of trinitrotoluene are affected by light in an apparently similar way, as in the instance of α– isomer, turning brown on exposure to sun. However, the chemical nature of the process has not been investigated.

PREPARATION AND CONSTITUTION OF UNSYMMETRICAL TRINITROTOLUENES

The following reactions give an indication of structure and the mode of preparation of the isomers:

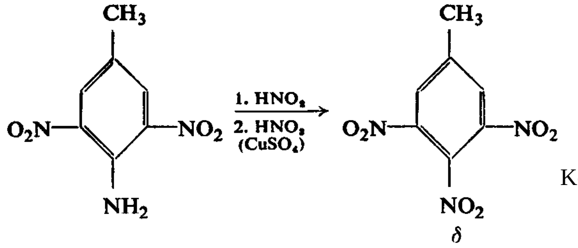


Will [37]
Brady and R. N. Williams [153]
Scott and Robinson [154]



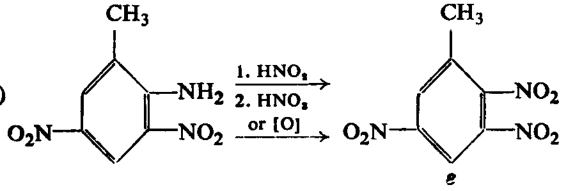
Will [37]

(δ)



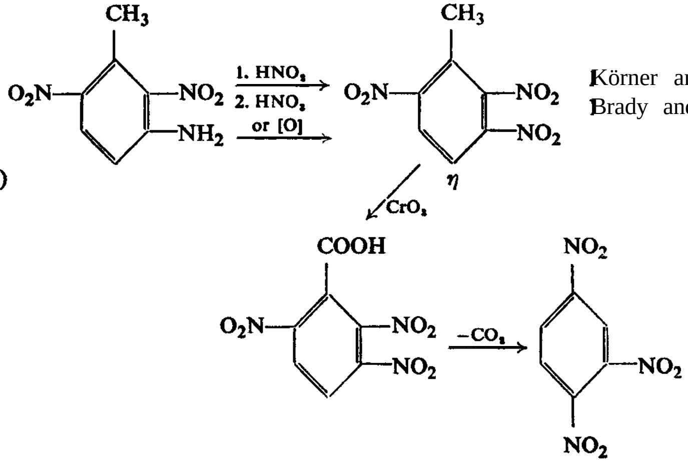
Körner and Contardi [155]

(ε)



Körner and Contardi [156]
Brady and R. N. Williams [153]

(η)



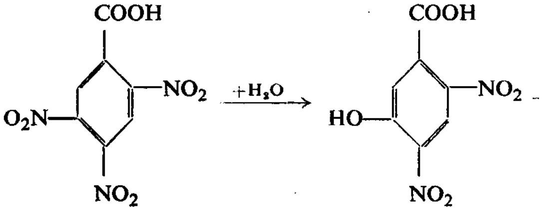
Körner and Contardi [158]
Brady and Taylor [136]

OTHER BY-PRODUCTS IN THE NITRATION OF TOLUENE

Apart from the unsymmetrical isomers of trinitrotoluene, other by-products are formed in the nitration process, owing to oxidation or decomposition processes.

Oxidation leads to the formation of di- and tri-nitrocresols, impurities frequently met with in TNT. Nitrocresols are mainly formed during the nitration of toluene to mononitrotoluene (Noelting and Forel [11]). If they have not been removed from mononitrotoluene by washing with alkalis, they undergo either further nitration to trinitrocresol, or oxidation to oxalic acid. Trinitrocresol may be removed from TNT by mild alkali washing (e.g. with a $NaHCO_3$ or a sodium sulphite solution).

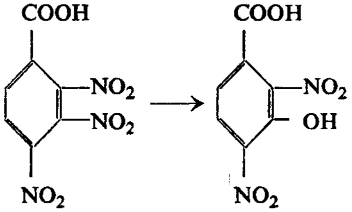
During the trinitration the methyl group is oxidized to the carboxyl group. The trinitrobenzoic acids behave in different ways in the course of hot washing of crude TNT. Thus 2,4,6-trinitrobenzoic acid is readily decarboxylated and sym-trinitrobenzene results (p. 254). According to Schmidt [147], 2,4,5-trinitrobenzoic acids gives rise to hydrolytic denitration to yield 2,4-dinitro-5-hydroxybenzoic acid (I).



I

(31)

It is probable that 2,4-dinitro-3-hydroxybenzoic acid (II) can also be formed in the similar way :



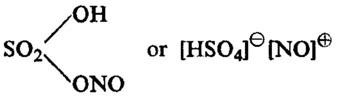
II

(32)

Also hydroxy-2,4,6-trinitrobenzoic acid (III) can be present among the other by-products in the formation of trinitrotoluene.

Hydroxynitro acids (I), (II) and (III) are (according to Schmidt) washed from the crude TNT and are present in the wash-waters. Trinitrobenzoic acids remain in TNT as impurities. The trinitrobenzoic acids formed are readily decarboxylated. CO_2 is evolved and only trinitrobenzenes remain in TNT as its impurities.

As a consequence of the strong oxidation processes occurring mostly during the trinitration (naturally at the expense of nitric acid) a relatively large quantity of nitrous acid is formed, which in sulphuric acid medium gives nitrosyl sulphuric acid :



$$SO_2\begin{cases} OH \\ ONO \end{cases} \quad \text{or} \quad [HSO_4]^{\ominus}[NO]^{\oplus}$$

According to Kobe and Lakemeyer [17], the nitrosylsulphuric acid represents about 17 wt. % of the total amount of spent acid from the trinitration. Its presence would subsequently considerably affect the process of the nitration of toluene to the mononitro-product, since it makes 14-17 wt. % of the acid used for the mononitration.

According to Gorst [2], the rate of the oxidation reactions falls with increase in the value Φ, or in other words with the increase of concentration of H_2SO_4 in the nitrating mixture or in the spent acid. A diagram (Fig. 102) related to nitration of dinitroxylene is given on the (p. 396).

Sapoihnikov (according to Gorst [2]) established that the losses of nitric acid during the nitration of DNT to TNT amount to 70-75% due to oxidation processes, the rest (25-30%) being due to evaporation of nitric acid.

Complete decomposition resulting from a vigorous nitration (with the loss of ca. 5% of toluene) may lead to the formation of the products: NH_3, CO, CO_2, etc. [158] (p 76).

Reduction products of nitric acid, such as nitrogen and nitrogen oxides can also be formed as the result of oxidation processes. Niederer [148] found that N_2 and NO were not formed in the nitration of nitro- to dinitrotoluene, while they were present in the nitration products of di- to tri-nitrotoluene. In addition to nitrogen and nitrogen oxide, carbon mono- and dioxide were formed in the last stage of nitration. Their amount and the CO to CO_2 ratio increased with temperature.

According to Eastman [158] the percentage of CO may be sometimes so high as to cause a gas explosion in the nitrator.

The break-down of the molecule, and the loss of the methyl group, may lead to the formation of tetranitromethane during the nitration process. This substance is always encountered in TNT as an impurity, and its presence can be established by its characteristic smell reminiscent of that of nitrogen oxides.

It has been suggested that tetranitromethane increases the sensitiveness of TNT to impact, friction and high temperature. That is, why the removal of this impurity is very advisable, the more so because in the course of time it transforms into nitroform, $CH(NO_2)_3$, an acid substance readily yielding salts which are sensitive to thermal and mechanical stimuli. The simplest way of removing tetranitromethane consists in treating it with sodium sulphite, which reacts in the following way:

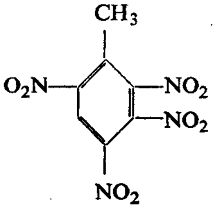
$$C(NO_2)_4 + Na_2SO_3 \rightarrow C(NO_2)_3SO_3Na + NaNO_2 \qquad (33)$$

The sodium salt of trinitromethanesulphonic acid is readily soluble in water. It is unstable and, according to Muraour [103], undergoes further hydrolysis:

$$C(NO_2)_3SO_3Na + H_2O \rightarrow CH(NO_2)_3 + NaHSO_4 \qquad (34)$$

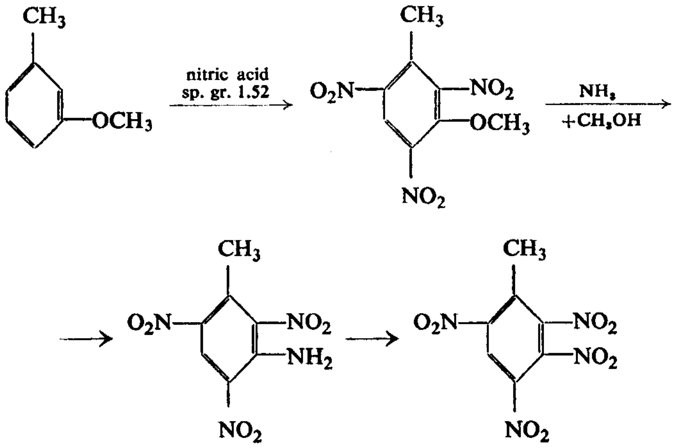
According to Kostevitch [159] tetranitromethane can be responsible for the formation of “tarry matters“.

TETRANITROTOLUENE



m.p. 136.5°C

The compound cannot be obtained by direct nitration of trinitrotoluene. It was first obtained by Holleman [149] from the methyl ether of *m*- cresol:



(35)

The starting product is nitrated with anhydrous nitric acid (sp. gr. 1.52) to the trinitro compounds. The methoxy group of the latter, on boiling with ammonia in methyl alcohol, can be substituted by an amino group.

The trinitro-m-toluidine thus obtained is oxidized in sulphuric acid solution with potassium persulphate. The yield of this stage of the reaction is about 85% of theory. The tetranitrotoluene thus prepared may then be recrystallized from nitric acid of a sp. gr. of 1.40.

Tetranitrotoluene is much more stable than tetranitrobenzene. It is considerably. more resistant to hydrolytic action of water. At room temperature the presence of trinitrocresol cannot be detected earlier than 24 hr; at 80°C only 57% of the product is converted within this period.

Holleman reported the following explosive properties of tetranitrotoluene :

Lead block test	327 cm^3
Sensitiveness to impact (2 kg falling weight)	50 cm

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CHAPTER IX

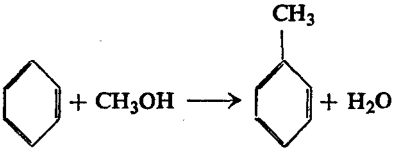
TNT MANUFACTURE

TOLUENE

TOLULENE is the principal raw material for the manufacture of TNT. It is produced from light oil and from the gases obtained by the dry distillation of coal.

In some oil producing countries (e.g. U.S.S.R.), toluene is obtained from aromatic fractions of petroleum or by aromatization of heavy petroleum hydrocarbons by cracking processes (in Poland studies on aromatization of petroleum were carried out by K. Smolenski [1] between 1922 and 1939). In war-time the demand for toluene for nitration was so large, that these two sources were inadequate. During World War II new methods of toluene manufacture on an industrial scale were developed starting from benzene and methyl alcohol and from n-heptane.

The reaction of toluene formation from benzene and methyl alcohol can be represented by the following scheme:

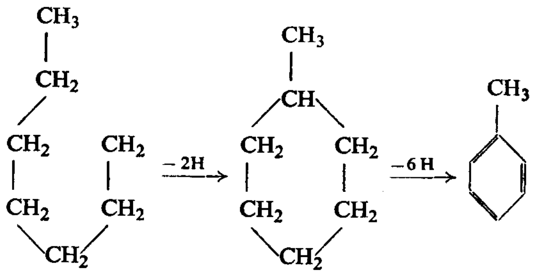

(1)

The reaction proceeds at a temperature of 340-380°C and at pressure of 30-35 atm in the presence of zinc diphosphate on silica catalyst.

Since under these conditions higher homologues of toluene (xylenes, etc.) can readily be formed, a large excess of benzene is used for the process. The yield of toluene obtainable by this method (calculated on methyl alcohol) is close to the theoretical one.

In Germany, during World War IL nearly 4000 tons of toluene were produced monthly by this method.

The method of preparation of toluene from n-heptane was mainly developed in the U.S.A. It is based on the following reaction:



(2)

It is carried out at 480-530°C at a pressure of 15 atm in the presence of a Cr_2O_3 + + MoO_3 catalyst, on a Al_2O_3 or MgO carrier. The yield obtained amounts to 72% of the theoretical.

Crude toluene obtained by this method contains 3-5% olefins, so it must be purified by refining with sulphuric acid, followed by washing with water and distillation.

Toluene for nitration must be of high purity, in fact almost chemically pure. The boiling range of the product should be 109-111°C, with at least 95% distilling within a range of 1°C. The specific gravity should be 0.870±0.002 at 15°C.

Only an insignificant amount of unsaturated aliphatic hydrocarbons is admissible in toluene for nitration. They may be detected by shaking a sample with concentrated sulphuric acid. If the toluene is pure, the sulphuric acid separates very quickly as a colourless or slightly yellow ("straw yellow") lower layer. If unsaturated hydrocarbons are present in significant quantities a stable emulsion is often formed, and the sulphuric acid turns brown or even black. Such a product cannot be used for nitration.

Nowadays an infra-red spectrophotometric technique is usually applied in testing toluene for purity (Gore and Patberg [2]).

It should be noted that toluene purity cannot be assessed by the ultra-violet technique, since strong bands produced by toluene (as about 262 mμ) mask those that may be produced by olefins.

Toluene obtained from petroleum should contain no more than 4% of paraffinic hydrocarbons. The content of the latter is determined by sulphonation of the toluene with concentrated sulphuric acid or with 20% oleum. Sulphonated aromatic compounds are washed out with water to leave the paraffin hydrocarbon which is not affected by oleum.

If the toluene contains a higher proportion of paraffinic hydrocarbons it can still be nitrated, provided the mononitration product is subjected to distillation (preferably with steam) to remove saturated hydrocarbons. According to Desseigne, Gladel, Guillemin and Sousselier [3], toluene containing 30-40% of saturated hydrocarbons can be treated in this way to obtain nitrotoluene suitable for further nitration.

The U.S.S.R. specification (OST 464) for nitration grade toluene requires the following properties (Table 81):

TABLE 81

	Toluene from coal	Toluene from petroleum
Specific gravity at 15°C	0.870±0.002	0.863-0.870
Boiling range	109-111°C	108.5-111°C
	(95% distils within a range of 1°C)	
Colouration with sulphuric acid (comparison with standard potassium dichromate solutions of concentrations x grammes per 1 l. of 50% sulphuric acid)	x 0.5	x 0.5
Bromine number (y grammes of bromine decolourized by 100 ml. of toluene)	y 0.8	y 0.8
Sulphonation test with 5% oleum	-	not less than 96 vol. % should be sulphonated

According to a German standard, toluene for nitration shall distil within a range not wider than 0.8°C.

NITRATION OF TOLUENE TO TNT

GENERAL REMARKS

The nitration of toluene to TNT is carried out by successive introduction of nitro groups. Such a method is justified from the points of view both of safety and economy as it permits the most efficient use of acids and produces a final product of high purity due to the purification of the intermediate products obtained in the separate stages of the process.

Nitration is commonly carried out in three stages, and less often in two Stages.

The principle of economical acid usage is simply achieved by using the spent acid from a higher nitration stage for the lower stage, after it has been fortified to the required concentration.

The diagram presented below illustrates the reactions occurring, and shows the average composition of the products and heat effects of the reactions. Another diagram (Gorst [4]) gives the yields of nitration of intermediate compounds.

THREE-STAGE PROCESS FOR MANUFACTURE OF TNT’

The three-stage nitration of toluene to TNT comprises the following processes:

I. $C_6H_5.CH_3$ -> $C_6H_4.CH_3.NO_2$ (MNT)

II. $C_6H_4.CH_3.NO_2$ -> $C_6H_3.CH_3.(NO_2)_2$ (DNT)

III. $C_6H_3.CH_3.(NO_2)_2$ -> $C_6H_2.CH_3.(NO_2)_3$ (TNT)

OLD FRENCH PROCESS

This process, as described by Pascal [5], was used in France both during World War I and in the early period of time between the two wars. Separate operations in the three-stage nitration process are carried out in the following way:

Nitration of toluene to MNT (“mononitration”). To introduce one nitro group into toluene a mixture of acids is used (sp. gr. 1.672) of composition:

HNO_3	28%
H_2SO_4	56%
H_2O	16%

Toluene (650 kg) is run into a nitrator, and 1580 kg of the nitrating mixture is added with vigorous stirring. The temperature in the nitrator should be maintained at 40°C by using a cooling jacket and a coil situated inside the nitrator. After the reagents have been mixed thoroughly the temperature of the mixture should be raised to 60°C and maintained then for 45 min to 1 hr. When the reaction has been completed the nitrator contents are cooled to room temperature and the stirrer is stopped. The liquid is allowed to stand still until quiet, and then the lower layer, i.e. the spent acid, is drained off.

The composition of the spent acid (sp. gr. 1.66) is:

HNO_3	trace
H_2SO_4	69%
H_2O	29%
NO_2	2%

From 650 kg of toluene 910-950 kg of MNT is obtained, i.e. 140-146 kg for 100 kg of toluene. Since the theoretical yield is 149 kg of MNT for 100 kg of toluene, the actual yield amounts of 94-98% of theory. Losses are due mainly to dissolution of the nitration product in the spent acid (up to 4.5% of the total amount of nitrotoluene).

Nitration of MNT to DNT (“dinitration”). The acid from the first stage of nitration, composed of:

HNO_3	32%
H_2SO_4	61%
H_2O	7%

is run into MNT over a period of 2 hr, with constant stirring. The amount of the acid should correspond to a 45% excess of HNO_3. During stirring the temperature should be maintained at 40°C for the first hour and at 50°C for the next hour.

When all the acid has been run into the nitrator the mixture is heated to 90°C and maintained at this temperature for half an hour. Then the nitrator contents are cooled to 60-65°C, i.e. to a temperature at which crude DNT remains liquid (m. p. 56-58°C).

Spent acid from dinitration has the composition:

HNO_3	2.5%
H_2SO_4	76.0%
H_2O	20.0%
NO_2	1.5%

DNT, being lighter than the spent acid (sp. gr. at 60°C - 1.337, at 80°C - 1.318) rises to the surface. The spent acid is drained off and DNT, while still hot, is run into a vessel with concentrated sulphuric acid.

From 100 kg MNT 130 kg of DNT are obtained (the theoretical amount is equal 133 kg), hence the yield amounts to 98% of the theoretical. When calculated on toluene, 188 kg of DNT are obtained from 100 kg of toluene (theoretically 198 kg), which corresponds to 95% of the theoretical yield.

Nitration of DNT to TNT ("trinitration"). An anhydrous mixture of acids is used for the third stage of nitration. Mixture of the composition

HNO_3	49%
H_2SO_4	49%
NO_2	2%

is run into the nitrator where it is heated to 80-90°C. Then the DNT from the preceding stage of nitration dissolved in concentrated sulphuric acid in 1: 1 weight ratio is added with stirring. Prior to mixing, the solution is heated to 60°C.

The resultant composition of the nitrating mixture is:

HNO_3	19%
H_2SO_4	80%
NO_2	1%

1500 kg of it are used for 1000 kg of DNT, this being one charge.

The two solutions are stirred for about 2 hr during which time the temperature of the liquid should rise to 105°C. The nitrator contents are then heated up to 120°C, and this temperature is maintained for one hour and a half.

In consequence of such drastic conditions of nitration several side reactions of oxidation and break-down processes take place, giving rise to the products mentioned above (trinitrobenzoic acid, trinitrobenzene, tetranitromethane). A decomposition reaction (p. 76) also gives off a large volume of carbon monoxide, which may form an explosive mixture with air. Several explosions of such mixtures have been described.

When nitration is completed, stirring is stopped. TNT separates from the spent acid, forming the upper layer (sp. gr. of TNT at 80°C is 1.467, and at 100° it is 1.443).

Spent acid from trinitration has the composition:

HNO_3	1.5%
H_2SO_4	92.0%
H_2O	4.0%
NO_2	2.5%

Separation of the molten product by decantation at this moment would result in heavy losses, as the solubility of TNT in hot acid is rather high (3.5% at 50%). For this reason the separation of TNT may be carried out in one of the following ways:

1. The reaction mixture is run into a cooling crystallizer. TNT solidifies on the surface of the liquid, forming a crust which is stripped off and washed with water. To the remaining acid 7% water is added, thus changing the solubility of TNT in the acid and causing a second batch of TNT to rise to the surface.

2. Another method of TNT separation from spent acid consists in bringing the TNT to crystallization point by stirring and adding water to the nitrator contents until cool. The reaction mixture is then transferred to filters to separate the crystals from the acid.

From 100 kg of DNT 102 kg of TNT are obtained (theoretical yield 124 kg), which makes about 82% of the theoretical yield.

When calculated on toluene, 190 kg of TNT are obtained from 100 kg (instead of 246 kg calculated theoretically) which makes the actual yield nearly 77% of theory.

Acid usage control. The French method is based on the use of the spent acid from trinitration for dinitration after it has been fortified, and on further utilization of the spent acid from dinitration in the mononitration stage. The composition of the mixtures is calculated as described above.

The spent acid obtained from mononitration by the method described should contain traces of nitric acid (0.2-0.4% of HNO_3). Its absence may be an indication that the amount of nitric acid used for the nitration was insufficient and consequently that part of the toluene has remained unnitrated. In such cases the portion of acid used for the next batches should be richer in HNO_3, since in the old French method the unreacted toluene is not distilled off from the mononitrotoluenes.

The H_2SO_4, content in the spent acid should not be less than 70%. A lower content is not advisable, for a less concentrated sulphuric acid may attack the iron equipment.

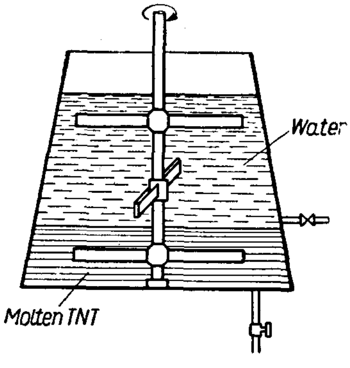


FIG. 78. Wooden tank for washing TNT (Pascal [51]).

Washing the TNT and preparing it for final purification. Crude, separated TNT, as described above, is transferred to a separator - a heated iron vessel, in which a temperature of 80°C or somewhat higher is maintained for about 3 hr in order to keep the product therein in a molten state. The remaining spent acid flows down to be then drawn off and added to the main portion of the spent acid. The molten TNT is transferred to a tank in which a preliminary washing (deacidification) is effected. For this purpose wooden tanks, shaped like truncated cones. are used. They are of about 20 m^3 capacity and are equipped with stirrers (Fig. 78).

15 m^3 of water heated to 85°C are run into the tank where this temperature

is maintained by introducing live steam. 4000 kg of molten TNT (the amount obtained from 4 nitrators) are run into the tank and stirred for half an hour. Then the stirrer is stopped and water decanted off. This operation is repeated 3-4 times, then the molten TNT is drained off at the bottom of the tank into pans (2 m x 0.6 x x 0.12 m), six of which are placed on top of each other on carts (Fig. 79).

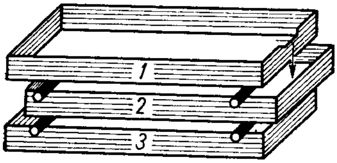


FIG. 79. Pans for crystallization of TNT (Pascal [5]).

The construction of these pans is such as to allow TNT to flow down to the lowest pan after the upper ones have been filled. The TNT solidifies slowly in the and forming large crystals, separated from lower melting impurities, which accumulate in the lowest pan in the form of oil. This product is a grade III TNT ("liquid TNT") used for the manufacture of mining explosives. The main product is removed from the pans, crushed with wooden hammers, and ground finally in a cylindrical mill. During the grinding TNT is sprayed with water to prevent it from emitting dust. The ground TNT is ready for further purification.

OLD BRITISH METHOD [6]

Some features of the British method which was developed during the 1914 1918 period are worth mentioning. One of them was the use of toluene derived from petroleum (Borneo petroleum), as well as toluene from coal.

Petroleum fractions distilling from 95°C to 115°C containing 55-60% of toluene, were used. The remainder constituted aliphatic hydrocarbons which would not nitrate under the conditions of the process. The MNT thus obtained, containing some petroleum components, was purified by distilling off the petroleum fraction.

Detoluation. Another characteristic feature of this method was the extraction of higher nitrated toluene derivatives, dissolved in the spent acids. The latter were conveyed to denitration and distillation (concentration) only after the nitro compounds present in them had been extracted with nitrotoluene, an operation which was called "detoluation". Primarily it consisted in stirring the spent acids, heated to 75-80°C with a quantity of crude MNT, amounting to one quarter of the acid volume. A slight amount of nitrotoluene became nitrated due to the presence of the unreacted HNO_3 in the spent acid.

Later the detoluation operation was combined with partial nitration of MNT to DNT, by adding to the spent acid a certain quantity of nitric acid from the recovery operation (denitration).

Detoluation consisted of two stages, carried out in a detoluator and in a superdetoluator (Fig. 80).

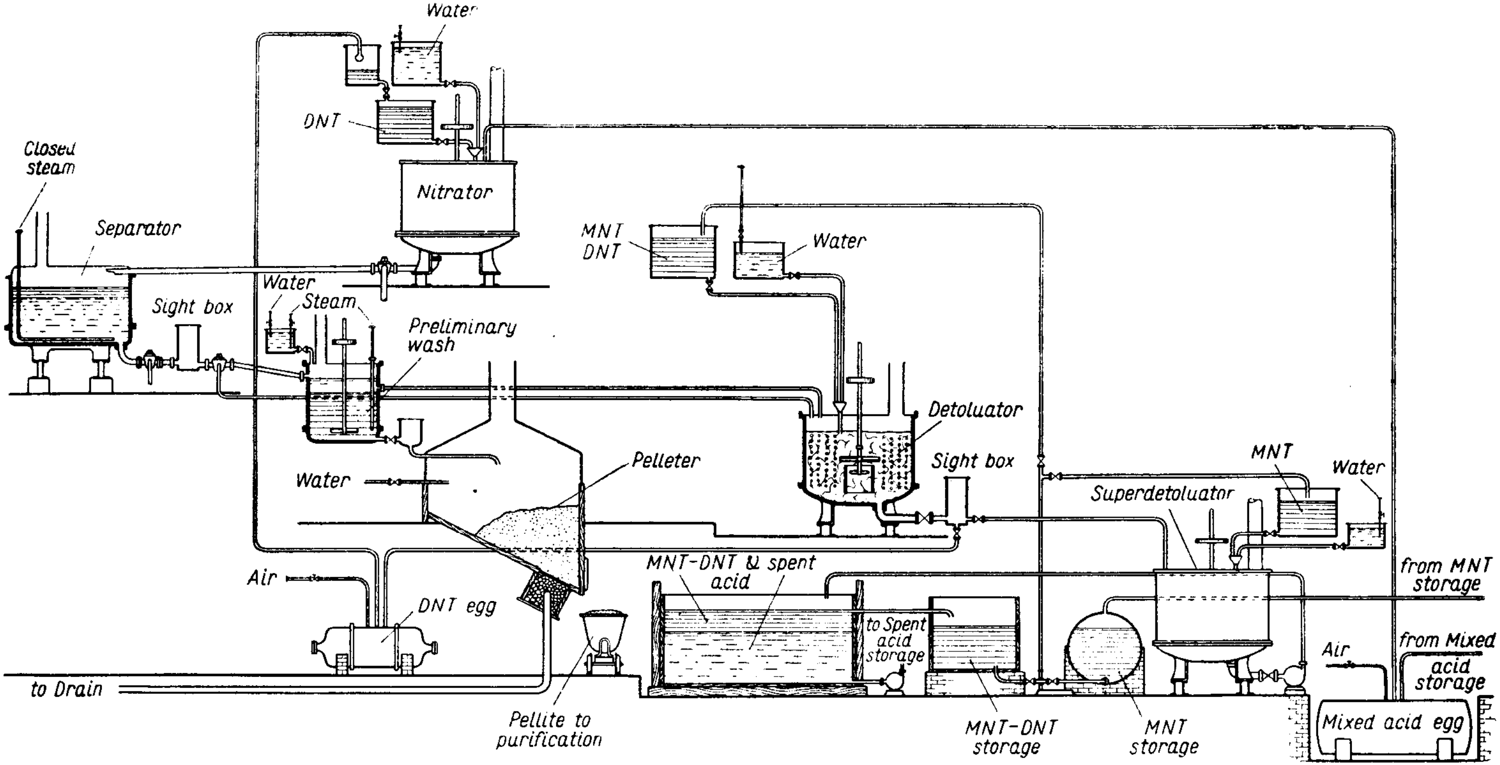


Fig. 80. Diagram of the lay-out of manufacture of TNT with detoluation [6].

The product of trinitration was drained off to a separator, where a temperature of about 80°C was maintained by means of a steam heating coil. When the product had set in two layers the lower one, i.e. the spent acid in a quantity of about 5000 kg, was transferred to the detoluator, into which a mixture of MNT and DNT from a superdetoluator was run with simultaneous cooling and stirring. While maintaining a temperature of 75-80°C by cooling, some 240 kg of 50% nitric acid were introduced into the detoluator and after the mixture had been stirred for half an hour it was cooled to 50°C. About 160 1. of acid water from the preliminary washing of TNT were then added.

Stirring was continued for another 15 min after which the contents were allowed to remain at rest for 30 min in order to set in two separate layers. The batch was then drained off through a sight-glass, the "twice used" acid being directed into the superdetoluator, and the nitro compounds to a pressure-egg, which in turn conveyed them into a tank. From this the nitro compounds were transferred for further trinitration.

Mononitrotoluene along with the acid from which nitro compounds had been partly removed (the "twice used" acid) were run into a superdetoluator, a temperature of 50°C being maintained. Then about 200 1. of water were added to reduce the concentration of H_2SO_4 below 73%. When the mixture had been cooled to 20-25°C stirring was stopped and the nitro compounds were separated and transferred to the detoluator (as described above).

Spent acid of an average composition

H_2SO_4	71.2%
HNO_3	trace
HNO_2	3.0%
organic matter (nitro compounds)	0.4%
H_2O	25.4%

was conveyed to denitration and concentration.

The spent acid from trinitration contained nearly 3.5% of nitro compounds before detoluation.

The composition of the detoluation product was:

30-40% of MNT
40-50% of DNT
20-30% of TNT

It was an oily liquid with a specific gravity of 1.29-1.30.

The extraction of acids with nitrotoluene not only made possible the utilization of the dissolved nitro compounds, but it also enabled direct use to be made of the diluted nitric acid (50% of HNO_3) from the distillation of the spent acid, so that concentration of this acid was not necessary. Apart from the extraction, a partial dinitration took place, the whole process consisting of the following stages:

Toluene -> Mononitration -> Detoluation and preparation of the mixture of MNT, DNT and TNT -> TNT.

Nitration of MNT and DNT to TNT. The mixture of nitrotoluenes was converted into TNT in the following way:

The nitrator was charged with 4800-5000 kg of acids in the following proportion :

H_2SO_4	79.5%
HNO_3	17.8%
H_2O	2.7%

Then crude DNT from the superdetoluator was added at a temperature of 66°C (maintained by heating). The temperature was then raised to 100°C at a rate not higher than 50°C per 10 min. Nitration ended at this temperature and the melting point of a sample of TNT in the nitrator, after it had been acid washed, was 72.5°C (this corresponded to the melting point 76°C of the dry product).

After nitration was completed, 550 1. of water were run into the nitrator to reduce the solubility of the TNT in the acid, and the mixture was then transferred to a separator, where TNT was separated from the spent acid.

After 30-45 mm the acid was drained off through the sight-glass to a detoluator, and the molten TNT to a preliminary washing tank fitted with a mechanical stirrer made of acid resistant material. 160 1. of boiling water were fed into the washing tank prior to the TNT. The mixture was kept boiling by direct steam heating.

Stirring was discontinued after 5 min and after another few minutes the acidic water (containing about 14% of acid) was drained off and transported to the detoluator as described above.

The washed, molten TNT was poured in streams into a granulator, to which a stream of water was also directed, so as to make two streams collide. TNT solidified at once in the form of granules at the bottom of the granulator. Water was run away through a filter, and the TNT, still wet, was unloaded for final purification. The impurities it contained were:

water	about 19.0%
H_2SO_4	0.3%
HNO_3	1.0%
tetranitromethane	0.15%

OLD U.S.S.R. METHOD (ACCORDING TO GORST [7])

The main feature of the old method used in the U.S.S.R. is the presence of separation columns which are combined with each of the three nitrators. Also the spent acid from the third nitration stage is kept for some time in a column in which the nitro compounds swim to the top. The columns are ca. 4 m high and of ca. 2 m diameter. They are made of sheet iron, clad inside with lead.

The flow-sheet is given in Fig. 81. Toluene flows from the tank (1) through the measuring tank (2) to the mononitrator (4). The acid flows through the measuring tank (3). After nitration the products pass through the pressure-egg (5) to the separating column (6). The mono-spent acid flows through (7) to denitration, and the MNT through (8) to the “bubbler” (10) fed through (9) with the spent acid from dinitration.

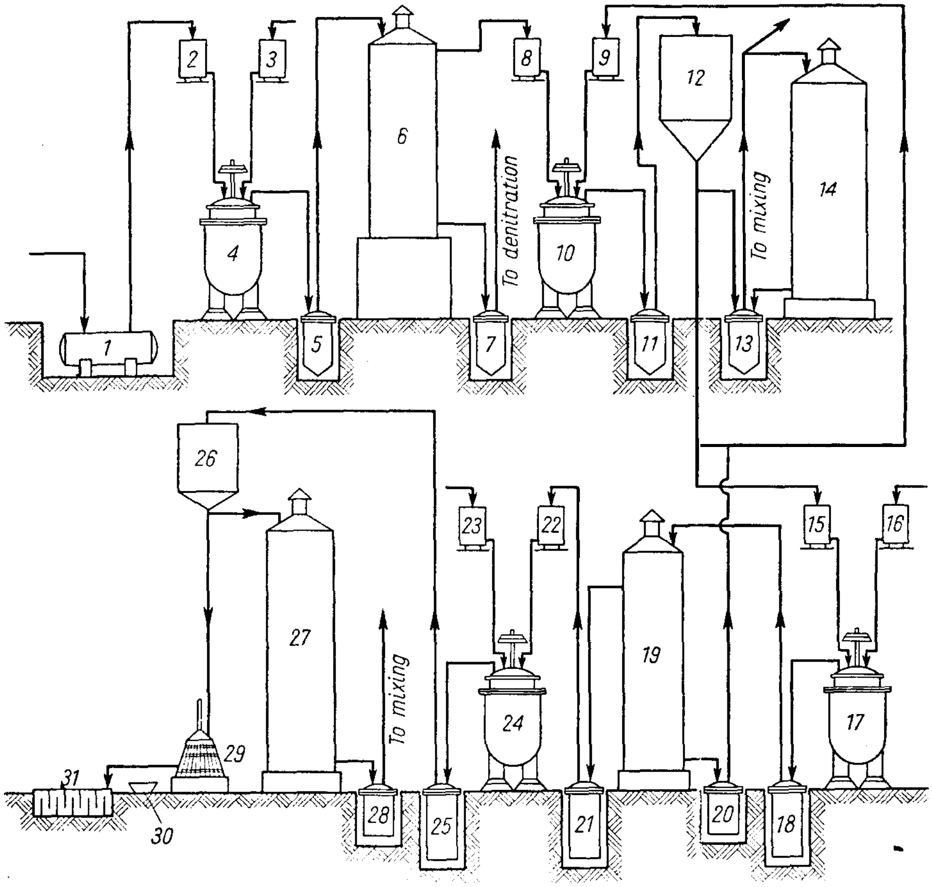


FIG. 81. Flow sheet of the old method of manufacture of TNT in U.S.S.R. (Gorst ([7]).

Here the acid is stirred with MNT to extract dissolved DNT. The mixture from the "bubbler" passes through (11) to the separator (12). The acid freed from DNT enters the separation column (14) and from the column passes to the mixing house to make mononitration acid.

MNT enriched with DNT flows from (12) through (25) to the dinitrator (17) fed with the acid through (16). After nitration the contents pass through (18) to the seperating column (19). The separated acid flows through (20) and (9) to the "bubbler" (10).

The separated DNT flows from the column via the egg (21) and the measuring tank (22) to the trinitrator (24). The nitrating acid flows in from the measuring tank (23). The nitrator contents pass through (25), to the separator (26). TNT from the separator flows to the washing vat (29) and the spent acid to the column (27). Spent acid is sent through the egg (28) to the mixing house. Washed TNT is poured into the pans (39) where it solidifies. The wash water enters the labyrinth (31) and after geos to waste.

The spent acid from the trinitration stage is partly used to make mono- and di-nitration acids, and the rest is diluted to 70-72% H_2SO_4 to separate dissolved

TNT and then sent to denitration. Excess of spent acid from dinitration (14) is diluted to separate dissolved nitro compounds and also sent to denitration.

The main features of the nitration conditions are given below.

TABLE 82

MONONITRATION OF TOLUENE

	Nitration acid	Spent acid
HNO_3	27-28%	0.5%
H_2SO_4	54-55%	68.5%
H_2O	17-19%	18.7-18.8%
N_2O_3	-	1.5%
Nitro compounds		0.7-0.8%
Quantity of the nitrating mixture	103% of theoretical	
Temperature of nitration :		
on mixing reagents	15-40°C	
after ,, ,,	40-50°C	
Time :		
in winter (better cooling)	12-13 hr	
in summer	30-36 hr	
Yield of MNT	95% of theoretical	

TABLE 83

DINITRATION OF MNT

	Nitration acid	Spent acid	
		before “bubbling”	after “bubbling”
HNO_3	23%	2.5%	0.8%
H_2SO_4	67%		
H_2O	10%		
Nitro compounds	-	4%	0.7-0.8%
Quantity of the nitrating mixture	111% of theoretical		
Temperature of nitration :			
on mixing reagents	20-80°C		
after ,, ,,	80-105°C		
Time	8 hr		
Yield	95% of theoretical		

Mononitration of toluene. The nitrator is filled with toluene and nitration acid is added (Table 82).

Dinitration. The nitrator is filled with MNT and nitrating mixture is added (Table 83).

Trinitration. The nitrator is filled with DNT and nitrating mixture is added (Table 84).

TABLE 84
TRINITRATION OF DNT

	Nitration acid
HNO_3	17.5-18.5%
H_2SO_4	81.5-82.5%
H_2O	-
Quantity of nitrating mixture	164% of theoretical
Temperature of nitration :	
on mixing reagents	72-77°C
after „ „	115°C
Time	6-6½ hr

GERMAN METHOD

This method known from the description of the process at the Krümmel. factory was used by the German explosives industry during World War II. Figure 82 represents a flow diagram of the manufacture of TNT by this method.

The characteristic features of the method were:

(1) two-stage mononitration, i.e. a preliminary and a final one;
(2) use of a nitrating mixture prepared from fresh acids for mononitration;
(3) purification of MNT prior to further nitration to DNT;
(4) low temperature during the trinitration process (max. 96°C);
(5) exclusive use of iron in the plant; such units as the washing vessels for TNT being constructed from materials other than wood.

Mononitration. For the nitration of toluene a mixture T_1 of the composition:

HNO_3	28%
H_2SO_4	56%
H_2O	16%

was used.

The nitrating mixture is prepared from fresh concentrated nitric acid, 55% regenerated nitric acid (from the denitration of spent acid), and 96% sulphuric acid recovered by distillation. The mixture of acids is fed into the nitrator from a metering tank through a vacuum started siphon. Toluene is conveyed to the nitrator from another metering tank by means of compressed nitrogen. Air is considered as too dangerous to use, because the explosibility of mixtures of toluene vapour with air.

Plant for mononitration consists of two cast iron pre-nitrators, each having a capacity of 0.5 m3 and a main cast iron nitrator of 15 m^3 capacity. Toluene and acid are run into the pre-nitrators, a toluene to acid ratio of 1 : 2.5 being maintained. The mixture is transferred to the main nitrator through an overflow in the quantity necessary to fill the nitrator (10-12 m^3). A temperature of 34-40°C is maintained in both nitrators by means of a cooling coil.

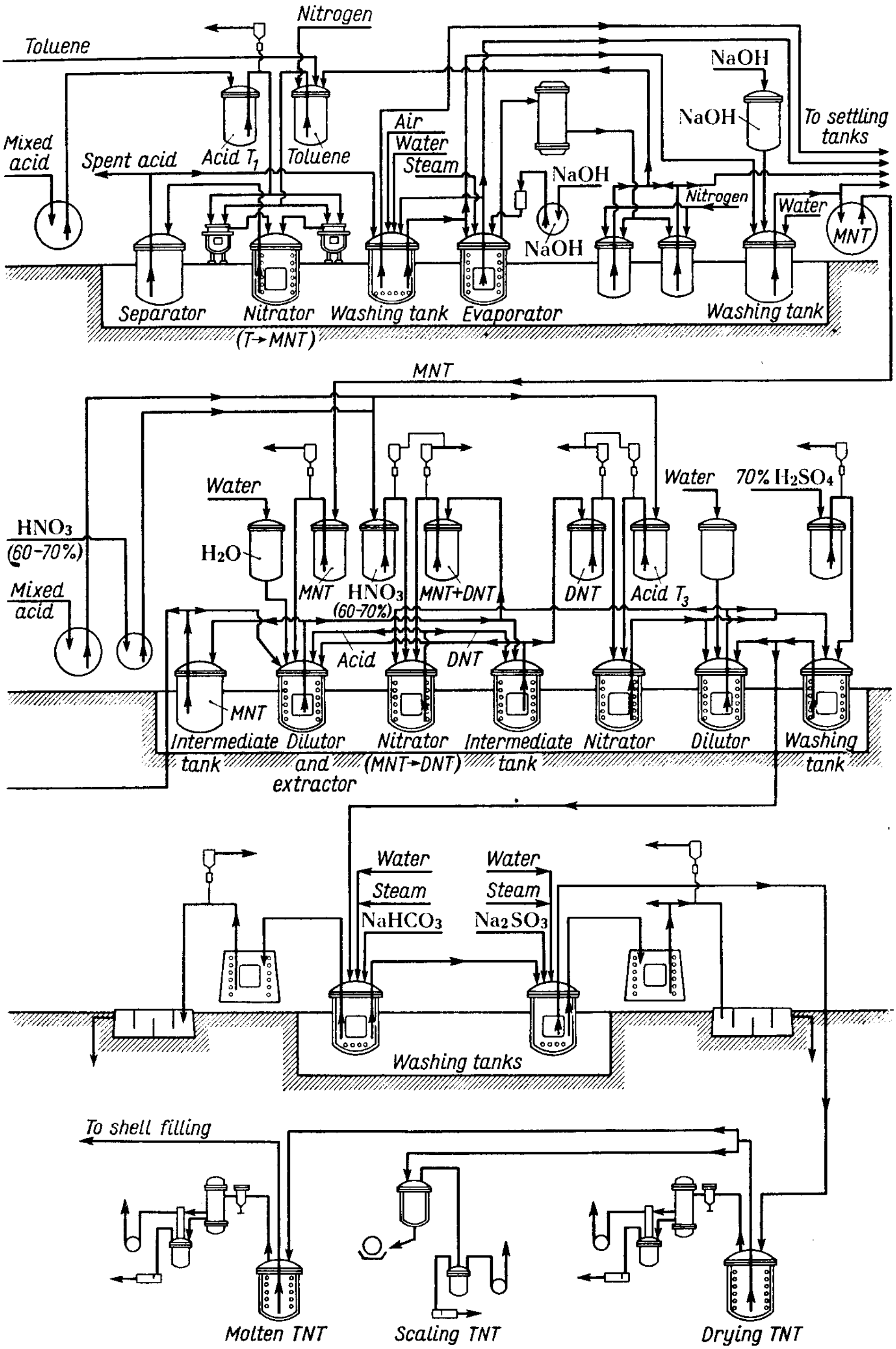


FIG. 82. Flow sheet of TNT manufacture in Krümmel.

The aim of dividing the operation into two stages is to achieve the most effective thermal control, since the conversion of toluene to mononitrotoluene is the most exothermic of all the stages of the reaction, as already mentioned in the section dealing with the theory of nitration. The operation is effected in 5-6 hr. 5000 kg of MNT is obtained from each charge of the nitrator.

When nitration has been completed the reaction mixture is transferred by compressed air to a cast iron separator with a capacity of 15 m^3, where it is allowed to remain at rest for 6 hr to separate into two liquid phases. Then the spent acid is conveyed to a special cast iron tank, where it stays for a few days to recover the temainder of the MNT, which is collected from the surface and added to the toluene to be mononitrated. The spent acid, having a composition:

H_2SO_4	70.0%
NO_2	0.5%
H_2O	29.5%

is conveyed to denitration, which yields 67-68% sulphuric acid. Subsequently this is concentrated by distillation to obtain a 96% product.

MNT thus prepared is washed with water in a wrought iron tank, lined with sheet lead. Washing is effected by vigorous stirring until the product is free from acid (test with Congo red paper). The neutralized MNT is transferred to a so-called distillation unit (of cast iron), where it is mixed with a dilute solution of NaOH, (ca. 1%), the latter being used in a quantity equal to 1 wt. % of MNT (i.e. about 50 kg of NaOH). Washing with alkali not only aims at a complete removal of acids, but also it converts nitrocresols impurities into water soluble nitrocresolates.

Live steam is passed through the mixture of MNT and alkali. The unnitrated toluene and benzene (the latter is a common impurity of toluene) are thus expelled. The steam is introduced until MNT begins to distil, after all the hydrocarbons or other volatile impurities have been expelled. The condensate, containing toluene and MNT, is either recycled for nitration to liquid nitro compounds, e.g. for mining explosives, or is used as a solvent for varnishes.

The alkali layer is separated by decantation and distilled. The MNT recovered is added to the main product. The latter is conveyed from the distiller to a washing tank where it is washed with water, then again with alkali and finally with a sodium carbonate solution. The moist MNT is conveyed by means of compressed air to a cast iron tank for temporary storage.

From 100 parts of toluene 140-144 parts of MNT are obtained by this method, containing about 4% of *m*- nitrotoluene.

Dinitration. Dinitration is carried out in two stages. The first consists of the following operations. The spent acid from trinitration, of the composition:

HNO_3	4-5%
NO_2	34%
H_2SO_4	80%
H_2O	11-13%

having a temperature of about 85°C is fed into a cast iron nitrator of 15 m^3 capacity and cooled to 30°C.

The MNT which has already been used for the extraction of the spent acid from dinitration and which contains some DNT, is introduced at first slowly and then as HNO_3 is used up in the nitration to DNT, the flow rate is gradually increased. The temperature in the nitrator rises to 60-65°C and then falls as the nitric acid is consumed. When all the MNT has been run in, the temperature falls to 55°C. Then the second stage begins. Nitric acid of a concentration of 60-70% of HNO_3 is added. The rest of the MNT is nitrated to DNT, the temperature rising to 70-72°C. The nitration is considered complete when MNT no longer steam-distils from a sample taken from the nitrator.

The reaction mixture is allowed to remain at rest for one hour, then the acid and DNT are separated. The composition of the spent acid is:

HNO_3	0.6%
NO_2	5-6%
H_2SO_4	78-80%
H_2O	13.4-16.4%

The spent acid is transferred to a cast iron dilutor-extractor, and the acid containing DNT goes to a cast iron tank for temporary storage.

The spent acid in the dilutor-extractor is diluted with water to reclaim the greater part of the dissolved DNT. The following composition of the spent acid is obtained on dilution :

HNO_3	0.5%
NO_2	4-5%
H_2SO_4	73%
H_2O	21.5-22.5%

The reclaimed DNT is added to the main yield of DNT, and the spent acid in the extractor is stirred with MNT. Thus the rest of HNO_3 is used for nitration to DNT, and at the same time the dissolved DNT is extracted. The MNT obtained, containing dinitrotoluene, is used later for dinitration.

Spent acid from the extraction process has the following composition:

NO_2	44.5%
H_2SO_4	73-74%
nitro compounds	0.2-0.3%

It is transferred to an intermediate storage tank, where it remains for 4-5 days. During this time the rest of the MNT rises to the surface. It is collected and added to the main portion, while the spent acid is conveyed to distillation.

Trinitration. This can be effected either by adding acid to dinitrotoluene or by the reverse operation.

The acid liquid DNT is metered and fed into a cast iron nitrator of 12 m^3 capacity by means of compressed air. Then acid T_3 of the composition:

HNO_3	24%
H_2SO_4	70%
SO_3	6%

is added. This T_3 mixture is prepared from concentrated nitric acid and 27% oleum. Alternatively, the nitrator may be fed first with acid and then with DNT.

The DNT to acid ratio is 1:2.5-2.6 4000 kg of TNT are obtained per batch, The reaction is completed in 35 hr, and the post-reaction period is 24 hr.

If acid is added to the DNT in the nitrator, the temperature within is kept at 83-85°C, and then raised to 96°C while if DNT is added to the acid, a temperature of 74-78°C should be maintained. When the two substances have been mixed, the temperature is gradually raised to reach 96°C in one hour.

The whole process lasts for 6 hr. Then the reaction mixture is allowed to remain at rest for half an hour, to separate the product from the acid. After separation, the molten TNT is conveyed by means of compressed air to a cast iron washing tank of 8 m^3 capacity and the spent acid to a wrought iron diluter of 15 m^3 capacity.

The TNT in the washing tank is stirred, while hot, with nearly 70% sulphuric acid, to wash out nitrogen oxides and the rest of the HNO_3 or nitrosylsulphuric acid. Then it is separated from the acid and transferred to a separate, building for final washing. TNT, after it has been washed with sulphuric acid, contains l-2% of HNO_3 and l-2% of H_2SO_4.

The spent acid, to which the acid from TNT washing has been added, is diluted with sufficient water to obtain the composition given above. The dilution results in further separation of TNT, which is added to the main portion. The diluted spent acid is conveyed to dinitration.

Nitration plant. The nitrators for mononitration (both the pre-nitrators of 0.5 m^3 capacity and the main nitrators of 15 m^3 capacity) are made of cast iron. The same material is used for all other parts of the plant in which not too concentrated acids are processed, e.g. dilutors, washing tank, tanks for nitro compounds, etc.

Those parts of the plant which are used for operations with concentrated acids (e.g. nitrators of 15 m^3 capacity for di- and tri-nitration) arc made of wrought iron.

Washing tanks for the final washing of nitro compounds with water (the water from the operation is slightly acid) are made either from stainless steel or from wrought iron lead lined or they may be constructed of bricks bonded by an acid resistant cement and lined with sheet lead and with acid resistant tiles (Fig. 83).

All pipes for conveying molten TNT from one part of the plant to another are heated either by hot water or steam jackets.

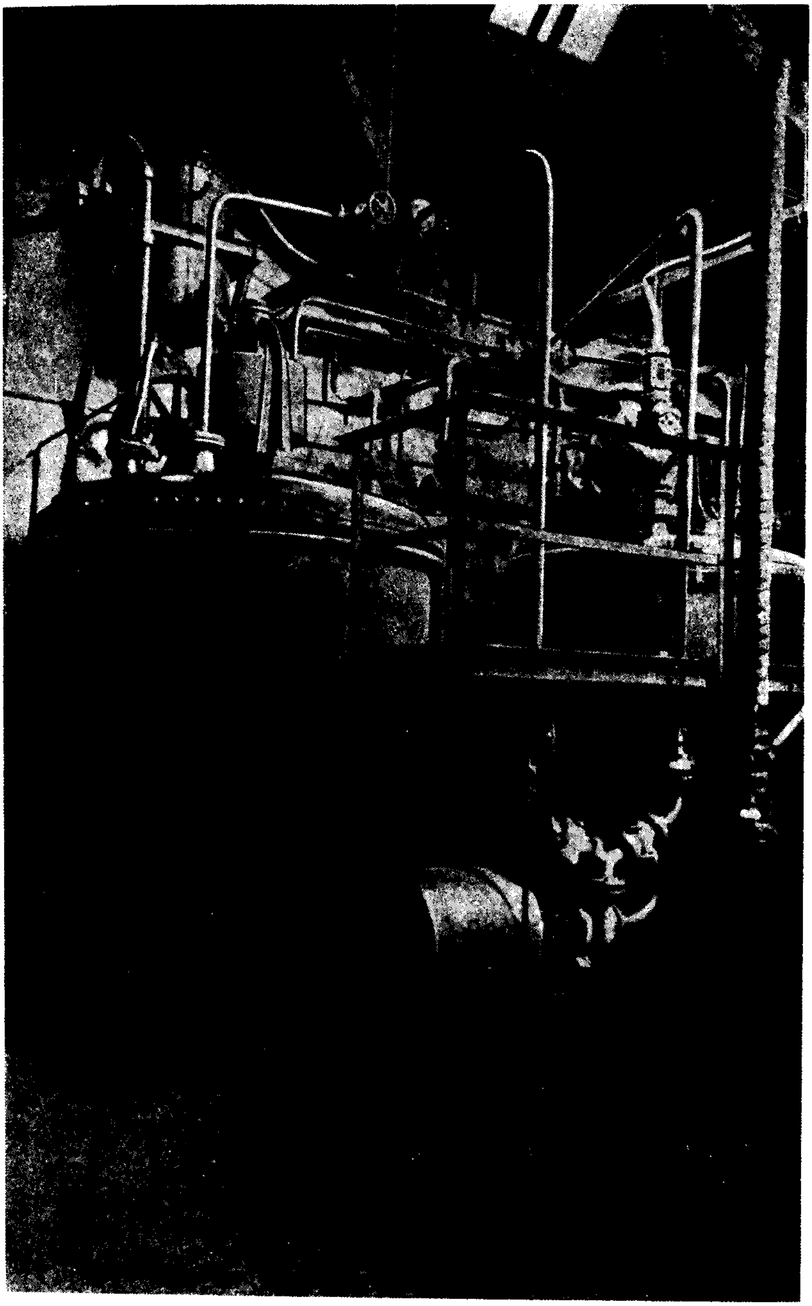


FIG. 83. Washing tank for TNT (Bofors Nobelkrut).

TWO-STAGE MANUFACTURE OF TNT (OLD ITALIAN METHOD)

In Italy a two-stage process of nitration has been used:

Toluene -> Dinitrotoluene -> Trinitrotoluene

For the nitration of toluene to dinitrotoluene a nitrating mixture of the composition :

HNO_3	28%
H_2SO_4	60%
H_2O	12%

is used.

Crude DNT, after it had been separated from acid and washed with water, was sometimes purified by sulphitation. This material partly freed from isomers and derivatives of m-nitrotoluene, was further nitrated.

The trinitration did not differ much from that described above. The mode of separating crystalline TNT from acid is worth mentioning. In this method the nitrator played the role of a crystallizer after nitration had been completed. The reaction mixture was cooled with continuous stirring until crystallization of the TNT began. To initiate the crystallization some water was added to the nitrator. Some of the crystalline TNT obtained in a previous batch might also be added if necessary.

TNT formed crystals which, while still in a hot state, were separated from the spent acid in a vacuum filter or in a centrifuge. The degree of TNT purity could be regulated by temperature during crystallization. A very pure product could be obtained, by using a relatively high temperature (e. g. 75°C).

From the spent acid TNT of lower quality was obtained on cooling. By using a lower temperature of crystallization in the nitrator, crystals of grade II TNT were obtained which in turn could be purified by sulphitation.

Belenkii [8] describes the U.S.S.R. process of crystallization of TNT in the nitrator as follows. TNT crystallization begins at 76°C. This temperature rises by 0.5°C owing to heat of crystallization. By this time the quantity of TNT dissolved in the spent acid amounts to about three quarters of the total. At the initial stage of crystallization, at a temperature of 76°C to 75°C cooling should be very slight. Usually the flow of cooling water to the coil is stopped.

As soon as the temperature falls to 75°C the nitrator contents should be cooled vigorously and simultaneously the speed of rotation of the stirrer should be reduced to avoid pulverizing the crystals. When the temperature has fallen to 30-35°C cooling is discontinued, and almost pure α– trinitrotoluene is filtered off. If the Process of crystallization is properly carried out most of the impurities will remain in the acid.

The TNT is filtered off in a vacuum tank and washed, first with 70% and then with 45% sulphuric acid, each used in the proportion of 800 kg for 1000 kg of TNT, and finally several times with water. By using acid of a gradually reduced concentration for washing a very effective removal of oily impurities of DNT and of isomers of trinitrotoluene can be achieved.

The water-washed TNT contains 0.3-0.5% of acid. This value falls to 0.005% after repeated washing with boiling water.

Pure TNT may be granulated. For this a stream of molten TNT is introduced into a vat, at a place where two jets of cold water impinge on each other (Fig. 84). In this way a product melting at 79.5-80.2°C can be obtained.

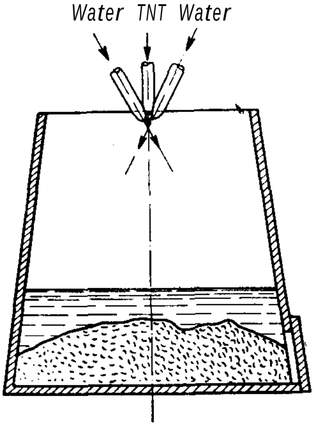


FIG. 84. Granulation of TNT.

The purity of the TNT obtained depends to a great extent on the size of the crystals formed. The best results are achieved when the crystals are of equal size and l-2 mm in diameter.

If grade I crystalline TNT is required the acid free TNT is sulphitated. In this way the melting point may be raised to 80.5°C.

MATERIAL BALANCE

Belenkii [8] reported data on the weight of acids used for 1000 kg of crude TNT (Table 85).

TABLE 8.5

QUANTITY OF ACIDS USED FOR 1000 KG OF CRUDE TNT

Process	Mixed acid (87.3% of HNO_3 and 8.4% of H_2SO_4)		Oleum (104% H_2SO_4) kg	93% sulphuric acid (as H_2SO_4) kg	Spent acid from trinitration kg
	H_2SO_4 kg	HNO_3 kg			
Mononitration	34.4	342.0	-~		664.5
Dinitration	35.0	349.0	197.6		841.0
Trinitration	52.2	518.3	1990.0	178.0	
Total	121.6	1209.3	2187.6	178.0	1505.5

The following nitric acid balance for the nitration of over 800 tons of toluene is given below (according to British data of 1914-1918). The balance takes into account both the quantity of nitric acid introduced into TNT in the form of nitro groups and that lost in various ways:

nitric acid used for the formation of NO_2 groups	79.64%
oxidation losses in the form of "fumes" and in wash waters from trinitration	11.22%
losses in mononitration ("fumes", washing out with water)	1.08%
losses at denitration	1.75%
losses in the nitric acid plants	6.31%
Total	100.00%

CONTINUOUS METHODS OF NITRATION

EARLIER METHODS

Although various descriptions of the continuous nitration of aromatic hydrocarbons have been known for a long time (e.g. patents granted to the companies: Meister, Lucius and Brüning in Höchst [9]; Weiler-ter-Meer in Uerdingen [10]; Westphalisch-Anhaltische Sprengstoffe A. G. [11] and a well-known patent granted to Kubierschky [12]), until recently these methods were not widely used. Particularly in the explosives industry, conservatism and fear of the adoption of any new untraditional methods not known to be safe, have been strong enough to prevent their realization. Hence most of the proposed methods have not been put into practice.

Methods of continuous nitration of aromatic hydrocarbons may be based on one of the following principles:

1. *Nitration in the vapour phase.* In methods of this kind (e.g. the Wilhelm method [13]) a continuous stream of vapours of the aromatic hydrocarbon and nitric acid or nitrogen dioxide is introduced into the reactor. Sulphuric acid is not used in this reaction.

One drawback of this method common to all processes taking place in the gaseous phase, is the necessity of using very large units, much larger than the capacity of the reactors for liquid processes. These methods have not found any practical uses.

2. *Partial pressures method.* Othmer and his co-workers [14-16] have suggested amethod in which a mixture of hydrocarbon and nitric acid of about 61% concentration is boiled. The water liberated in the reaction is distilled off with part of hydrocarbon, as an azeotrope. The two components are separated in a receiver into two layers, the water being drained off and the hydrocarbon recycled. As a result of the reaction mono- and di-nitro derivatives can be obtained. The method has been developed on the laboratory scale only.

3. *Counter-current method.* The method was suggested by Kubierschky [12]. The nitrator for nitrating benzene to nitrobenzene takes the form of a column. A mixture of nitric and sulphuric acids is introduced at the top while a mist of hydrocarbon is fed in at the bottom. The middle part of the column plays the role

of nitrator. The nitration product collects at the top, where it flows off continuously, while the spent acid, which concentrates at the bottom, always flows downwards.

There is no need for a stirrer as the reacting liquids are mixed by the natural flow resulting from the difference in specific gravities of the components. Because of certain drawbacks inherent in the difficulty of removing the heat of reaction, and as an emulsion may be formed, the method has not found any permanent practical uses.

4. *Co-current method.* Such methods are described in patents, granted to Meister, Lucius and Brüning [9] and to Weiler-ter-Meer [10]. The nitrating mixture is fed to the nitrator simultaneously with the hydrocarbon to be nitrated. A set of nitrators arranged in series may be applied to make the nitration more complete.

In industrial practice the co-current and co-current-counter-current methods are used. Thus, for example, the process in single nitrators may be based on a co-current principle while a number of nitrators may be connected in such a way as to work as a battery of counter-current system.

MODERN METHODS

The continuous methods are in many respects superior to the batch methods. One of the advantages of the continuous methods is that a much lower quantity of explosive accumulates at any moment in the plant. According to A. B. Bofors [17], in a plant with a daily production of 7.5 tons of TNT by the batch process, 10 tons of explosive were accumulating at any moment in a volume of plant of ca. 50 m^3. The corresponding figures for a plant with twice the capacity run continuously are 4 tons and 12 m^3 respectively.

With regard to the hazards involved, the modern continuous methods offer a much higher degree of safety, thanks to automatic regulators which keep control over the rate of feed into the nitrators and separators, the temperature of the reaction etc. In the event of a breakdown in the power supply (which usually involves danger due to the stoppage of stirring) all proportioning apparatus automatically stops and the reacting quantities in the nitrators are too small to produce any alarming rise of temperature.

All the reactors are provided with regulators controlling the supply of cooling water so as to keep the temperature constant. The regulators are so connected that in the case of a power interruption, they will fully open the feed of cooling water. Accordingly since no special action is required of the operator, he may simply leave the building when a power failure occurs.

One of the advantages of the modern methods is the small size of the apparatus. According to A. B. Bofors [17], a continuous plant with a daily production of 15 to 40 tons requires a floor surface of only ca. 150 m^2 in a one-storey building.

British method

The detoluation method was developed as a continuous method of manufacturing TNT in the Oldbury plant which came into operation in 1917.

In this plant each of the nitrators is connected with a separator, into which the liquid from the nitrator overflows and where the nitro compound is separated from the acid. The upper, nitro compound layer then flows to the next nitrator, containing a more concentrated acid, while the lower acid layer passes through a siphon to another nitrator, where less vigorous nitration takes place. Both liquid phases-that of the acid and that of the material being nitrated-flow in counter-current to each other. Figure 85 represents a schematic diagram of a unit for continuous nitration (after MacNab [18]).

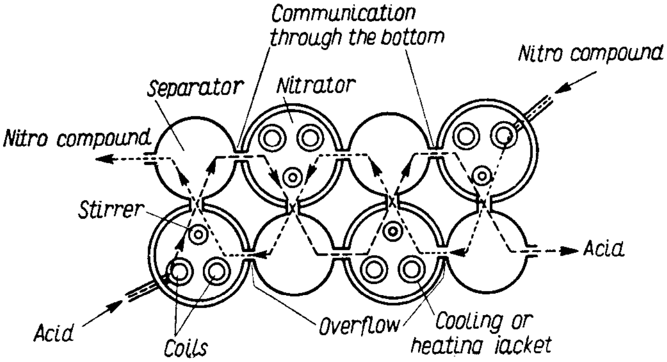


FIG. 85. Diagram of the British continuous nitration of toluene to TNT (according to McNab ([18]).

The unit comprises 14 nitrators and 14 separators. The first nitrator is fedwith nitrotoluene, prepared in another unit by the batch process. Nitrators from (2) to (14) are fed with acids of an increasing concentration. The acid in the "middle" nitrators, from (5) to (22), is of the following composition:

HNO_3	8-10%
NO_2	1%
H_2SO_4	80-82%
H_2O	11%

Into nitrator (24) a nitrating mixture prepared from 96% sulphuric acid and anhydrous nitric acid is introduced. The spent acid flowing from nitrator (2) to nitrator (I) is detoluated here by agitating with nitrotoluene whence it flows away as waste acid of the composition:

HNO_3	1%
NO_2	4%
H_2SO_4	78-80%
H_2O	14-16%
organic matter	1-1.5%

In the nitrators the following temperatures are maintained:

Nitrators	1-2	40°C
	3	70°C
	4-13	100°C
	14	90°C

The composition of the nitration products obtained in the separate nitrators is reflected by the melting points of the products:

Nitrator	3	15°C	Nitrator	9	55°C
	4	35°C		10	63°C
	5	50°C		11	69°C
	6	45°C		12	72°C
	7	41°C		13	76°C
	8	35°C		14	77°C

The formation of trinitrotoluene begins in nitrator 5. For 1000 kg of TNT

470-480 kg of toluene
1090-1160 kg of HNO_3
410-440 kg of H_2SO_4

are used in the process.

German method

During World War II a continuous process for nitrating toluene to TNT developed by J. Meissner [19] and patented in 1941 was introduced at the Schlebusch factory in Germany. The nitration unit consisted of 5 nitrators and 4 separators, as shown in the schematic diagram in Fig. 86. Both the nitrators and the separators are arranged in a cascade so as to enable the liquid to flow down from higher vessels to lower ones. In this way the nitration mixture can be transferred from the nitrator to the separator, where the nitro compound rises to the surface and flows off through a drain between the separator to the next nitrator. The waste acid flows down from the bottom of the separators to storage tanks.

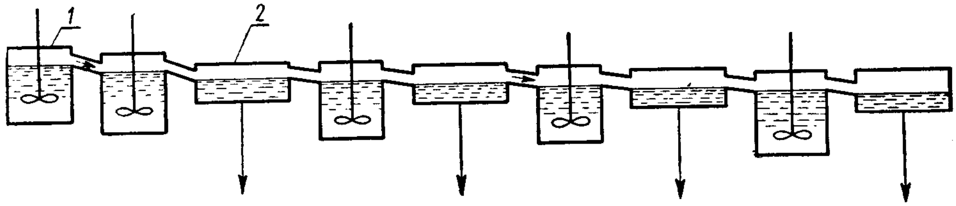


FIG. 86. Diagram of the German continuous nitration of toluene to TNT (CIOS XXIV 4).

The nitrators are 1.5 m high and 1 m in diameter. The separators are 0.75 m high and 1.5 m in diameter. Both are fabricated from cast iron.

Recently F. Meissner, Wannschaff and Othmer [20] have published some data on J. Meissner's continuous method of preparation of TNT, which is an improvement of an earlier patent of Meissner's.

The design of the plant is based on the combination of the co-current process with the counter-current-battery system. The plant consists of three aggregates, each of them comprising the following stainless steel parts:

(1) tanks for reactants and metering tanks for the continuous supply of nitrating mixture and hydrocarbon;

(2) the main nitrator ;
(3) one or more supplementary nitrators;
(4) a vessel for extraction of the waste acid (detoluator);
(5) two separators.

A schematic diagram of such a nitration unit with a washing column and a separator is shown in Fig. 87.

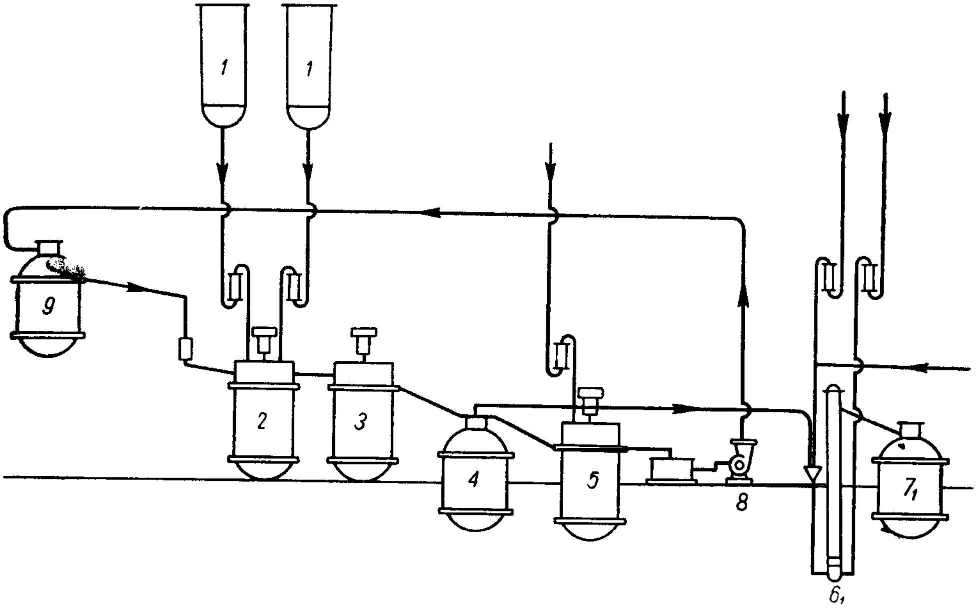


FIG. 87. Flow-sheet of continuous nitration of toluene according to J. Meissner ([20]).

The acid and toluene are introduced from tanks (1) to the nitrator (2), in which the main part of the nitration proceeds. From here the contents pass to another nitrator (3), and if necessary to still another where the reaction is completed. The nitrators are arranged in series, each of them being operated co-currently. The reaction mixture passes from nitrator (3) to separator (d), where the separation of the nitro compound from the waste acid takes place. The nitrotoluene then flows to a system of washing tanks ((6) is the first of these). The waste acid passes to vessel (5), also continuously fed with toluene. By stirring the spent acid with a very small quantity of toluene, the former is freed from any nitro compounds present and at the same time the nitric acid still remaining in the spent acid (1-3%) reacts with toluene to yield nitrotoluene. The purified acid along with toluene is transferred by pump (8) to separator (9), where they are separated. The toluene, still containing some nitrotoluene, is introduced to the main nitrator (2), in a continuous way, thus realizing the counter-current principle and the spent acid, now containing only about 0.3% of HNO_3 and not more than 0.5% of aromatic compounds, goes direct to concentration, previous denitration being unnecessary here.

Nitrators for continuous nitration are of about one twentieth the size of reactors for the batch process. They are equipped with very efficient stirrers and fitted with an external jacket and a coil for conducting away the reaction heat. Rotameters, measuring with an accuracy of about 1%, are used for proportioning the reagents.

The nitrotoluene produced in the first aggregate is sent to the second one, where further nitration to dinitrotoluene takes place in a similar way as that described above. Finally, in the third aggregate, nitration to trinitrotoluene occurs.

For the first nitration stage (toluene to mononitrotoluene) a mixture of 96-98% sulphuric acid and 60% nitric acid is used. Sulphuric acid is taken in such as quantity as to obtain the concentration of about 70% of H_2SO_4 in the acid after the first stage of nitration.

The loss of sulphuric acid is about 1% of the quantity used. A 1.5% excess of acid is used over the required amount theoretically. The yield of nitrotoluene is 98% of theory.

The quantity of alkali required for the neutralization of the wash water does not exceed 0.5% of the weight of nitrotoluene.

The unit is easy to operate. It is claimed that at an output of 20-60 tons of TNT a day (larger units are not advisable) not more than one skilled worker is needed.

The separation of the production unit of mononitrotoluene from the next stages of nitration is desirable so as to provide the mononitration unit with a unit for removing m-nitrotoluene by distillation. A mixture of *o*- and *p*- nitrotoluene or *o*- nitrotoluene alone is then used for further nitration. In the latter case *p*- nitrotoluene is utilized for the preparation of dyes (from *p*- toluidine, derivatives of stilbene, etc.) and pharmaceuticals (*p*- aminobenzoic acid.)

Swedish Bofors-Norell method

The Bofors-Norell process [21] was tried out in 1940-41 and has now been in full-scale operation for nearly two decades. The process includes both continuous nitration of toluene or mononitrotoluene to trinitrotoluene and continuous crystallization of the product from dilute nitric acid.

The nitration is carried out continuously in a series of nitrators through which the nitrating acids and toluene or nitrotoluenes pass in counter-current. Each nitrator is joined with a separator.

According to A. B. Bofors both nitrator and separator have been designed in such a way that no pumps or conveyors are needed to transport the nitrating acid and the nitrated product between the different nitrators. Reactants are supplied continuously in quantities adjusted by means of proportioners. The continuous flow of waste acid from the mononitration stage and also of trinitrotoluene keeps the plant running constantly.

One of the features of the method is its lower temperature as compared with the former Bofors discontinuous method which required a temperature up to 140°C at the last stage of nitration.

All nitrators are provided with regulators controlling the supply of cooling water. According to A. B. Bofors, the raw material consumption per 1000 kg TNT is as follows:

toluene	450 kg
nitric acid (99%)	1000 kg
sulphuric acid (100%) supplied in the form of 95% sulphuric acid and oleum	1850 kg

A flow sheet and general view of the Bofors plant is given in Fig. 88 and 89 respectively. A general lay-out is given below (Fig. 101).

Swedish-Norwegian Chematur and Norsk Spraengstoffindustri method

This method [22] patented in Sweden in 1953 employs stepwise nitration of mono- and/or di-nitrotoluene to trinitrotoluene in a series of counter-current units, each unit consisting of a nitrator and a separator.

The principle of the design of the unit is given in Fig. 90. Nitrator N consists of a U-vessel with two legs or shanks (1) and (2) joined by pipe (6). The components of the reaction are introduced through inlets (4) and (5). Liquid can be kept in circulation from leg (1) to leg (2) and back by the turbine-wheel (8) on the driving-shaft (7). By regulating the speed of the turbine (8) and adopting suitable proportions for pipes (3) and (6) it is possible to keep the liquid at a higher level in leg (2) than in leg (1). Separator S communicates with the nitrator through pipe (9). The separator is shaped as a rectangular box (10) with distributor (II) for the mixture coming from the reactor, an outlet (12) for the separated light component and an outlet (13) for the heavy component. At some distance from the inlet and between the levels of the outlets for the separated components there is also another outlet (14) for partly separated emulsion. This outlet has adjustable plates (15) and (16) to make it possible to adjust the opening of the outlet with reference to its level in the separator. The partly separated emulsion is led back to the reactor through pipe (18) and regulating valve (17). To control the temperature of the reaction mixture the unit is equipped with heat exchangers (19) and (20). The separator may also have a heat exchanger jacket not shown in the diagram.

The unit is operated in the following way. The reactants are introduced through inlets (4) and (5), mixed with the help of turbine (8) and circulated through pipe system (1), (3) and (6) chemical reaction and physical exchange being simultaneously effected. They are continuously transported to the separator in the form of an emulsion. In the separator the components are separated, the light component (nitro compounds) rising to the surface and flowing off continuously through outlet (12). The heavier component (spent acid) sinks to the bottom and is removed continuously through outlet (13). In the area between the separated components the partly separated emulsion is withdrawn and led to mixing part of the reactor. This transport is possible because the level of the liquid in the separator through leg (2) is higher

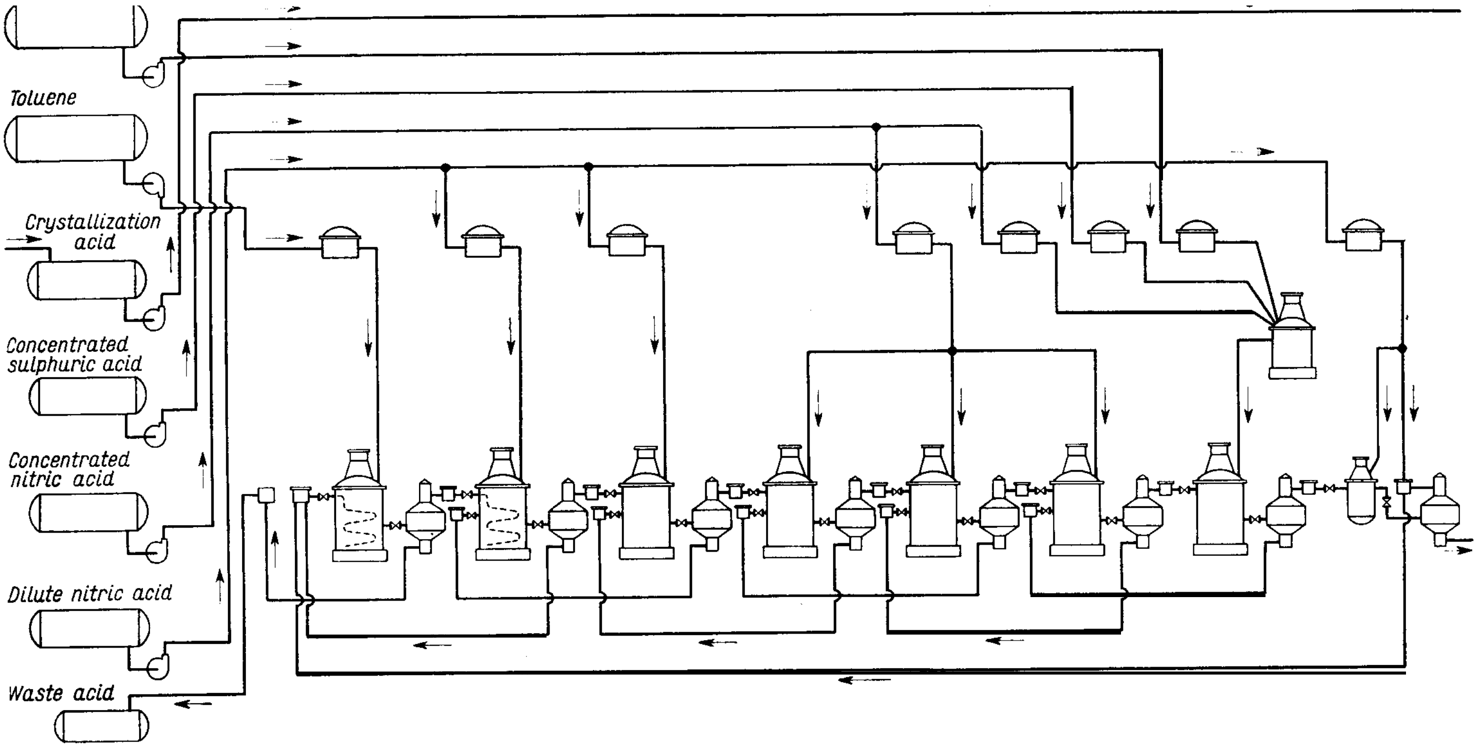


FIG. 88. Flow-sheet of Bofors-Norell method of continuous manufacture of TNT ([17]).

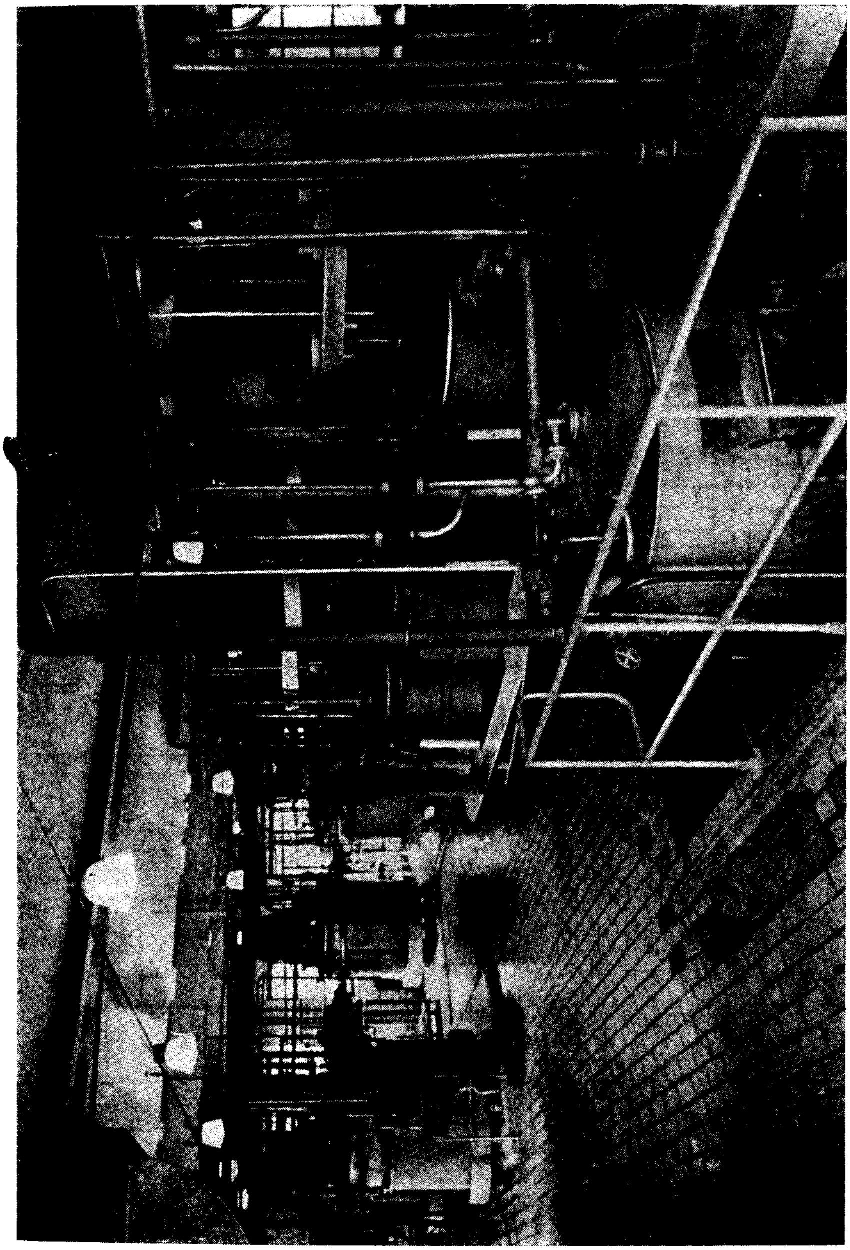


FIG. 89. General view of Bofors plant for continuous manufacture of TNT (Bofors-Norell method). Nitration and crystallization of TNT.

than in leg (1). The rate of feed of partly separated emulsion can be regulated by means of valve (17).

With plates (15) and (16) adjusted to lower levels of the fedback currents through pipe (18) they will be more enriched with the heavy component and this component will therefore be concentrated in the system.

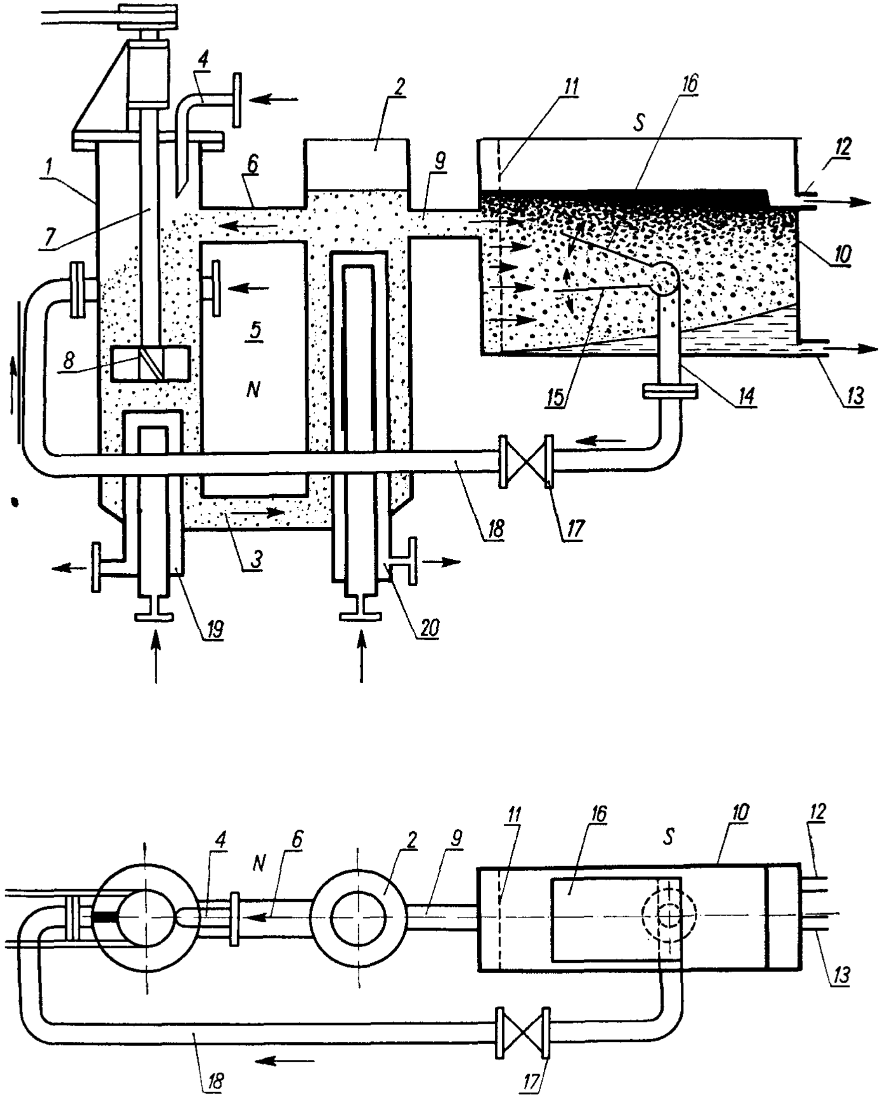


FIG. 90. Nitrator for continuous manufacture of TNT (Chematur method ([22]).

If eighteen nitrating units are applied, the composition of the nitrating mixtures and the temperature during the process will be as follows (Table 86).

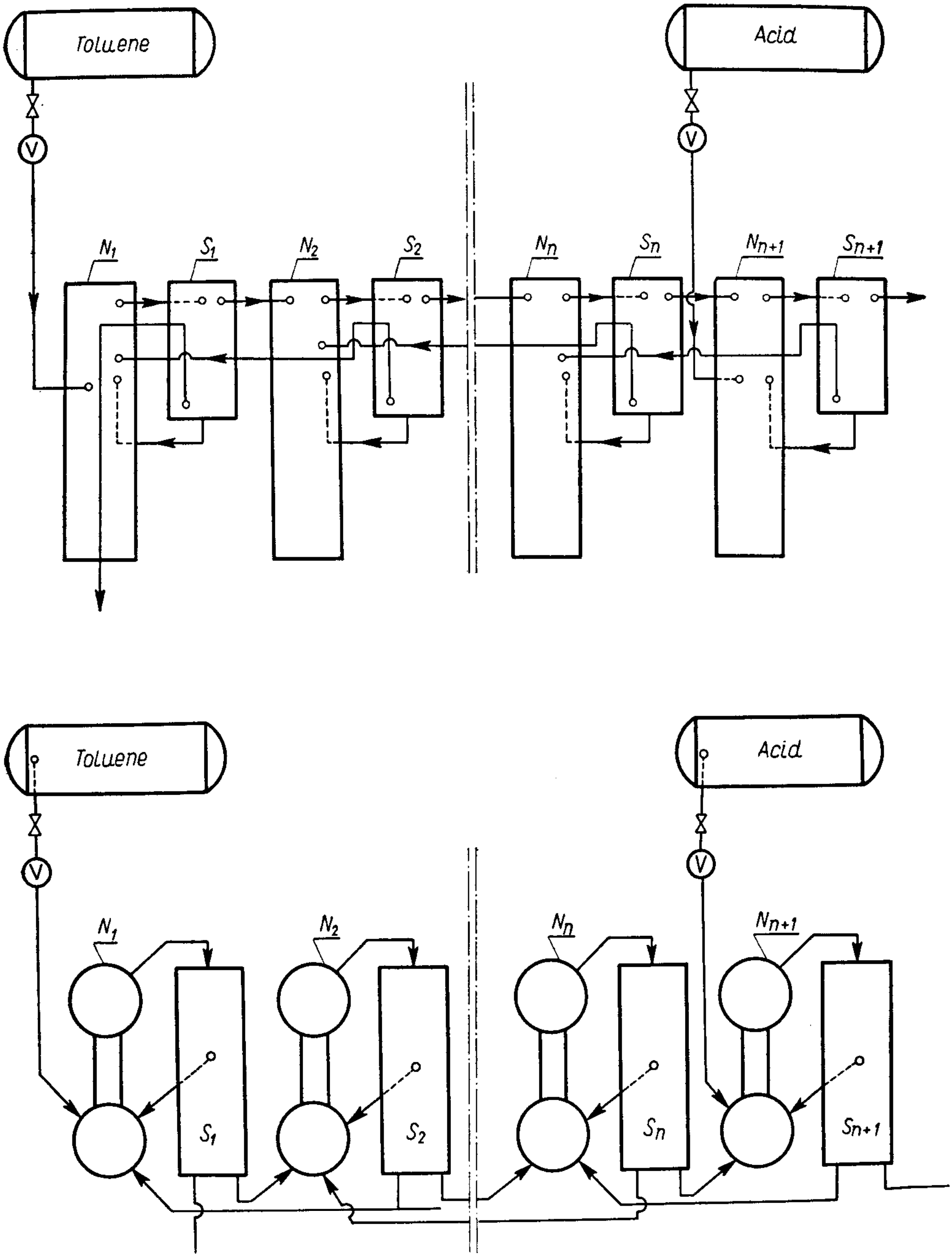


FIG. 91. Diagram of a system of nitrators (N) and separators (S) in the Chematur method of continuous manufacture of TNT [22].

The yield of TNT is as high as 97-99% of theory.

If an unfractionated mixture of the mononitrotoluene isomers is used (i.e. the product of straight nitration of toluene), TNT with a melting point of 78.7°C results. If the starting material is free from *m*- nitrotoluene, e.g. if pure *o*- nitrotoluene is used, TNT with a melting point of 80.6°C is produced.

TABLE 86

Nitrators Nos.	Composition of nitrating mixtures, %			Temperature °C
	HNO_3	H_2SO_4	H_2O	
1-3	0.9	89.2	9.9	65
4-6	3.0	90.1	6.9	75
7-9	7.9	87.8	4.3	80
10-12	7.5	89.8	2.7	85
13-15	7.5	91.4	1.1	90
16-18	7.7	91.8	0.5	90

PURIFICATION OF TNT

In the purification of TNT the following impurities have to be removed:

(1) traces of nitric and sulphuric acids;

(2) unsymmetrical isomers;

(3) products of incomplete nitration;

(4) by-products (tetranitromethane, trinitrobenzene, nitrobenzoic acids, nitrocresols, etc.).

The aim of final purification is to remove all those products which are present TNT and which are more reactive than TNT itself (isomers, nitrocresols, nitrobenzoic acids etc.) or which can easily give oily exudation products (isomers, lower nitrated substances).

The oily exudation product (TNT-oil) is very undesirable for the following reasons :

(a) Exudation produces porosity of the TNT charge and reduces its density. This reduces its explosive effect. In artillery shells it can produce a dislocation of the charge on firing, compression of the air included in the cavities, and prematured explosion.

(b) The oily products can penetrate into the threaded parts of the shell and form “fire channels” through which the ignition of propellant can ignite the charge.

(c) The oily products can penetrate into the detonating gaine if the charge of the gaine is unprotected by a metal envelope (e.g. former English gaines made up of TNT in a silk bag). The oily products reduce the detonating powers of the gaine.

The first purification step is thorough washing of the TNT with hot water, in washing tanks or by emulsification.

PURIFICATION BY CRYSTALLIZATION

In the past the TNT, washed free from acids, was further purified by crystallization. For this purpose 95% alcohol was mostly used. Since alcohol is not a very good solvent for TNT, in several countries it was customary to add a certain quantity of benzene (e.g. 5%) as in Germany before World War II. In other countries toluene was added. Since benzene and toluene vapours are more toxic than that of alcohol, in some U.S.S.R. factories alcohol alone was used for the crystallization.

Various other solvents for the crystallization of TNT have been suggested: carbon tetrachloride (U.S.A., World War I), benzene, *o*- nitrotoluene (Stettbacher [23]). More modem method consists in crystallizing TNT from nitric acid (see below under continuous method of crystallization).

With the outbreak of World War I the shortage of alcohol compelled German factories to give up the crystallization method and to confine purification either to thorough washing with hot water or to crystallization by dissolving the TNT in concentrated sulphuric acid followed by precipitation with water (Vender's method [24]). The precipitation could be controlled by adding sufficient water to allow lower nitrated and unsymmetrical derivatives of TNT to remain in solution.

After the war the method of purification by crystallization was not resumed, as purification by means of sodium sulphite was introduced.

The reason why the use of alcohol for crystallization was abandoned can be ascribed to the constant risk of fire when handling a large quantity of this volatile and inflammable solvent. Attention had been drawn to this by the explosion which took place in the TNT drying building at the Allendorff factory in Schbnebeck in 1909. The cause of that dangerous explosion which destroyed both the crystallization building and the drying building was fire started by ignition of the mixture of alcohol vapour and air. It is very likely that the fire started in a centrifuge where TNT had been separated from the solvent after crystallization. The crystallization of TNT from alcohol solution had been the cause of many other fires, so when sulphitation was developed it was readily adopted.

Although the purification of TNT by sodium sulphite was widely used after World War I a number of factories continued with the crystallization method using among other solvents toluene, which directly after crystallization was used for nitration.

In the United States a method of purifying TNT by washing with xylene is used (after Clift and Fedoroff [25]). The method is based on the view that the isomers of $\alpha-$ trinitrotoluene are located mainly on the surface of the grains of solid TNT. For purification, TNT is mixed with xylene in the cold, then the latter is filtered Off on a vacuum filter. The operation is repeated with a smaller quantity of xylene the mixture is passed again through a filter and the rest of the xylene is removed by pressing to a content of 3-4%. Finally the product is dried under vacuum, at 60°C. The xylene from the washing operation is sent to distillation.

The residue left after the solvent - alcohol (in the earlier crystallization method) or xylene (from the washing technique) - has been distilled off, is a semi-solid substance consisting of α– trinitrotoluene, its isomers, dinitrotoluenes and other nitro compounds, all of them found as impurities in TNT.

The mixture, known as "TNT oil", generally melts within a wide temperature range, for example from room temperature up to 60°C. It may be used as a component of ammonium nitrate explosives for the mining industry.

The "exudation process" is a modified purification by crystallization. At present it is applied to purify grade III TNT and to recover impurities present in TNT for use as "TNT oil" in the preparation of explosive compositions. The process may be carried out in two ways.

In one of them TNT, scattered over sloped flat pans (Fig. 79, p. 351), is put into a chamber heated to 60°C. After several hours the low-melting impurities segregate as oil which collects in a special vessel placed below the pans.

Another method consists in melting TNT in tilting kettles (converters) heated by steam or hot water which are then left at rest at room temperature or slightly higher (e.g. 30°C) for slow crystallization. Under such conditions large crystals of TNT are formed immersed in an oily mixture of other nitro compounds. The latter is removed by breaking the solidified substance and inclining the kettle so as to enable the oil to run out.

The oily product has been used as an ingredient of coal mining explosives as so-called "liquid TNT". This material also comprised the liquid mixture of nitro compounds forming the residue after distillation of alcohol (or any other solvent) used for crystallization of TNT.

In an earlier Russian method (Belenkii [8]) crude, granulated TNT was washed with hot water in wooden tanks lined with sheet lead, and equipped with an air bubbler.

For a batch of 1000 kg of TNT 1000 l. of water were used at a time. The water was brought to boiling by direct heating with steam (1-2 hr). After boiling for 5 min heating and air mixing were stopped, and the TNT allowed to settle at the bottom. After 10-15 min the water was separated by decantation. This operation was repeated 6-8 times with new portions of fresh water, until the acidity of the TNT fell to 0.02% (calculated on H_2SO_4). The whole washing process took about 7 hr. The use of lead-lined tanks for the first two washings, and a wooden tank for the next ones proved advantageous,

Norell [26] invented a continuous method of crystallization of TNT from nitric acid. A diagram is given in Fig. 92, according to the A. B. Bofors patent.

The crystallizing vats (1).-(5) are provided with heating jackets (3) and stirrer (4). The vats communicate through the overflow (7) and pipes (6). The last crystallizer has an outlet (8) provided with a screw type conveyer to remove a semi-solid mixture of crystals of TNT plus mother liquor.

The first vat is provided with pre-crystallizer (9) and a stirrer (10). The molten TNT (II) and solvent (12) (i.e. nitric acid) is introduced to the pie-crystallizer in which TNT

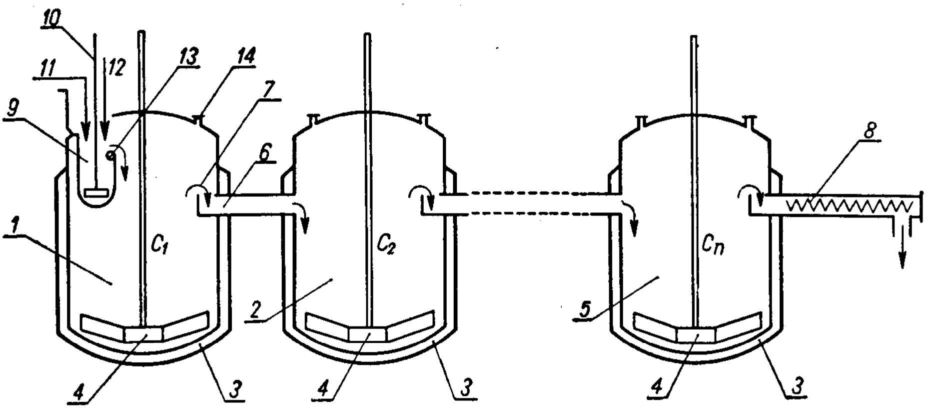


FIG. 92. Continuous crystallization of TNT (Bofors-Norell method [26]).

is dissolved. The solution flows to the crystallizer (1) through an overflow weir (23). Mechanical impurities are held back by the weir. The crystallizer decks are provided with apertures (24). Vat (1) is heated, vat (2) is cooled. Here crystallization begins, and is ended in vat (5).

SULPHITATION AND DRYING OF TNT

There are various methods of purification of the TNT with sodium sulphite.

French method

In the French method the ground TNT is mixed with a 7.5% solution of Na_2SO_3 at room temperature for 2 hr. The operation is carried out in wooden vats, 1.3 m high and 1.3 m in diameter (Fig. 78), using 750 kg of TNT and 750 1. of the solution at a time. Then the mixture in the vat is drained off to a vacuum filter, where the TNT is filtered off, washed with water four times, and sent to a drier.

For drying, an iron vessel of construction similar to that of the nitrator, is charged with TNT (2250 kg). The TNT is melted by passing steam through the jacket of the drying vessel, after which dry air is passed from the bottom through the molten product.

The vessel is covered by a hood with a ventilation pipe through which the moisture escapes (Fig. 93). Initially a temperature of 90°C is maintained, and toward the end of the operation it is raised to 105°C to let the rest of moisture escape.

@he-dry, molten TNT is -subsequently flaked. The equipment for this, operation consists of a rotating steel drum (I), cooled by water from inside. The lower part of the drum is dipped in molten TNT, the temperature of which is about 80°C (Fig. 94). The cooled surface of the drum causes the TNT to solidify on it, and a bronze knife (2) scrapes off the TNT coating in fine flakes, which fall into hopper (3). Flaked TNT is the most convenient form for transport, storage and further use, and is therefore the most widely used form of this substance. Alternatively pure TNT is sometimes used in the form of granules, obtained by granulating in cold water. For this purpose the installation described on p. 364 may be used, in which a stream of molten TNT ejected under pressure impinges on two streams of cold water at their point of contact (Fig. 84). Grains of TNT together with water fall into a tank, and are conveyed to a centrifuge or to a vacuum filter. To remove water the product is dried in a tunnel or tray drier at 50-60°C, i.e. at a temperature below its melting point.

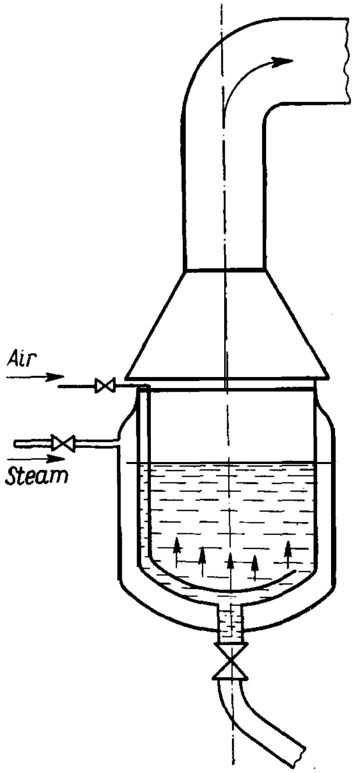


FIG. 93. Vessel for drying TNT.

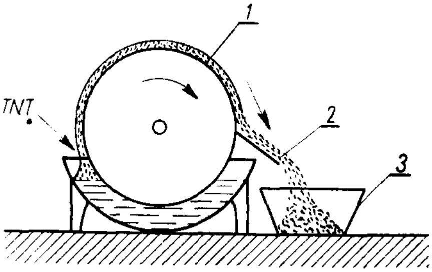


FIG. 94. Flaking of TNT.

The water and liquors from washing and sulphitation of TNT contain some TNT both dissolved and suspended. For recovering the latter the water and wash liquor are conveyed to "labyrinth" tanks equipped with baffles barring the passage of suspended TNT, which settles at the bottom. In this way a certain amount of lower grade TNT may be recovered.

British method

In the British method, crude, granulated TNT prior to sulphitation is washed either batchwise - an operation not differing from the one described above - or continuously.

The plant for continuous washing (Fig. 96) consists of a rectangular trough, 8 m long, 1.4 m wide and 1.3 m high. The trough is made of cast iron sections screwed

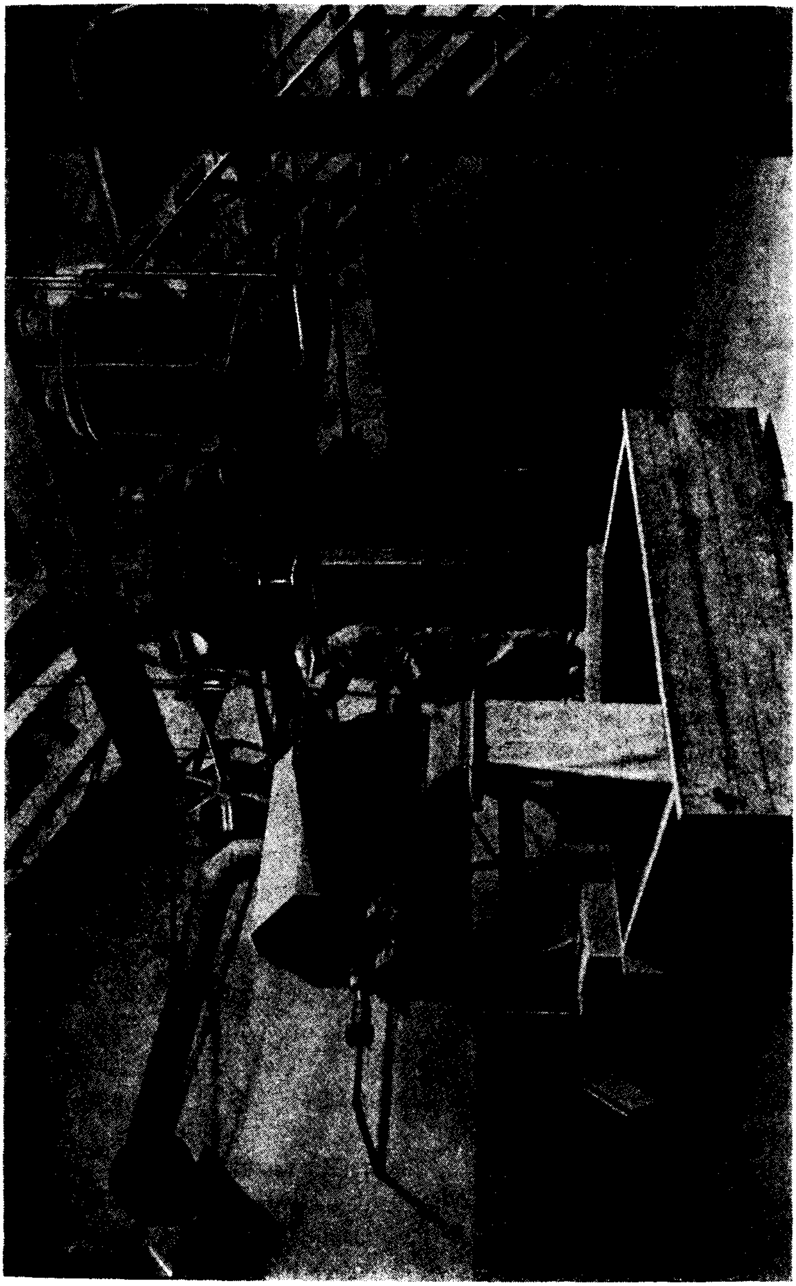


FIG. 95. General view of drying and flaking TNT (Bofors Nobelkrut).

together to form a unit. It is divided into sections by vertical walls, each section consisting of two parts: a larger one for mixing the TNT with water (mixers), and a smaller one for separating both phases (separators).

The vertical walls are provided with holes to allow both molten TNT and water to flow through. Each segment is also provided with horizontal perforated iron plates. The mixers are equipped with stirrers, rotating at high speed, which can direct the contents of the unit upwards or downwards.

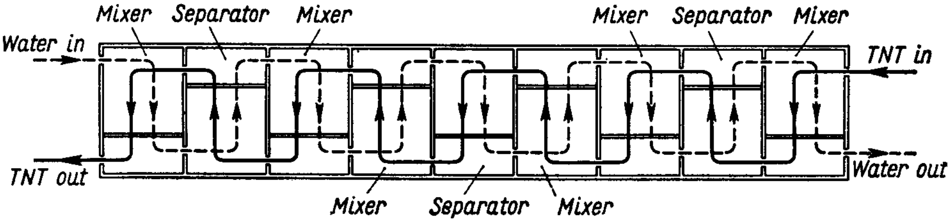


FIG. 96. Continuous washing of TNT (British method [6]).

It can be seen from the diagram that the molten TNT to be washed flows in counter-current against a stream of hot water. In the mixers, emulsification of the TNT in water takes place. The emulsion then passes through an overflow at the top or at the bottom of the mixer (depending on the direction given by the stirrer) to the separator, where the TNT collects at the bottom and flows to the adjacent mixer by an outlet near the bottom. Water rises to the top of the separator and passes in counter-current through an overflow to another mixer. By direct steam heating a temperature 80-100°C is maintained in the trough. The cover of the latter is provided with vent ducts for escaping vapours.

For 1000 kg of TNT about 2500 1. of water is used. The output amounts to 1.5 tons of TNT per hour. After washing the acidity of TNT falls to 0.1-0.2% of H_2SO_4

The sulphitation of TNT is carried out in a unit illustrated in Fig. 97.

The granulated, crude TNT is washed with hot water in a wooden vat A, equipped with a stirrer rotating at a speed of 75 r.p.m., and with a sheet metal lid connected to a ventilating pipe. The mixture in the vat is heated by steam introduced through a silicon-iron pipe. The acidity of the TNT falls after washing to below 0.1% of H_2SO_4. The number of washing operations depends on the initial acidity.

The molten, deacidified TNT is drained off to a crystallizer, placed below. The crystallizer consists of a wooden cylindrical vessel, 0.9 m high and 2.8 m in diameter, equipped with a wooden stirrer.

For crystallization the molten TNT is run from vessel A into a crystallizer filled with water, heated to 90-100°C. The ratio of water to the TNT should be 1:1 by volume. The content of the crystallizer is allowed to cool. At about 75°C the TNT begins to crystallize. After the temperature has fallen to 50°C (in about 4 hr from the time the crystallizer was loaded) sodium sulphite solution is added and the mixture is allowed to react for half an hour at a temperature of 40-45°C. The concentration of Na_2SO_3 in the crystallizer is 34%. The weight of the Na_2SO_3

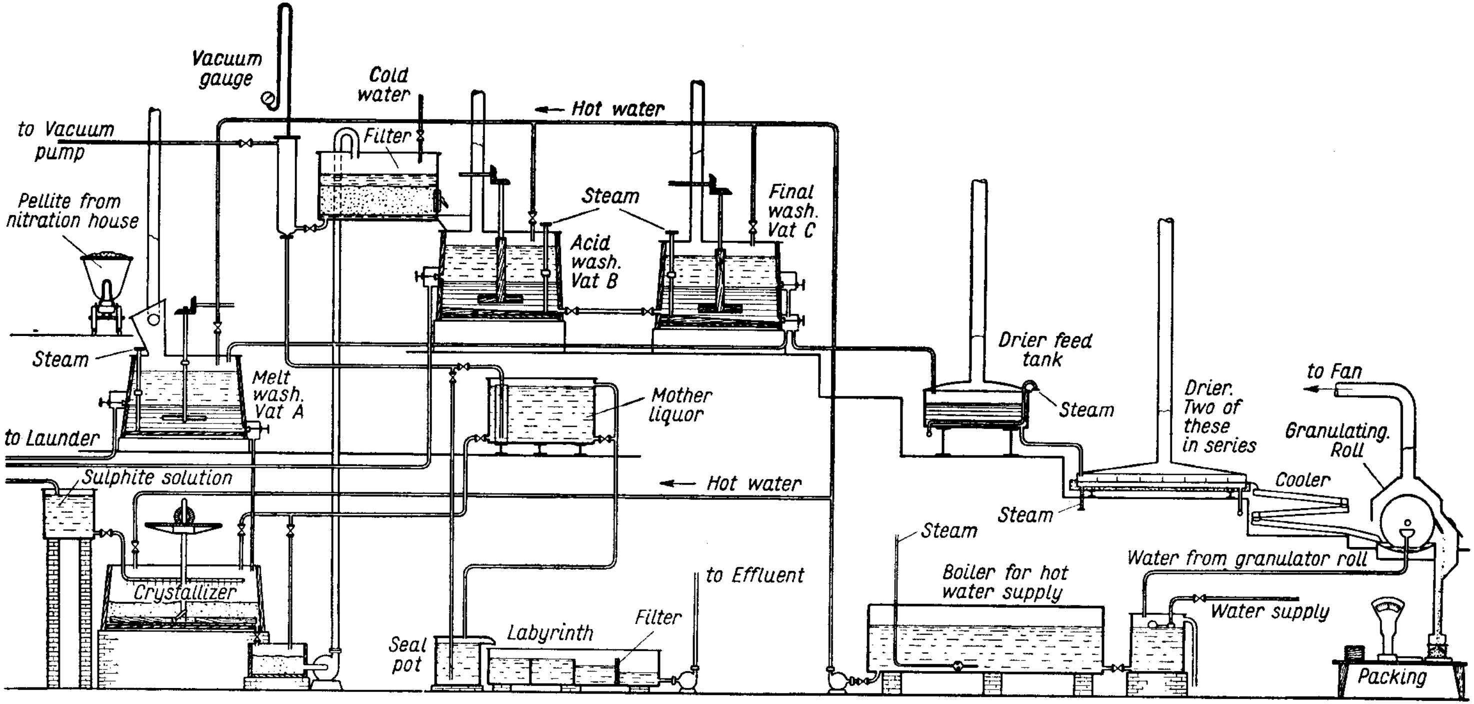


FIG. 97. Sulphitation of TNT (British method [6]).

used amounts to 3.54% of the weight of the TNT. The designers of this method believe that the uniform, Ime crystals formed in the crystallizer are most suitable for the sulphitation process.

The suspension of crystals in sodium sulphite solution is pumped upwards by a rotary pump to a vacuum filter through a small tank in which the suspension is diluted with water. After the TNT has been separated from the liquor it is washed with cold water until its pink colour, produced during the sulphitation process, disappears. The aluminium filter plate in the filter bowl should be covered with linen cloth, which in turn is covered with a layer of pure, granulated TNT.

After sulphitation and washing, the TNT is transferred to tank *B*, containing water acidified with sulphuric acid (up to 0.1%). Here the TNT is freed from any traces of basic sodium sulphite. The acidified, molten TNT is then transferred to tank C for final washing with pure, hot water. The washing is repeated several times, until the wash water proves neutral.

The solution of sodium sulphite from filtration of the TNT is collected in an intermediate tank from which part may be directed back for the sulphitation and part to a settling tank (labyrinth). There a certain amount of TNT slurry sets and may be utilized as the grade III TNT.

The washed TNT is then transferred to a tank where it is kept in the molten state and thence through a bronze wire gauze (for retaining any impurities) it is poured in a thin layer on to a tray for drying. The tray is steam heated to keep the TNT at a temperature of 105-115°C. Due to this temperature and the thin layer of the product, drying takes only a short time. Free from moisture, hot TNT is allowed to flow via a spout (in which it is cooled to about 98°C) into a flaker. The drum and the knife of the flaker are made of bronze. The drum is 60 cm in diameter and is rotated at a speed of about 4.5 r. p. m. (Fig. 94).

All pipes for conveying the molten TNT are heated by steam located below the TNT pipes, both being heat insulated.

German method

In a German method, applied at the Krümmel factory, the crude acid TNT, after it has been washed free from nitrosylsulphuric acid, is washed several times with water at a temperature of 90°C in brick washing vats lined with sheet lead, or in stainless steel tanks. The deacidification is finally followed by neutralization with an $NaHCO_3$ solution of concentration about 1%. The product obtained in this stage has a freezing point of 78.8-78.3°C.

For further purification molten TNT and hot water in equal volumes are run into a cast iron tank of 15 m^3 capacity, where the TNT is emulsified by vigorous stirring. The emulsion is cooled to 74-76°C and treated with a 25% solution of sodium sulphite, used in such a proportion as to obtain a final concentration of sodium sulphite in the mixture of 2.5%. During the sulphitation process 5-6% of trinitro compounds and 0.2-0.3% of tetranitromethane (calculated on the TNT) go into solution.

After half an hour the stirrer is stopped, the solution is separated by decantation and the TNT left behind is washed with water again at 85-90°C. If TNT of very high purity is required (m. p. 80.6%) it is sulphitated once more with a 0.5% solution of sodium sulphite.

The washed TNT is then air dried in a water heated tank of capacity 15 m^3, at 85-90°C. At this stage of manufacture samples are taken for determining the freezing point of the product. Finally the dry TNT is flaked on a steel drum with a bronze knife.

Continuous methods

Continuous washing with sodium sulphite was also applied at Schlebusch (Fig. 98).

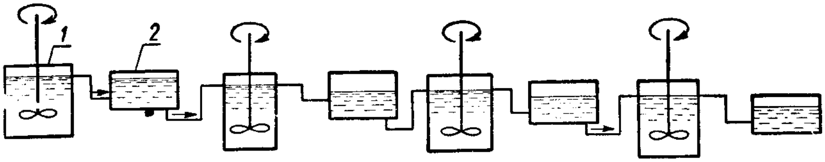


FIG. 98. Continuous washing with sodium sulphite of TNT in Schlebusch (CIOS XXIV - 4).

The purifying unit consisted of four washing tanks (I) and four separators (2). As in the nitration plant the vessels were arranged in cascade. The first washing tank was for washing the TNT with water, the next one for washing with sodium sulphite and the last two again for washing with water. Each was 0.5 m high and 0.8 m in diameter.

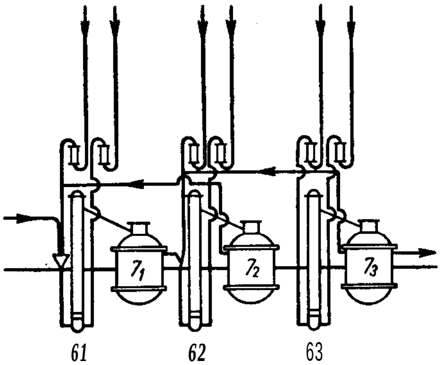


FIG. 99. Meissner’s continuous process of washing nitrotoluenes including TNT (co-currentsounter-current method [20]).

Meissner’s continuous process for washing nitrotoluenes, applied also for TNT (Fig. 99), belongs to the co-current-counter-current type. The quantity of water used should be as small as possible, thus reducing the losses of nitrotoluenes to a minimum. The nitro compound, separated from acid in the separator (4) (see the diagram in Fig. 87) flows to the washing column (6,), fed with fresh water. A mixture of the nitro compound and water flows off at the top of the column to the separator (7_1), where the nitro compound separates from acid washings. The washings (being the upper layer in the separator) are drained away, while the nitro compound flows to the next column (6_2), fed with the water from the third separator (7_3). A calculated weight of alkali is added to column (6_2) to neutralize any acid present. The neutralized mixture of the nitro compound and wash water flows off at the top of column (6_2) to separator (7_2) The water separated from the nitro compound is drained away while the nitro compound is transferred to column (6_3), whence it overflows to separator (7_3.) The nitro compound from the third separator passes to further nitration or to a drier, while water is led to column (6_2)

The equipment is made of stainless steel, those parts that hold alkaline or neutral liquids may be made of carbon steel. The washing columns are equipped at the bottom with air injectors for emulsifying the nitro compounds in water. To avoid any hazards the plant is not equipped with mechanical stirrers.

To remove any acid present the TNT is water-washed, neutralized with a solution of sodium hydrogen carbonate, then with a solution of sodium sulphite and finally washed several times with water.

SCHEMATIC DIAGRAM OF A PLANT FOR CONTINOUS TNT MANUFACTURE

A schematic diagram of such a plant is shown in Fig. 100. Separate buildings are denoted :

1. Packing department
2. Granulation
3. Sulphite washing and TNT drying
4. TNT washing
5. Nitration of nitrotoluene to di- and tri-nitrotoluene
6. Absorption
7. Concentration of sulphuric acid
8. Concentration of nitric acid
9. Preparation of washing solutions
10. Compressor house
11. Boiler house
12. Acid storage tanks for di- and tri-nitrotoluene
13. Acid storage tanks for mononitration
14. Distillation and mononitrotoluene separation plant
15. Toluene and mononitrotoluene separation tanks
16. Mononitration plant
17. Mononitrotoluene washing plant
18. Safety embankments
19. Safety walls for shielding passages.

A schematic diagram of a plant operated by the A. B. Bofors system is shown in Fig. 101.

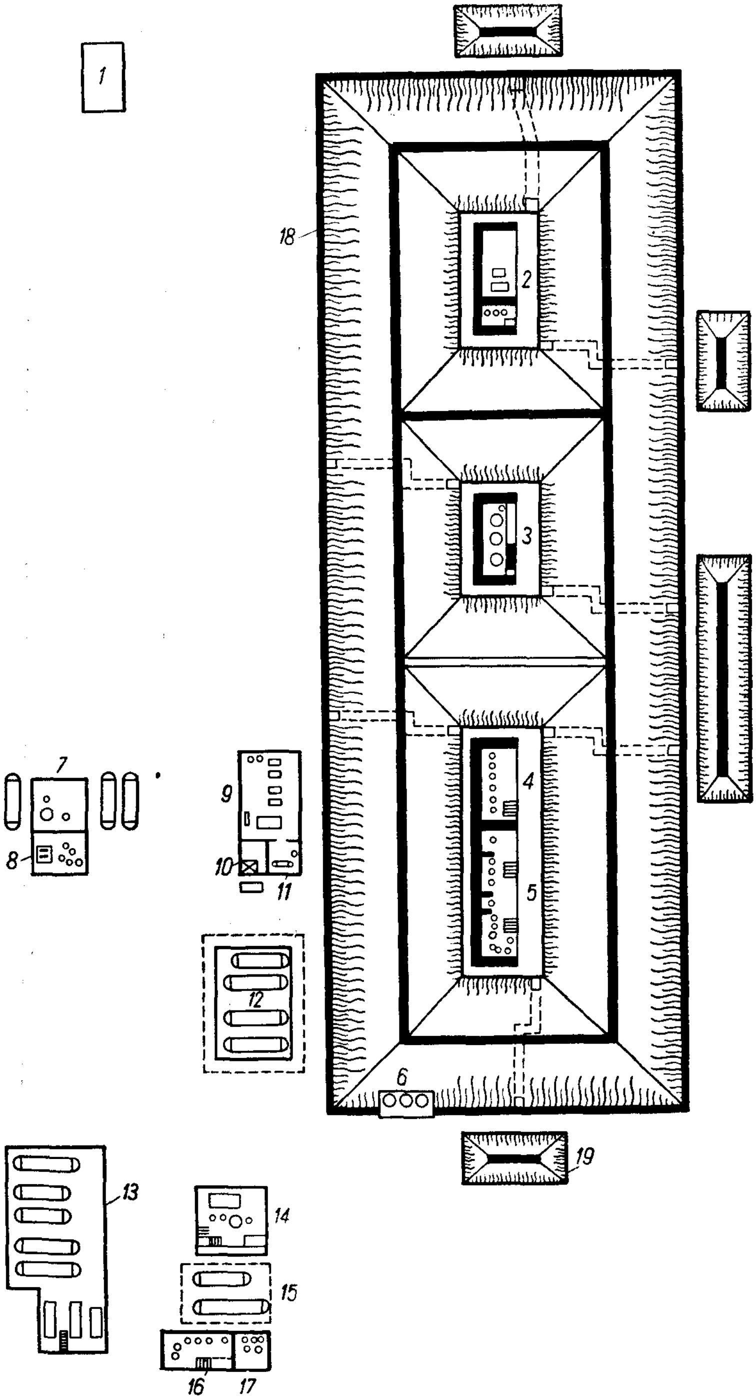


FIG. 100. Lay-out of a plant for continuous TNT manufacture according to Meissner [20].

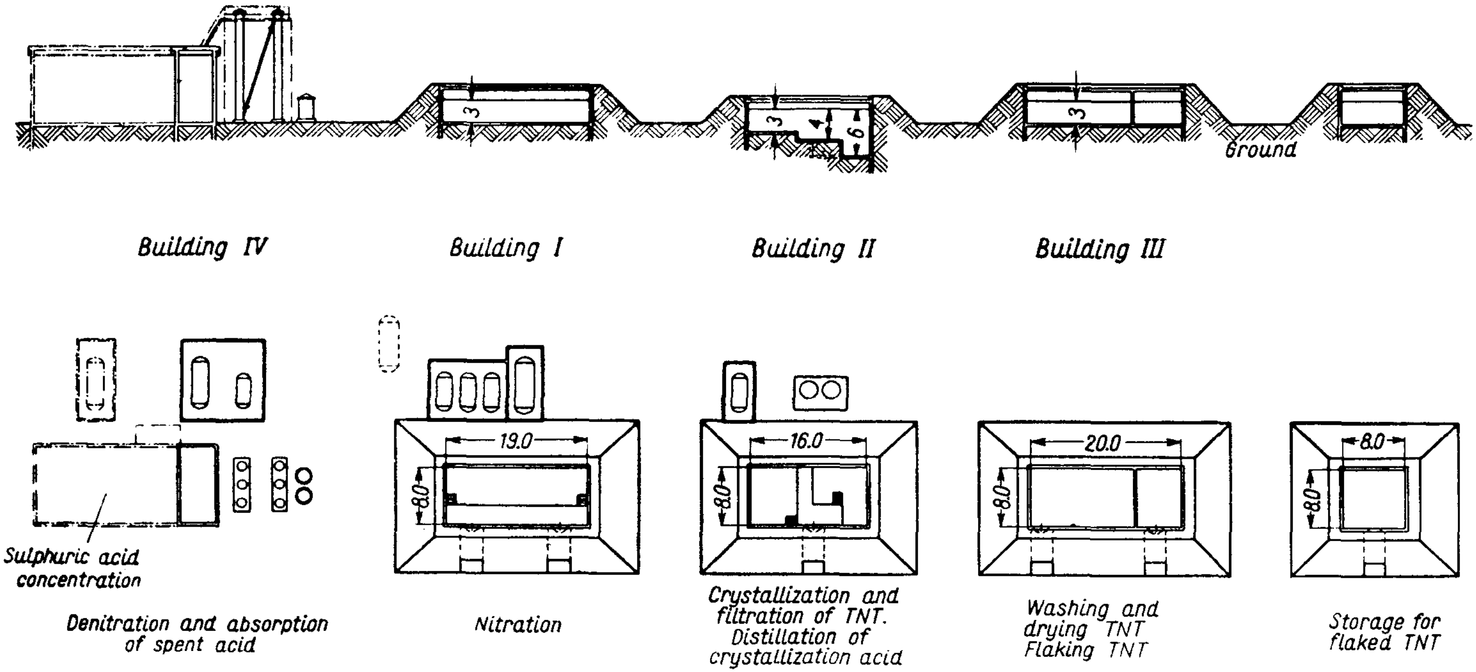
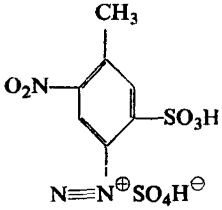


FIG. 101 Lay-out of a Bofors plant for continuous TNT manufacture [17]. (Dimensions in meters).

UTILIZATION AND NEUTRALIZING OF SULPHITATION LIQUORS

The sulphitation liquors contain dinitrotoluenesulphonic acids in a quantity amounting to about 4% of the TNT produced. In a period of intensive manufacture of TNT this may be of considerable importance from an economic point of view. This is why the problem has arisen of how to utilize the organic compounds contained in sulphitation liquors.

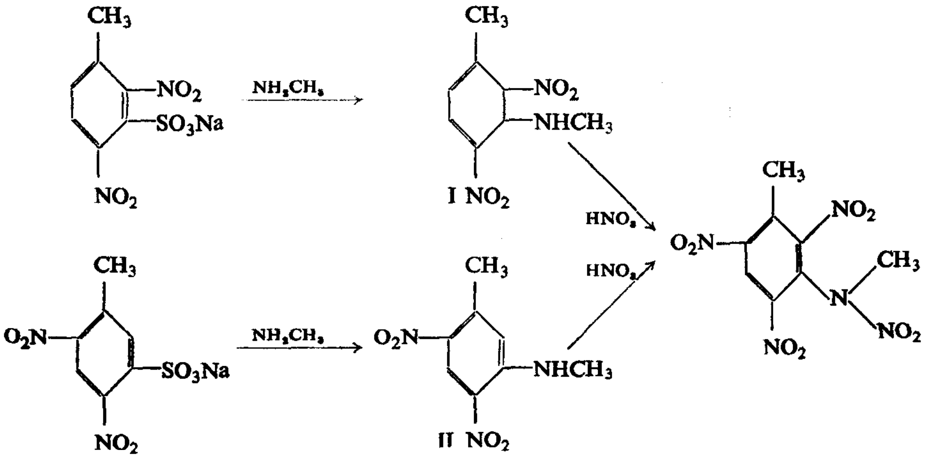
Batik [27] found that the acidification of sulphitation liquors with an inorganic acid resulted in the formation of $NaHSO_3$, which reduced the nitro- to the amino group. Simultaneously, due to the presence of $NaNO_2$, diazotization took place and a red diazonium salt



was precipitated.

The compound may be utilized for further reactions, for example in dyestuffs manufacture.

British Technical Records [6] mentioned another approach to the problem of utilization of sulphitation liquors. According to these data, attempts were made in Great Britain during World War I to make use of the reactivity of the sulpho group in the *ortho* or *para* position to the nitro ones. By acting with methylamine, N-methyldinitrotoluidine (I and II) was obtained, which, when further nitrated, yielded “methyltetryl”. All the methods mentioned proved uneconomical.



Gornall and R. Robinson [28] suggested reducing sodium dinitrotoluene sulphate (e.g. the sodium salt of 2,4-dinitrotoluene-3-sulphonic acid) to yield *m*- toluenediamine-3-sulphonic acid which could serve as an intermediate for obtaining azo dyes. Oxidation of sodium 2,4-dinitrotoluene-3-sulphonic acid with potassium permanganate in alkaline medium gave 2,4-dinitro-3-sulphobenzoic acid, also an intermediate for azo dyes.

WASTE WATERS

The problem of the neutralization of waste water from the manufacture of TNT, and the possibility of utilizing the dinitrotoluenesulphonic acids present in them acquired a considerable importance during World War II, owing to the enormous output of TNT. In Germany alone the production of TNT was over 20,000 tons a month, whereas during the World War I it averaged merely 3000 tons a month.

Such a high output involved the use of tremendous quantities of water. According to Kratz [29], for an production of TNT of 4000 tons monthly, 40,000 m^3 of water were used daily. Most of this was used for cooling, while the quantity of waste water containing nitro compounds and acids amounted to 5000-6000 m^3. Kratz believed this consumption of water to be abnormally high, and caused by hasty production.

Kratz has classified the "acid" waters according to their origin as follows (Table 87):

TABLE 81

Origin of water	Output m^3/hr	Colour and appearance	Acid content	Colour after purification with lime milk
Process water	50	brick-red turbid	4 g/l. H_2SO_4 2 g/l. HNO_3	dark red
Condensed water from concentration of sulphuric acid	100	almost Colourless, clear	2 g/l. H_2SO_4 0.3 g/l. SO_2	pale pink
Wash water	80	from light to dark brown from clear to turbid, with suspension	5 g/l. H_2SO_4 2g/l. HNO_3 (changeable)	dark red

Channels for discharging waste water should be open gutters or loosely closed troughs. The channels should be built of acid resistant bricks, joined by asplit (phenolic resin).

The removal of dinitrotoluenesulphonic acids from waste waters prevents a difficult problem since due to their high solubility they are difficult: to absorb on carbon or on anion exchangers, or to extract with dibutyl phthalate.

The water may be decolourized by chlorination, but this requires large quantities of chlorine. Biological processes can lead to destruction of TNT, but the sulphonic acids remain unaffected.

For this reason, according to Kratz, the most rational way of removing TNT and salts of nitrosulphonic acids from the water is by simply distilling off the water and then destroying the non-volatile residue.

Since this method is expensive as regards capital and operating costs, Kratz has suggested a method of treatment for acid waste water from the TNT manufacture consisting in agitating with 5-10% milk lime.

The reaction with calcium hydroxide is rather slow, so agitation should go on for some time (5-15 min). The mixture is then allowed to remain at rest for clarification. Treatment with milk of lime neutralized the acids and caused the precipitation of several coloured compounds, among others the products of the reaction of trinitrotoluene with calcium hydroxide. The amount of calcium oxide consumed in the process is 700 tons monthly, at an output of 4000 tons of TNT a month.

SAFETY IN TNT MANUFACTURE

The manufacture of TNT is one of the safest operations in the explosive industry. Nevertheless, any negligence about safety regulations may have disastrous consequences. Because the manufacturing process is regarded as safe, the fact must not be overlooked that less experienced personnel may disregard the regulations.

The most hazardous operation in TNT manufacture is nitration, primarily mono- and tri-nitration. In mononitration the hazard is due to the extremely violent reaction of the unreacted hydrocarbon with the nitrating mixture, and to the fact that nitro derivatives of cresols are formed in the process, along with nitrotoluenes. The last stage - trinitration - is dangerous due to the drastic conditions of the reaction which requires concentrated acids and a high temperature. The earlier method of trinitration at which temperatures up to 120°C were applied, was particularly hazardous. If the mononitrotoluene has not been freed from nitrocresols, trinitration is still more dangerous, due to the high reactivity of nitrocresols, and their liability to undergo oxidation. The formation of carbon monoxide may also be a cause of an explosion in the course of trinitration [33] (p. 339).

The spent acid from trinitration has also been the cause of several disasters, although it had been considered safe to handle. The most noteworthy example of this occurred in the Reinsdorf factory in Germany in 1935. The hot spent acid flowed down to open iron tanks, where, as the liquid cooled, a mixture of di- and Tri-nitrotoluenes rose to the surface. It was skimmed off from time to time and transferred to a washing tank, where it was washed with water. On skimming, a rubber glove and a shelf left on the brim of the tank with some cotton wool on it, fell into the tank. The reaction between the spent acid and the rubber and cotton wool initiated violent decomposition and fire. An attempt to extinguish the flames failed, and soon the nitro compounds on the surface of the spent acid exploded. The explosion and fire spread over several nearby tanks, then to the nitro compounds in the washing tank. As a result the whole plant for the recovery of nitro compounds was destroyed. In addition to this the explosion tore away the roofs of some nearby buildings, among them drier buildings located at a distance of about 660 m. Parts of the tank thrown off by the explosion into one of the driers detonated the TNT present, and in another they caused the ignition of the load. Similar explosions or fires spread over further buildings of the TNT factory. Moreover, a neighbouring nitroglycerine plant also exploded. This disastrous explosion cost 82 human lives and in addition 104 people were seriously and 700 were lightly injured.

Accidents caused by spontaneous explosion of finished TNT are also known. Some of them could be ascribed to the presence of traces of trinitrocresol salts. Others were presumably caused by products of decomposition of trinitrotoluene under the influence of sunlight or alkaline compounds used for deacidification of the TNT. Still others were due to the high sensitiveness of molten TNT to impact. This is why the drying of TNT should be regarded as a very dangerous operation.

Descriptions of several explosions that took place in French factories, may be very instructive. As an example, the explosion in the St. Chamas TNT factory in 1936 which caused the death of 53 people. Investigations showed that the explosion occurred after about 2000 kg of TNT in a drying tank had caught fire. The TNT in question was that recovered from the spent acid from trinitration ("plastic TNT"). It is known that such a product contains various impurities, among them the isomers of α– trinitrotoluene, nitrocresols etc. It had first been washed with water at 90°C then with a 6% solution of sodium carbonate, and again with water. The drying was effected at 85°-90°C by passing air for 8 hr. In the case described, as the drying TNT still contained some acid, 7 kg of sodium carbonate (i.e. 0.35% in relation to TNT weight) were added to the tank with the drying TNT which at the time contained only a very small quantity of water. This must have led to the formation of typical decomposition products of TNT brought about by reaction with alkalis. It is highly probable that these compounds were the first to ignite. whereupon the flames spread over the whole drier.

A number of explosions in French TNT factories which occurred during 1917-18, in particular the one at Neuville-sur-Saone (1917) which caused the destruction of the whole plant, were presumably due to the decomposition of the products of reaction of metals, such as lead or iron, with TNT under the conditions described in a paper by Kovache and Thibon [31]. Products readily decomposed, and sensitive to friction and impact, were formed in various parts of the plant where contact between these metals and the TNT could occur in the presence of dilute nitric acid, for example in the TNT washing tank and granulators. Similar compounds were found in a nitrator where part of the TNT in close contact with metals was subjected to the action of nitric acid vapours, for example around the seals at the stirrer shaft bearings.

Similar compounds were also found in an iron sulphitation tank. TNT is inflammable, although this occurs under specific conditions of prolonged action of glowing material.

Steele [32] described the following accident in the amatol section of an ammunition factory. A worker smoking a cigarette (in spite of the regulations) threw it away when he saw a foreman coming up. The burning cigarette fell on a sack filled with TNT. After a while the jute sack caught fire causing the TNT to ignite, and then to explode. This involved the explosion of the amatol in a mixer located in the same premises. The explosion tore away the wooden roof, and its fragments scattered on to other buildings causing further explosions. Soon all buildings of the factory were on fire and destroyed and 11 lives were lost, mainly in fire fighting.

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CHAPTER X

NITRO DERIVATIVES OF HIGHER BENZENE HOMOLOGUES

HIGHER benzene homologues, which have more or longer side chains than toluene, undergo oxidation more readily during the nitration process than toluene or benzene. They should therefore be nitrated with great care; the higher homologues in particular should be nitrated at a temperature as low as possible. As a rule the range of permissible concentrations of nitrating acids is narrower than for nitration of benzene or toluene. An excess of nitric acid should also be avoided. For example Kobe and Langworthy [1] gave the following data on the nitration of *p*- cymene to the mononitro derivative. An 89% yield can be obtained by nitration at 10°C, with a mole ratio of nitric acid to *p*- cymene of 0.9 and a weight ratio of sulphuric acid to *p*- cymene of 4.0, initially using a sulphuric acid concentration of 85 weight % and very vigorous stirring.

NITRO DERIVATIVES OF XYLENES

m- Xylene is the most important of the three xylene isomers *(ortho-, meta-* and *para-)* as a starting material for the preparation of nitro derivatives, as it enables three nitro groups to be introduced into the 2-, 4, and 6- positions. *Ortho*- and *para*- xylenes can give a stable system when only two nitro groups are introduced, for when three groups are introduced one of them is compelled to occupy an inappropriate position and may easily undergo substitution reactions.

Xylene for nitration should therefore be as rich in the *m*- isomer as possible. The requirements for the nitration of xylene will be discussed on pp. 406-412.

The presence of two methyl groups on the benzene ring greatly facilitates the introduction of nitro groups. In consequence less concentrated mixtures may be used for the preparation of trinitro-m-xylene (TMX) than for TNT.

On the other hand, the methyl groups are easily oxidized so the nitration should be married out under conditions less favourable for oxidation, for example at a temperature as low as possible. Low concentration of the nitrating mixture also facilitates oxidation reaction of xylene. Gorst [2] reported that the rate of oxidation is reduced with increase in the factor Φ or concentration of H_2SO_4 in nitrating mixtures. This can be seen in the diagram (Fig. 102) illustrating the nitration of DNX to TNX. The quantity of N_2O_3 evolved during the reaction was taken as a criterion of the intensity of the oxidation reactions.

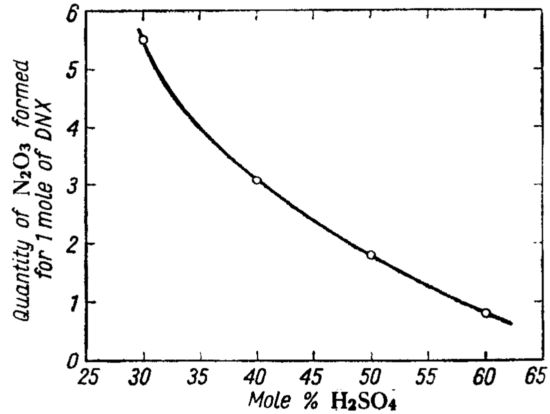


FIG. 102. Oxidation of dinitroxylene as a function of the concentration of sulphuric acid in nitrating mixtures (Gorst [2]).

Ortho- and *para-* xylenes are particularly easy to oxidize. One of the reasons why TNX has not been more widely used as explosive is that it is difficult to isolate m-xylene from the corresponding light oil or petroleum fractions (p. 406). Owing to the presence of its isomers commercial m-xylene, when nitrated, gives a mixture of nitro compounds, often containing oily components that exude easily and which are highly undesirable where a high purity product is required (e.g. for filling shells). In addition to this, trinitro-m-xylene has other disadvantages, viz.: its high melting point, which makes it difficult to fill shells by pouring, and its relatively low explosive power, which corresponds approximately to that of dinitrobenzene. An advantage of TNX is its low toxicity.

In spite of its drawbacks, during World War I France, Russia, and the United States used commercial trinitroxylene as an explosive, mostly in mixtures with other nitro compounds, or with ammonium nitrate, when these countries were short of nitration grade toluene. In the period between the two World Wars trinitroxylene was manufactured in the U.S.S.R and France and on a small scale in Poland.

Trinitroxylene is known as Ksilil (U.S.S.R.), Xylite (France), Ksylit (Poland) and TNX.

The commercial product, according to Kravchinskii [3], melts partially at 120-125°C and completely at 160-177°C, and solidifies at 160-162°C, while chemically pure 2,4,6-trinitro-m-xylene melts at 182°C.

The grades of commercial TNX as classified by their melting points are:

I grade	m. p.	170°C
II grade	m. p.	160-162°C

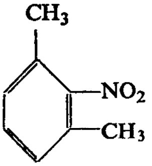
In addition grade III trinitroxylene may also be available. This is an oily product used like nitrated solvent-naphtha, for special purposes (e.g. in coal mining explosives).

Nitro derivatives of xylene were first mentioned in a work by Bussenius and Eisenstück [4], in 1860, on various products obtained from petroleum. The authors investigated among others the Hannover oil fraction, boiling from 75°C to 180°C. This fraction contains easily nitrated aromatic hydrocarbons. Among the products obtained in nitration, there was a crystalline compound melting at 169°C of composition, corresponding to that of trinitroxylene, as confirmed by analysis. A similar substance of higher purity, melting, at 177°C was obtained by Beilstein [5] in 1864 by nitration of xylene.

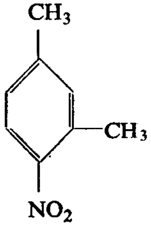
Systematic studies of the nitration of xylene and of the constitution of the products obtained were carried out by Noelting and Fore1 [6] and Blanksma [7]. During World War I in Russia Solonina [8] and Filippov [8a] and in France Marqueyrol and Loriette [9] developed methods of preparing nitroxylene in an industrial scale.

ISOMERS OF MONONITRO-m-XYLENE (MNX)

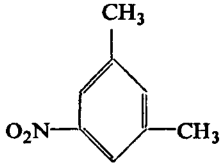
Three isomers of mononitro-m-xylene are known, viz.: 2-,4-, and 5-nitro-m-xylenes :



b. p. 225.5°C



m. p. 2°C
b. p. 246°C



m. p. 74°C
b. p. 273.7°C

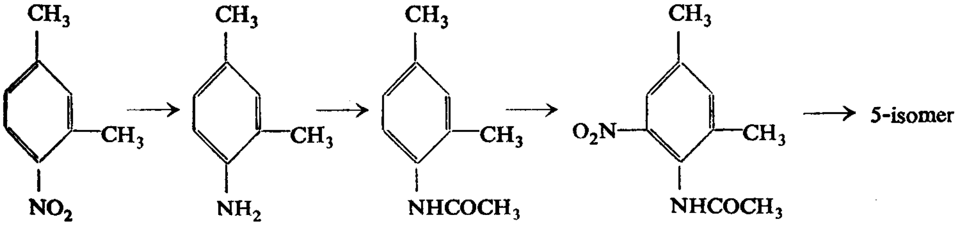
All three isomers can be obtained by nitrating m-xylene using a nitrating mixture of the composition:

HNO_3	25-28%
H_2SO_4	56-59%
H_2O	16%

The nitration temperature should not exceed 35-40°C.

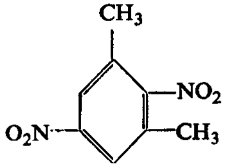
The principle products are the 2- and 4-isomers in the proportion of 25:75, while the 5- isomer is obtained only in an insignificant quantity.

The latter can be obtained from the 4- isomer (Wróblewski [46]):

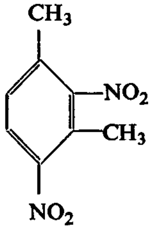


ISOMERS OF DINITRO-m-XYLENE (DNX)

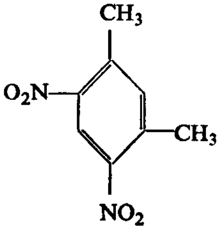
The following three isomers of dinitro-m-xylene are known:



m. p. 132°C



m. p. 82-84°C



m. p. 101°C

All three isomers can be obtained either by the nitration of *m*- xylene with a nitrating mixture such as:

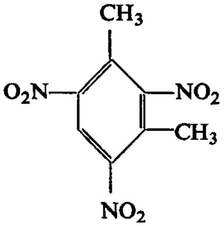
HNO_3	20%
H_2SO_4	65%
H_2O	15%

or by the nitration of mononitro-m-xylene with a mixture poorer in nitric acid (e.g. HNO3 - 10-12%, H_2O - 15%).

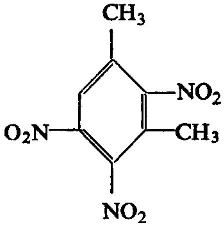
The 2- isomer predominates in the nitration product, while the 2,5- isomer formed in the nitration of 5-nitro-m-xylene is obtained only in small quantity.

ISOMERS OF TRINITRO-m-XYLENE (TNX)

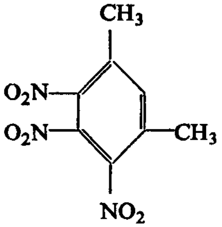
There are three isomeric trinitro-m-xylenes: 2,4,6-trinitro-m-xylene, 2,4,5-, and 4,5,6-trinitro-m-xylene :



m. p. 182°C



m. p. 90°C



m. p. 125°C

The 2,4,6- isomer is the principal component of the products of nitration of *m*- xylene. It constitutes the largest part of the purified commercial product. The 4,5,6- isomer is formed only in an insignificant quantity.

The composition of the nitrating mixture depends on whether *m*- xylene, nitro- or dinitro-m-xylene is to be nitrated. Usually more dilute mixtures are applied than for the nitration of toluene to trinitrotoluene.

For example, for the conversion of dinitro- to trinitro-m-xylene, a mixture containing 9-10% of water at a temperature up to 100°C is used.

m- Xylene can be nitrated to its trinitro derivative in one stage using a nitrating mixture containing ca. 20% of HNO_3 and ca. 3% of H_2O.

Physical properties of 2,4,6-trinitro-m-xylene

2,4,6-Trinitro-m-xylene crystallizes in white crystals at room temperature. It is only slightly soluble in concentrated sulphuric acid - at a temperature of 150-160°C 10% of it goes into solution. In fuming sulphuric acid the solubility is higher.

The solubility of 2,4,6-trinitro-m-xylene in organic solvents is much lower than that of α– trinitrotoluene (Table 88).

TABLE 88

SOLUBILITY OF 2,4,6-TRINITRO-m-XYLENB IN ORGANIC SOLVENTS

Solvent	At room temperature g/100 ml of the solvent	At boiling point g/100 ml of the solvent
Benzene	0.5	7.5
Toluene	0.5	20.5
Alcohol	0.05	0.55

The solubilities of trinitro-m-xylene (m. p. 180.5°C) in mixtures of benzene with alcohol (after Kravchinskii [3]) are given below (Table 89).

TABLE 89

SOLUBILITY OF TRINITRO-m-XYLENE IN MIXTURES OF BENZENE WITH ALCOHOL

Composition of the solvent, parts by volume		Solubility, g/100 ml of the solvents	
benzene	alcohol	at 8°C	at 20°C
1	0.5		0.71
1	1	0.32	0.45
1	1.5	0.24	0.29
1	2	-	0.2

At high temperatures 2,4,6-trinitro-m-xylene is readily dissolved by acetic acid and by aniline. 2,4,6-Trinitro-m-xylene forms eutectics with aromatic hydrocarbons and their nitro derivatives. Some of the available data are tabulated (Table 90).

The steam volatility of 2,4,6-trinitro-m-xylene is low. At a temperature of 100°C it begins to sublime. It can be purified by sublimation at 150-170°C. The thermal conductivity of 2,4,6-trinitro-m-xylene at 25°C is 0.00057 (Prentiss [12]).

chemical properties of 2,4,6-trinitro-m-xylene

2,4,6-Trinitro-m-xylene is not affected by hot concentrated sulphuric and hydrochloric acids, but it reacts with alkalis in the presence of alcohol or acetone, yielding an intense blue addition product.

2,4,6-Trinitro-m-xylene forms addition products less easily than α– trinitrotoluene. Undoubtedly the two methyl groups present in the ring reduce its ability to form addition compounds.

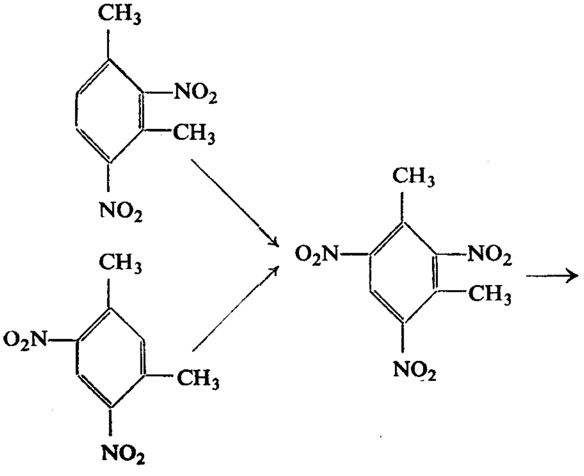
TABLE 90

EUTECTICS WITH 2,4,6- TRINITRO-m-XYLENE

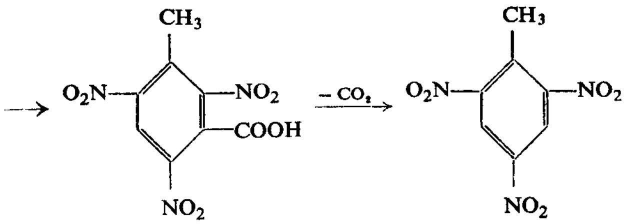
The second component	%TNX by weight	m. p. °C	Authors
Anthracene	64.4	151.2	Jefremov and Tikhomirova [10]
m- Dinitrobenzene	17.8	76.4	
2,4-Dinitrotoluene	6.0	67.7	Bell and Sawyer [11]
Naphthalene	7.6	76.0	Jefremov and Tikhomirova [10]
p- Nitrotoluene	2.0	50.5	Bell and Sawyer [11]
Picramide	23.5	110.8	Jefremov and Tikhomirova [10]
Picric acid	21.7	105.8	"
Picryl chloride	12.8	73.2	"
Tetryl	23.5	110.8	"
sym-Trinitrobenzene	16.4	104.6	"
	(Solid solution, system V of Roozeboom)		
2,4,6-Trinitro-m-cresol	17.2	84.6	Jefremov and Tikhomirova [10]
Trinitroresorcinol	37.5	141.3	„
2,4,6-Trinitrotoluene	8.0	75.2	„
	(Solid solution, system V of Roozeboom)		

According to Jefremov and Tikhomirova [10], 2,4,6-trinitro-m-xylene contrary to both sym-trinitrobenzene and 2,4,6-trinitrotoluene does not combine with such hydrocarbons as acenaphthene, anthracene, phenanthrene, fluorene or naphthalene.

The constitution of 2,4,6-trinitro-m-xylene was determined by Grevingk [13]. He nitrated both 2,4- and 4,6-dinitro-m-xylene and obtained the same product.

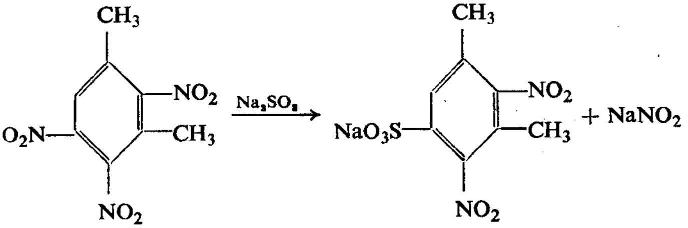


(1)



Then, by oxidizing one of the methyl groups to a carboxyl group with chromic acid, he obtained a carboxylic acid which on losing CO_2 was converted to α– trinitrotoluene.

The isomers of 2,4,6-trinitro-m-xylene formed in the nitration process may of course be removed from the product by crystallization or by reacting with sodium sulphite, the substitution of a nitro group by a sulpho group taking place, e.g.:



(2)

The reaction proceeds much more slowly than with the unsymmetrical trinitro derivatives of toluene.

Explosive properties of 2,4,6-trinitro-m-xylene

2,4,6-Trinitro-m-xylene is more sensitive to impact than TNT. This can be explained by the presence of a large number of substituents on the benzene ring. As Wohler and Wenzelberg [14] found, it could explode at only about half the impact energy needed for the explosion of TNT.

Other authors, however, declare that the sensitiveness of trinitro-m-xylene is only slightly higher than that of TNT. Taking 100 as figure for picric acid, the sensitiveness of TNT is 127 and that of trinitro-m-xylene is 120.

The explosive properties of trinitro-m-xylene, as measured by Kravchinskii [3] are: initiation temperature, 330°C; lead block expansion test, 270 ml (for TNT this author gives 285 ml); rate of detonation, 6600 m/sec (d = 1.51).

Kast [15] found the explosive power of 2,4,6-trinitro-m-xylene to be similar to that of *m*- dinitrobenzene.

The heat of formation of 2,4,6-trinitro-m-xylene equals +18.3 kcal/mole.

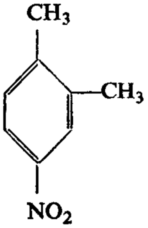
Applications of TNX

Trinitroxylene is used as an additive for fusible explosive compositions mixed with TNT, with TNT and picric acid, or with ammonium nitrate (Vol. III). For the compositions of various eutectics with trinitroxylene see p. 400.

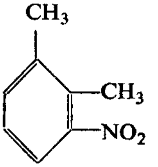
MONONITRO DERIVATIVES OF *o*- AND *p*- XYLENES

Ortho- and *p*- xylene nitrate more readily than *m*- xylene. They are also more readily oxidized especially during mononitration as well as during vigorous nitration to trinitro derivatives. For this reason the yields obtained in the nitration of *o*- and *p*- xylene are lower than those obtained with *m*- xylene.

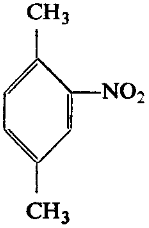
The following mononitro derivatives are known: 4-nitro- and 3-nitro-o-xylene and 2-nitro-p-xylene :



m. p. 30°C
b. p. 258.8°C



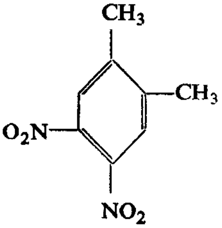
m. p. 9%
b. p. 250-8°C



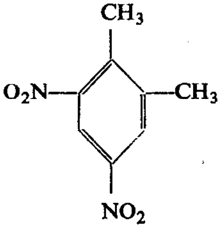
b. p. 234-239°C

DINITRO DERIVATIVES OF *o*- AND *p*- XYLENES

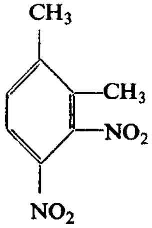
The following dinitro-o-xylenes are known: 4,5-, 4,6- (or 3,5-), 3,4- and 3,6-*o*- xylene :



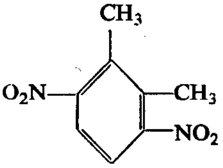
m p. 115°C



m. p. 75-76°C

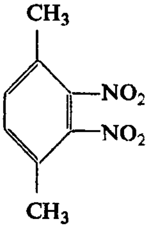


m. p. 82°C

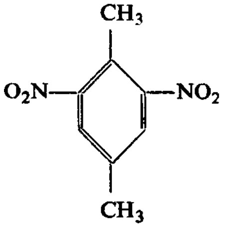


m. p. 56-60°C

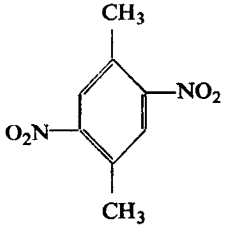
Among dinitro derivatives of *p*- xylene the following three isomers are known : 2,3-, 2,6- and 2,5-dinitro-p-xylene :



m. p. 93°C



m. p. 123-129.5°C

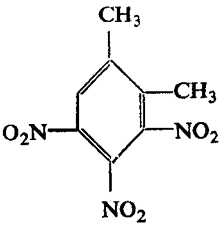


m. p. 147-148°C

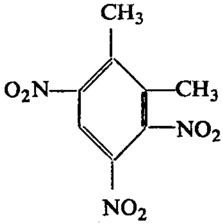
Nitration of *p*- xylene mostly yields the 2,3- and 2,6-isomers.

TRINITRO DERIVATIVES OF OF AND *p*- XYLENES

At first *o*- xylene was believed (Noelting and Thesmar [16]) to be without trinitro derivatives, until Crossley and Renouf [17] obtained a trinitro compound, which they separated into two isomers - 3,4,5- (or 4,5,6-) and 3,4,6- (or 3.5,6-):



m. p. 115°C

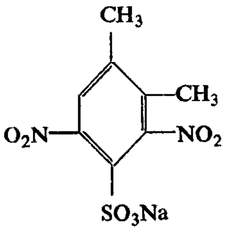


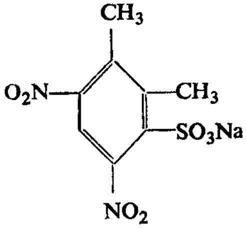
m. p. 72°C

Later these observations were confirmed by Marqueyrol and Loriette [9]. From 100 parts of *o*- xylene, 130-135 parts of trinitro derivatives are obtained.

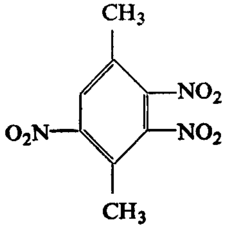
To separate the isomers use is made of their different solubility in 75% sulphuric acid. The mixture of isomers is dissolved in the acid at 120-130°C, and then cooled; only the 3,4,5-isomer crystallizes then. The 3,4,6-isomer left in the acid can be precipitated from the solution by adding water. The 3,4,5-isomer can be purified by crystallization from 75% sulphuric acid, the 3,4,6-isomer by crystallization from alcohol.

Both isomers react with sodium sulphite to form the corresponding sulpho derivatives :





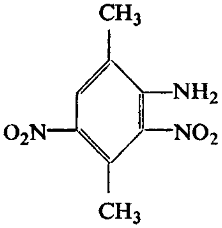
Only one trinitro-p-xylene exists, viz. 2,3,5- or 3,5,6-trinitro-p-xylene :



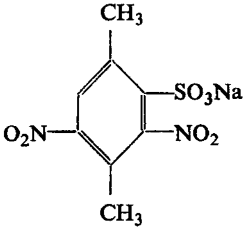
m. p. 139-140°C

It was first obtained by Noelting and Geissmamr [18] in a yield of 150 parts Per 110 parts of *p*- xylene.

With an alcoholic solution of ammonia, trinitro-p-xylene gives dinitroxylidine:



which reacts with sodium sulphite to form a sulpho derivative:



The solubility of the trinitro derivatives of *o*- and *p*- xylene in various solvents is higher than that of trinitro-m-xylene. Here are the comparative data on the solubilities in 100 ml of 95% alcohol at 8°C (after Kravchinskii [3]):

2,4,6-trinitro-m-xylene	0.024 g
3,4,5-trinitro-o-xylene	0.874 g
3,4,6-trinitro-o-xylene	1.159 g
2,3,5-trinitro-p-xylene	0.325 g

MANUFACTURE OF TRINITROXYLENE (TNX)

Xylene

The success of the nitration process, from the point of view of the quality and yield of the product as well as of safety, depends to a considerable extent on the quality of the xylene used. For nitration, both xylene from coal pyrolysis and from petroleum is used. In both cases *m*- xylene is the main component of the crude substance.

The average composition of xylene from coal is:

o- xylene	10%	(b. p. 141°C, sp. gr. 0.863)
m- xylene	66%	(b. p. 139°C, sp. gr. 0.862)
p- xylene	20%	(b. p. 136°C, sp. gr. 0.861)
ethylbenzene	4%	(IL p. 136°C, sp. gr. 0.876)

Xylene obtained by cracking heavy petroleum hydrocarbons has approximately:

20-47% of *o*- and *p*- xylene, 30-45% of *m*- xylene, 12-25% of ethylbenzene and 8-10% aliphatic hydrocarbons.

The composition of the xylene obtained by distillation of Borneo petroleum is much the same as that of the xylene from coal.

Due to a relatively high content of the *m*- isomer xylene derived from coal or xylene from Borneo oil is the most convenient starting material for the preparation of nitration grade xylene.

Small differences in the boiling points of the xylene isomers make the preparation of pure *m*- xylene by distillation impossible. Nevertheless, boiling ranges of fractions suitable for nitration can be established.

Dobrianskii [19] tabulated the boiling points of the isomeric xylenes under various pressures (Table 91).

TABLE 91

BOILING POINTS OF ISOMERIC XYLENE

Pressure mm Hg	ortho	meta	para
740	143.50	137.90	137.20
750	144.00	138.40	137.70
755	144.25	138.65	137.95
760	144.50	138.90	138.20
765	144.75	139.15	138.45
770	145.00	139.40	138.70

According to Soviet data (Kravchinskii [3]), from the fraction of commercial xylene boiling below 136.5°C a nitration product of low value is obtained, melting at a low temperature owing to its high content of oily products. The fractions boiling in the range 136.5-140°C are much more convenient for nitration, since the product obtained has a melting point of 164.5-166°C.

Fractions boiling in the temperature range 140-141.5°C again yield a lower quality product containing a high proportion of oil.

Taking this into consideration, specifications (as in the U.S.S.R.) require a fairly narrow boiling range for xylene, for example, 95% of the product should distil between 136.5-140°C or 136.5-141.5°C.

The specific gravity of the xylene at 15°C should be 0.862±0.002. Only a slightly yellow colour (straw yellow) produced by treating xylene with sulphuric acid is permissible.

A low specific gravity of the fraction indicates a high content of *p*- xylene, while a high specific gravity indicates a high content of ethylbenzene. A low boiling point is an indication of high proportions of ethylbenzene and *p*- xylene in the xylene and a high boiling point indicates the presence of large amounts of *o*- xylene.

Since analytical results do not give a clear idea as to the usefulness of xylene for nitration, nitration tests on a laboratory scale are recommended.

Recent German specifications for nitration grade xylene require determination of the freezing point of *m*- xylene, which should not be lower than -52°C. 100% of the xylene should distil within 1-2°C.

Separation of the xylene isomers by freezing. Besides the distillation method for separating *m*- xylene a method of separating the isomers by fractional crystallization, with freezing out, is used. The method is based on differences in the freezing points of the isomers:

o- xylene	f. p. -27.1°C
m- xylene	f. p. -54.8°C
p- xylene	f. p. +13.2°C

Such big differences enable the *o*- and *p*- isomers to be separated readily from *m*- xylene.

A drawback of this method is that the mixture has to be cooled to a very low temperature, which is costly. Further, if very pure *m*- isomer is to be prepared, it should be crystallized out, which is a very expensive operation as it requires cooling to a temperature below -55°C.

Chemical method of separating *m*- xylene. The method is based on the different capacities of the isomers to undergo sulphonation, and on the different extent to which the sulphonic acids are hydrolysed. It has been shown that *o*- and *m*- xylene can be sulphonated with concentrated sulphuric acid under conditions which leave *p*- xylene unaffected. *m*- Xylenesulphonic acid can be hydrolysed to *m*- xylene at a temperature too low for the hydrolysis of *o*- xylenesulphonic acid.

In practice, the process is effected as follows. Crude *m*- xylene, containing 60-70% of *m*- xylene, is mixed with sulphuric acid (sp. gr. 1.84) whereupon the temperature rises to 45°C. Then the mixture is heated to 50°C and allowed to remain at this temperature for 2 hr. Under these conditions sulphonation of the *o*- and *m*- isomers takes place. The sulphonic acids may be separated from unconverted *p*- xylene either by extraction with water or by expelling the *p*- xylene by steam distillation.

The temperature of the aqueous solution of sulphonic acids is brought to 130°C. Hydrolysis of sulphonated *m*- xylene follows :

$$C_6H_3(CH_3)_2SO_3H + H_2O \rightarrow C_6H_4(CH_3)_2 + H_2SO_4 \qquad (3)$$

The sulpho derivative of *o*- xylene undergoes hydrolysis only at 160°C and it remains unaffected during the reaction. This permits the separation of *m*- xylene from an aqueous solution of sulphonic acid.

The *m*- xylene isolated in this way is of very high purity. When nitrated it yields a product having a melting point only slightly lower than that of chemically pure 2,4,6-trinitro-m-xylene.

One-stage preparation of TNX

The nitration of xylene to trinitroxylene may be carried out in one, two or three stages.

The one-stage nitration has the advantage of giving a higher yield of the nitro compound as compared with other methods. On the other hand it has also a drawback, as it requires larger quantities of acids. The one-stage method of nitration is recommended when the product must be obtained in a short time, and cost is of minor importance.

The method was used in Russia during the 1914-1918 War. It was worked out by Solonina [8] and applied in the Shterovka factory. As Kravchinskii [3] reported, the operation was carried out in the following way.

Nitrating mixture of a composition:

HNO_3	18-19%
H_2SO_4	78-79%
H_2O	3%

is run into the nitrator. Then the stirrer (120-150 r. p. m.) is started and cooling water is passed through the jacket and the coil of the nitrator. When the temperature reaches 12°C xylene is run into the nitrator at such a rate as to allow the whole quantity to be introduced in 4-4.5 hr (for 1 part by weight of xylene 13.5 parts of the nitrating mixture is applied). Thus, the excess of nitric acid used amounts to 43%). During the introducing of the xylene a temperature of 30-40°C is maintained, and by the end of the operation it is raised to 65-70°C.

When all the xylene has been run into the nitrator the temperature rises spontaneously to 90°C. This is a critical moment, as the rise of temperature is accompanied by vigorous oxidation and frothing of the reaction mixture, owing to the evolution of gases (mainly carbon dioxide and nitrogen oxides). The reaction mixture is likely to run over if the process is too vigorous. When the violent reaction has subsided the mixture is heated to 105°C, this temperature being maintained for one hour.

The whole operation takes nearly 7 hr, including half an hour for charging the nitrator, 6 hr for the nitration, and half an hour for unloading.

After nitration has been completed the mixture is sent to a settler and allowed to remain there for 2 hr for the nitro compound to settle. The product is separated from the spent acid on a vacuum filter, and then transferred by means of shovels or by a stream of water to a washing tank.

The composition of the spent acid is:

HNO_3	0.8-1.5%
NO_2	3-5%
H_2SO_4	81-82.5%
nitro compounds	3-4.5%
H_2O	8-11%

Trinitroxylene is washed in a lead-lined wooden tank (Fig. 103) first several limes with cold water (1 part of water for 1 part of the product), then with hot water (80-85°C) and finally with cold water again. In all, the washing is repeated 6-7 times, each washing taking about 1 hr.

Compressed air, introduced through a lead bubbler, is used for mixing the nitro compound with water.

When the acid content of the washings falls below 0.1%, the product together with the washing water is drained off to a centrifuge. At this stage the trinitroxylene still contains oily admixtures apart from water.

When heated, it melts partially at 120-125°C, and becomes completely molten at 160-177°C. The melting point of the main part of the product is 163°C.

By passing moist hot trinitroxylene through a centrifuge not only the water but also the oily components are removed. Under these circumstances the product loses about 12% in weight. The oily product separated along with water is allowed to settle in special tanks and should then be utilized for special purposes. After centrifugation, the trinitroxylene still contains 15-18% of water. As Kravchinskii believed, the melting point of the product could be raised from 168°C to 176°C as a result of centrifugation.

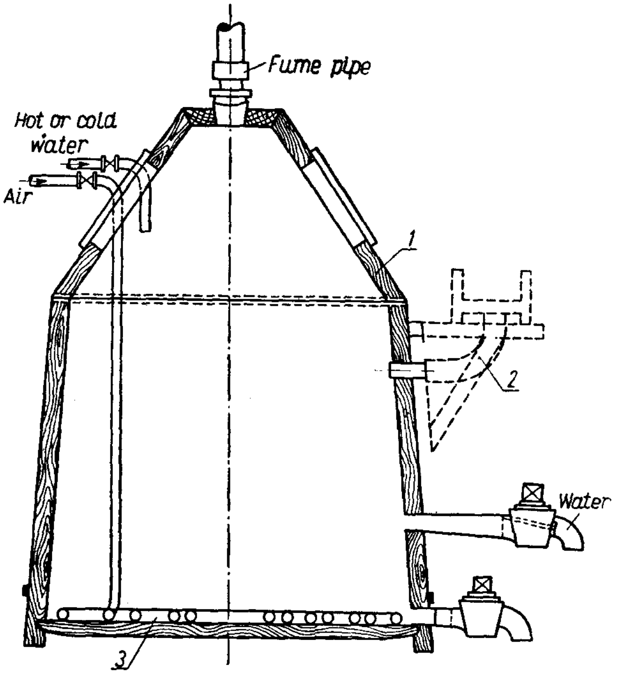


FIG. 103. Wooden vat for washing TNX: 1 - wooden lead lined walls, 2 - rubber sleeve to introduce TNX, 3 - lead bubbler (Kravchinskii [3]).

Two-stage preparation of TNX

The two-stage preparation of TNX consists in the nitration of *m*- xylene in two stages.

This method has been applied in the U.S.S.R, two modes being used:

Xylene -> DNX -> TNX
or Xylene -> MNX -> TNX

Nitration via DNX. In the first stage of the process - dinitration of xylene- the following nitrating mixture is used:

HNO_3	20%
H_2SO_4	65%
H_2O	15%

The mixture is run into the nitrator, and when it has attained a temperature of 25°C, feeding with xylene starts until the acid to xylene ratio is 6.5, which corresponds to an excess of HNO_3 amounting to 10% of theoretical. While adding xylene a temperature of 35-40°C is maintained. Then it is gradually raised to 100°C, where it is maintained for 14 hr.

After cooling (while stirring) the dinitroxylene, which is partly crystalline and partly oily, is separated from the spent acid by centrifugation. The melting point of the product ranges from 37° to 61.5°C.

From 100 parts by weight of xylene 163.8 parts by weight of dinitroxylene are obtained, the yield being 94% of theory.

The composition of the spent acid is:

HNO_3	1.7%
H_2SO_4	74.3%
H_2O	24.0%

The wet product is separated into two fractions - liquid (oily) and solid. Usually 20% of liquid and 80% of solid dinitro-m-xylene is obtained.

For the second stage of the process, i.e. trinitration, the DNX liquid or solid obtained is charged into the nitrator and acid of a composition:

HNO_3	18%
H_2SO_4	60%
H_2O	2%

is added.

For 1 part of DNX 3.2 parts of the nitrating mixture are run in, thus the excess of HNO_3 is 80% of the calculated amount.

Temperatures during the operation are maintained as follows: 50-55°C during addition of the acid, then 110°C for an hour, and finally 120°C for two hours. When nitration is completed, TNX is separated from the spent acid on a vacuum filter, after cooling to 20°C.

The spent acid from the process has the following composition:

HNO_3	6%
H_2SO_4	86%
H_2O	8%

From 100 parts of DNX 105 parts of TNX are obtained, which makes 86% of the theoretical yield.

From liquid DNX solid grade II TNX (m. p. 164°C) and liquid TNX are both obtained.

From solid DNX grade I crystalline TNX (m. p. 177°C) is obtained.

100 kg of *m*- xylene yield the following quantities of TNX:

147-154	kg of the grade I product
25.6	kg of the grade II product
1.0	kg of the liquid product.

Nitration via MNX. The process worked out by Filippov [8a] consists of two stages: mononitration followed by trinitration.

For one part of *m*- xylene, 2.5 parts of nitrating mixture of the composition:

HNO_3	25%
H_2SO_4	59%
H_2O	16%

are added. Thus, the quantity of HNO_3 amounts to 105% of theoretical. The nitrating mixture is prepared from the spent acid from trinitration.

During the introduction of the nitrating mixture into the nitrator a temperature of 30-40°C is maintained. After all the acid has been introduced and the mixture in the reactor has been kept at 40-45°C for two hours, it is cooled to 15-20°C, the stirrer is stopped, and after 15-20 min the nitro compound formed is separated from the spent acid.

100 parts of *m*- xylene yield 130-140 parts of MNX, which corresponds to 91-98% of theory.

For the conversion of MNX to TNX a nitrating mixture of the composition:

HNO_3	17.5%
H_2SO_4	79.0%
H_2O	3.5%

is added at a temperature of 10-12°C, the proportion of the reagents being 6 parts of the nitrating mixture for 1 part of mononitroxylene. Such a proportion corresponds to an excess of HNO_3 of nearly 25%.

During the first hour of the nitration process the temperature rises gradually to 50-60°C and finally reaches 65°C. Then the temperature is raised gradually to 110-120°C, and maintained then for 1 or l½ hr. After cooling, the trinitroxylene is filtered off, washed with cold, and then with hot (80-90°C) water, and finally the wet, hot product is separated from oily substance by centrifugation.

Spent acid from trinitration has the composition:

HNO_3	2-6%
H_2SO_4	82-85%
H_2O	11-15%

From 100 parts of MNX 170-180 parts of TNX are obtained; thus the yield is 70-80% of the theoretical.

The melting point of TNX prepared in this way is 164-166°C.

Three-stage preparation of TNX†

Mononitration. For 100 parts of *m*- xylene, separated from its isomers by sulphonation, 220 parts of a nitrating mixture of the composition:

HNO_3	28%
H_2SO_4	56%
H_2O	16%

are used.

The nitrating mixture is prepared from spent acids from di- and tri-nitration, by fortifying them with fresh concentrated acids.

The nitration temperature should not exceed 35°C. From 100 parts of *m*- xylene, 130-135 parts of MNX are obtained, i.e. the yield is 90-94% of the theoretical. Further procedure (separation of the nitro compound from the spent acid) is similar to that used in other nitration processes.

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† Soviet and French methods (according to Kravchinslcii [3] and Pascal [20] respectively).

Nitration of MNX **to DNX.** For 100 parts of MNX 140 parts of a nitrating mixture of the composition:

HNO_3	11%
H_2SO_4	74%
H_2O	15%

are used.

The mixture is prepared from the spent acid from trinitration by fortifying it with concentrated acids. During the mixing of mononitroxylene with the acid a temperature of 35-50°C is maintained. Then it is raised to 85°C and the reaction mixture is allowed to remain at this temperature for one hour. From 100 parts of mononitroxylene 137 parts of dinitroxylene are obtained, thus the yield is 95% of the theoretical.

Nitration of dinitroxylene to trinitroxylene. For 100 parts of dinitroxylene 230-300 parts of a nitrating mixture of the following composition are applied:

after Kravchiiskii [3]		after Pascal [20]	
HNO_3	10-15%	HNO_3	15-21%
H_2SO_4	76-81%	H_2SO_4	70-75%
H_2O	9-10%	H_2O	9-10%

The nitrating mixture is gradually run into dinitroxylene in the nitrator, at first at 60-70°C, and by the end of the procedure at 80-85°C. Then all is carefully heated to 95-100°C or 110-120°C.

When the reaction has been completed the nitrator contents are cooled and the product obtained is separated from the spent acid.

As Pascal [20] reported, from 100 parts of dinitroxylene 105 parts of trinitroxylene were obtained, the yield being 85% of the theoretical. In Table 92 the conditions and yields (calculated on toluene or xylene) obtained in the nitration of toluene and xylene are tabulated for comparison.

TABLE 92

COMPARISON OF NITRATION CONDITIONS FOR TOLUENE AND XYLENE (PASCAL [20])

		Product obtained					
		MNT	MNX	DNT	DNX	TNT	TNX
Composition of the nitrating mixture	HNO_3	28	28	32	11	19	15-21
	H_2SO_4	56	56	61	74	80	70-75
	H_2O	16	16	7	15	0	9-10
Maximum temperature, °C		60	35	90	85	120	95-120
Yield	obtained	143	130-135	188	178-185	190	170
	calculated	149	144	198	187	246	229
Yield ratio $\frac{\text{Xylene}}{\text{Toluene}}$		0.930		0.962		0.894	

Mononitration of xylene (I. G. Leverkasen method). To the nitrator containing I400 1. of spent acid from the previous nitration, 50 1. of xylene are added (thus the xylene is partly nitrated by the residual nitric acid still present in the spent acid). Then over a period of 3-4 hr, 1950 kg of xylene and about 3000 kg of a nitrating mixture :

HNO_3	28%
H_2SO_4	56.5%
H_2O	15.5%

are run in, the initial temperature of 15°C rising to 35°C by the end of the procedure.

Then over half an hour the rest of the acid is introduced so that the total quantity of the fresh nitrating mixture amounts to 4150 kg. The mixture in the nitrator is then stirred for another half an hour and conveyed to a separator where it is allowed to remain at rest for 2 hr so as to separate the nitro compound from the spent acid.

Part of the spent acid, having an average composition:

HNO_3	0.3%
NO_2	0.4%
H_2SO_4	70%
H_2O	29%

is sent to a concentration plant, while the rest is recycled to the nitrator.

The nitroxylene is washed with water until free from acid (test with Congo paper), then it is mixed with 150 1. of 30% sodium hydroxide solution at 70°C. Thus any nitroxylenols resulting from oxidation are removed.

The nitroxylene is then mixed with 50 kg of sodium carbonate and steam is passed through the mixture to remove unnitrated volatile compounds. The sodium carbonate dissolves in water and the aqueous solution thus formed is separated from nitroxylene.

The nitroxylene is further washed, this time twice with a 2.5-3% solution of NaOH at a temperature of 60°C and finally with water until quite free from alkalis.

From 100 kg of xylene 125 kg of nitroxylene can be obtained, which is 88.5% of the theoretical yield.

Purification of TNX

If trinitro-m-xylene has been prepared from pure *m*- xylene simple washing with hot water is sufficient to obtain a product of high purity. Otherwise, the removal of oily components by hot centrifugation is necessary. Additional purification by washing the product in the centrifuge with organic solvents (alcohol, benzene) may be applied. In consequence of the higher solubility of nitro derivatives of *o*- and *p*- xylene, mainly these compounds are removed.

A sodium sulphite wash may also be applied. According to Kravchinskii [3], the agitation of trinitro-m-xylene with a 7-9% solution of sodium sulphite at 70°C for 4 hr results in the complete removal of oily products. However, losses caused by this process may be considerable (15-25%), so that this method of purification does not always pay.

Drying. The trinitro-m-xylene, purified as above, and containing 13-18%

of water, is dried in tunnel or chamber driers at 60-70°C, until the water content falls to 0.1%. This operation takes 12-24 hr, depending on the type of drier. The finished product is a crystalline, slightly yellow powder.

NITRO DERIVATIVES OF OTHER HOMOLOGUES OF BENZENE

NITRO DERIVATIVES OF MESITYLENE

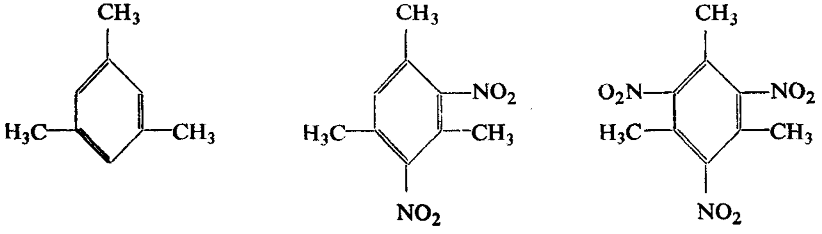
Trinitromesitylene is of some importance as an explosive due to the fact that the raw material - mesitylene - is easily obtainable by reacting acetone with sulphuric acid (Kane [21]).

However, as Tishchenko [22] reported, the yield of the reaction did not exceed 27% of the theoretical. Ipatiyev [23] found that mesitylene could be obtained in a yield up to 36% by reacting acetone with hydrogen chloride at a pressure of 100 atm.

Sucharda and H. Kuczynski [24] found that the yield could be increased to 47% by reacting the two compounds in sealed tubes at 145-195°C.

Cahours [25] obtained trinitromesitylene by treating mesitylene with a mixture of nitric and sulphuric acids. Repeating these experiments, A. W. Hofmann [26] obtained dinitromesitylene as well.

Nitration of mesitylene to di- and tri-nitromesitylenes proceeds with great ease :



m. p. 89°C m. p. 235°C

(4)

Dinitromesitylene can be obtained by dissolving mesitylene in fuming nitric acid, followed by the addition of water which causes dinitromesitylene to precipitate. For the preparation of trinitromesitylene by the Blanksma [7] method, mesitylene is dissolved in sulphuric acid (partial sulphonation taking place), and the solution is added to nitric acid (sp. gr. 1.52). Trinitromesitylene then precipitates, as white crystals, dissolved by organic solvents only with difficulty. Kholevo [26a] nitrated mesitylene with the nitrating mixture (27% HNO_3, 69% H_2SO_4, 4% H_2O) to yield trinitromesitylene.

The explosive power of trinitromesitylene is rather low - of the order of DNT. Its sensitiveness to impact, however, is relatively high - of the order of TNX -and much higher than that of DNT. This can be explained by the presence of the largest possible number of substituents on the ring.

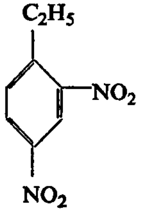
NITRO DERIVATIVES OF ETHYLBENZENE

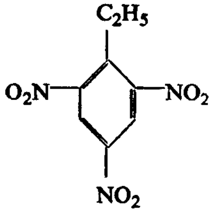
Ethylbenzene is always present in crude xylene and in solvent-naphtha. Since the boiling point of ethylbenzene (136°C) is identical with the boiling point of *p*- xylene, the two are difficult to separate. It is possible to do so by cooling. as the freezing point of ethylbenzene is -94.9%.

Fittig and Tollens [27] obtained ethylbenzene by synthesis from chlorobenzene and ethyl chloride. At first they believed it was xylene (basing their view on its boiling point). However, the substance did not yield a crystalline product when nitrated, as in the case of xylene, but an oily one, from which they inferred that the "ethylphenyl" they had obtained was not xylene.

Beilstein and Kuhlberg [28], by nitrating ethylbenzene with a mixture of nitric and sulphuric acids at a low temperature obtained two oily products which proved to be *o*- and *p*- nitroethylbenzenes.

Weisweiller [29], and later Schultz and Sander [30] obtained 2,4-dinitroethylbenzene and 2,4,6-trinitroethylbenzene:





2,4-Dinitroethylbenzene (b. p. 167.5% at 13 mm Hg, m. p. +4°C) was obtained by reacting ethylbenzene with a mixture of 2 parts of sulphuric acid (sp. gr. 1.84) and 1 part of nitric acid (sp. gr. 1.43). After the reaction had subsided the temperature of the mixture was raised to 125-130°C and kept at this temperature for 10 min.

For the preparation of trinitroethylbenzene (m. p. 37°C) ethylbenzene was treated with a mixture of nitric acid (sp. gr. 1.525) and 30% oleum, initially at 0°C, then the temperature was raised to 100°C and maintained there for 15-20 min. After cooling, the trinitroethylbenzene formed remained in the solution. By pouring the latter into water, the oily product was separated, which then solidified to form a crystalline mass.

With naphthalene and aromatic amines (e.g. aniline) trinitroethylbenzene forms addition compounds.

The explosive power of trinitroethylbenzene is rather low, so the compound itself is of no value. However, it is one of the chief components of liquid nitro-solvent-naphtha, and is sometimes used as an ingredient in the preparation of explosive mixtures.

p- Nitroethylbenzene is obtained as an intermediate in chloramphenicol (chloromycetin) synthesis.

NITRO-SOLVENT-NAPHTHA

Difficulties met in separating chemical individuals from higher fractions of light oil and lower fractions of middle oil stimulated attempts at the direct nitration of solvent-naphtha, the name given to a mixture of isomers comprising xylenes, ethylbenzene, pseudo-cumene (1,2,4-trimethylbenzene), ethyltoluene and mesitylene.

The mixture is obtained as a fraction boiling within the range 120-175°C. lt should be nitrated with great care, since it reacts violently with nitric and sulphuric acids. Nitration techniques have been described in a number of patents (Dahmen [31]; Blechner, Lopez and Distler [32]; Schultz [33]):

In most of the descriptions temperatures of 25-30°C are quoted for the first nitration stage and 80°C towards the end of the process. The nitrating mixture is prepared from concentrated sulphuric (sp. gr. 1.84) and nitric (sp. gr. 1.50) acids.

The product is a mixture of oil with a solid substance, the quantity of the latter depending on the fraction of solvent-naphtha used.

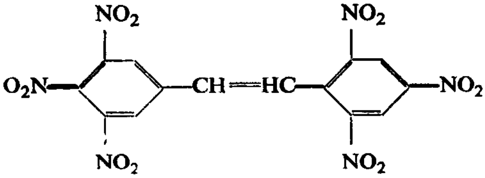
Thus, Blechner, Lopez and Distler [32] give the following data on the nitration of various solvent-naphtha fractions (Table 93).

TABLE 93

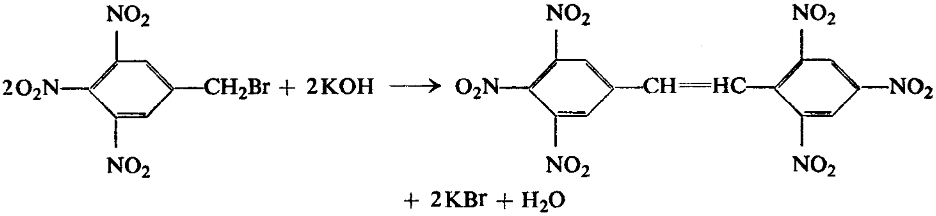
Fraction boiling within the temperature range, °C	Average yield	
	solid substance, %	oily substance, %
140-145	80	20
150-155	40	60
160-165	100	-

For some time nitro-solvent-naphtha was a widely used component of explosive compositions. Liquid fractions of the nitrated substance have also been used in the manufacture of mining explosives and even of smokeless powder, as an explosive solvent for nitrocellulose. In the latter case liquid nitro-solvent-naphtha acted as a substitute for part of the nitroglycerine. This type of smokeless powder was also manufactured in Poland in the period between the two World Wars (Kardaszewicz, Markiewicz and Smisniewicz [34]).

HEXANITROSTILBENE

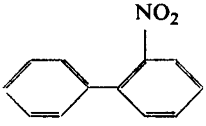


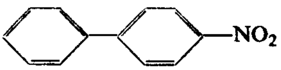
Pure hexanitrostilbene (m. p. 211°C, with decomposition) was obtained by S. Reich, Wetter and Widmer [35] by treating boiling trinitrobenzyl bromide with alcoholic potassium hydroxide:


(5)

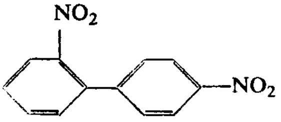
NITRO DERIVATIVES OF DIPHENYL

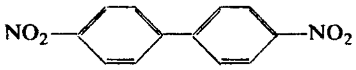
Diphenyl is nitrated with nitric acid in the presence of acetic acid to form a mixture of mononitro derivatives:


2-Nitrodiphenyl
m. p. 37°C

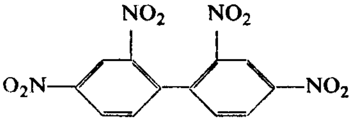

4-Nitrodiphenyl
m. p. 114°C

By boiling with nitric acid (98%) or with a mixture of nitric (77%) and sulphuric acids, diphenyl yields a mixture of 2,4'- and 4,4'-dinitrodiphenyl:


m. p. 93-94°C

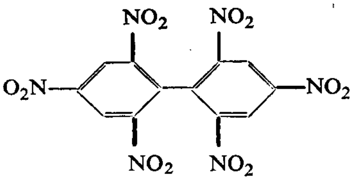

m. p. 233°C

By direct nitration no more than four nitro groups can be introduced into diphenyl, 2,4,2',4'-tetranitrodiphenyl being formed (Losanitsch [36]; Ulhnann and Bielecki [37]).


m. p. 163°C

Nowadays the compound is not used in the explosives industry since its explosive power is only slightly higher than that of dinitrobenzene, while on the other hand its melting point is too high, and diphenyl, the raw material for its manufacture, is available only in small quantities.

Its hexanitro derivative: 2,4,6,2',4',6'-hexanitrodiphenyl



m. p. 238°C

has evoked much more interest as an explosive.

The compound may be obtained by Ullmann and Bielecki's [37] method, which consists in heating picryl chloride with copper powder in a high boiling solvent like nitrobenzene, toluene or xylene.

Its explosive power is higher than that of hexanitro-diphenylamine (hexyl) by nearly 10%. According to a patent granted to Sprengstoff A. G. Carbonit [38] the lead block test figure for the product is about 360 cm^3. The initiation temperature of the explosive is high - over 320°C. It has also the advantage of being only slightly toxic (less than hexyl). On the other hand its application is limited by the cost of manufacture, which requires picryl chloride. Because of its high melting point it cannot be used in the molten state. So it should either be compressed or used as an additive in fusible mixtures with other nitro compounds.

NITRATION OF MIXTURES

During World War II a method of preparing mixtures of nitro compounds (e.g. TNT and TNX, or TNT and tetryl, see Vol. IV) was developed by the Germans. It consisted in the nitration of the corresponding lower nitrated compounds, namely a mixture of mononitrotoluenes plus mononitroxylenes was nitrated in two stages to form trinitro compounds. In this way a product containing 20% of TNX and 80% of TNT was obtained.

A mixture consisting of 45 parts of TNX and 50 parts of tetryl was prepared by mixing mononitroxylenes and dinitromethylaniline in suitable proportions and nitrating them. To the nitration product TNT was added in such a quantity as to obtain a mixture composed of 45% of trinitroxylene, 50% of tetryl and 5% of TNT. The mixture melts at 80°C; it does not need washing with a sodium bicarbonate solution, as is the case with TNT. A simple washing with hot water will suffice. The mixture has proved to be a fully adequate substitute for TNT.

NITRO DERIVATIVES OF POLYMERS

During World War II a large amount of research was carried out in seeking fully synthetic polymeric materials which could substitute a semi-synthetic polymer such as nitrocellulose. This research was connected with the immense development of plastics chemistry, which began shortly before World War II and is still advancing at a great pace.

NITROPOLYSTYRENE

Investigations on the nitration of polystyrene go back to 1845, to the experiments of Blyth and Hofmann [39], who reacted boiling nitric acid with glassy polystyrene, which was obtained from styrene of natural origin, namely from Styrax resin. The product prepared contained 10.6% of N.

During World War II several authors resumed the investigations. G. B. Bachman and his co-workers [40] nitrated polystyrene with nitric acid (sp. gr. 1.50) and obtained products of various degrees of nitration depending on the nitration temperature: at 50°C a product containing 10.0% of N was obtained, while at 150°C the product contained 11.2% of N.

A vast amount of research was carried out by Zenftman [41], who proved the action of a nitrating acid on polystyrene to be limited to the nitration of the superficial layer of polymer granules only. The inside of the granules remained unaffected. A necessary condition for obtaining complete nitration of the substance is to use a nitrating mixture which completely dissolves the polymer. According to Zenftman, nitrating mixtures of a composition ranging from the anhydrous one:

$$\left.\begin{array}{ll} \mathrm{HNO_3} & 70\% \\ \mathrm{H_2SO_4} & 30\% \end{array}\right\} \mathrm{I}$$

to that containing water:

$$\left.\begin{array}{ll} \mathrm{HNO_3} & 76\% \\ \mathrm{H_2SO_4} & 12\% \\ \mathrm{H_2O} & 12\% \end{array}\right\} \mathrm{II}$$

are good solvents for polystyrene.

With a mixture of type I, a product containing up to 14.4% of N can be obtained, while a mixture of type II gives a product with about 9.4% of N.

The nitration of polystyrene is carried out in the following way. To a mixture containing

$$\begin{array}{lr} \mathrm{HNO_3} & 73\% \\ \mathrm{H_2SO_4} & 26.5\% \\ \mathrm{H_2O} & 0.5\% \end{array}$$

finely ground polystyrene is added, a temperature of 18°C being maintained by cooling. The polystyrene to acid ratio is 1:20. After all the polymer has been added, the temperature is allowed to rise to 20°C. After one hour's stirring the polymer becomes completely dissolved in acid. After 4 hr from the beginning of the nitration process the solution is poured into water. Nitropolystyrene is then precipitated in the form of threads, which are washed with water, ground in a ball drum and again washed with hot water (90-95°C). From 100 g of polystyrene nearly 33 g of the nitrated product containing 13.4% of N can be obtained.

It has been shown by analysis that even under the most severe conditions of nitration only two nitro groups can be introduced into the benzene ring. The oxidation of nitropolystyrene to the corresponding nitrobenzoic acid (with MnO_2 in sulphuric acid) has shown, according to Zenftman [41], that the substitution occurs in the 4- and 2,4-positions of the benzene ring. Hence one can infer that during the nitration of polystyrene the first nitro groups take the position para to the vinyl group and then part of the rings undergoes further nitration, the next nitro groups taking the ortho position.

During the nitration, polystyrene undergoes partial degradation to an extent which depends on the nitration conditions and is greatest at the beginning of the reaction.

Nitropolystyrene is soluble in 90% nitric acid, nitroglycerine, nitrobenzene and cyclohexanone. It burns without melting. Zenftman and MacLean [42] suggested taking advantage of this by using the product as a combustible binder for explosive mixtures instead of nitrocellulose.

Médard [43] has examined the explosive properties of nitropolystyrene containing 13.9% of N, i.e. consisting of about 90% of the dinitro and 10% of the mononitro compound. In his investigations he compared nitropolystyrene with dinitrotoluene and found the former to be a less powerful explosive and less sensitive to impact.

The rate of detonation of nitropolystyrene of density 0.25 in a steel pipe 36-42 mm in diameter is only 1510 m/sec.

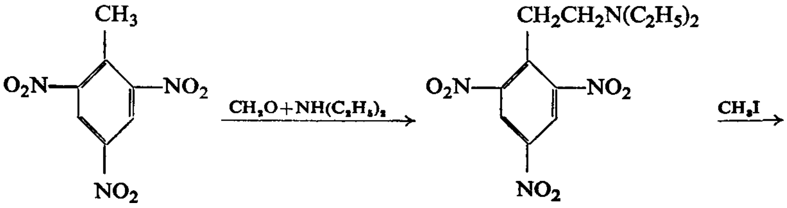
The density of nitropolystyrene is very low, due to its “fluffiness”. Médard suggested its use in the manufacture of ammonium nitrate mining explosives of low density, hence of a relatively low power. The following figures give some idea of such mixtures:

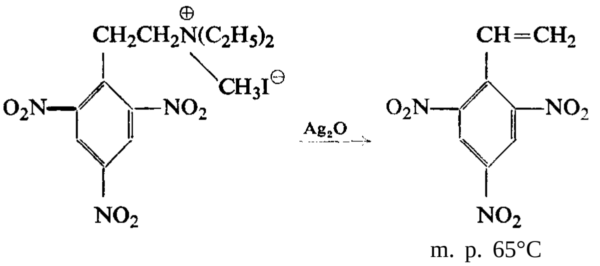
Nitropolystyrene	15%	12.75%
Ammonium nitrate	85%	72.75%
Sodium chloride	-	15%
Density	0.6	0.72
Lead block expansion test (picric acid = 100)		120
Rate of detonation	-	2720 m/sec

Attempts to prepare nitropolystyrene by the nitration of styrene followed by polymerization of the nitro derivatives, have failed.

Although it was possible to obtain the monomer 2,4,6-trinitrostyrene (Wiley and Behr [44]) every attempt to polymerize it has proved useless. This is understandable in the light of the fact that aromatic nitro compounds inhibit polymerization processes (p. 214). Similarly 2,4-dinitrostyrene has not been polymerized.

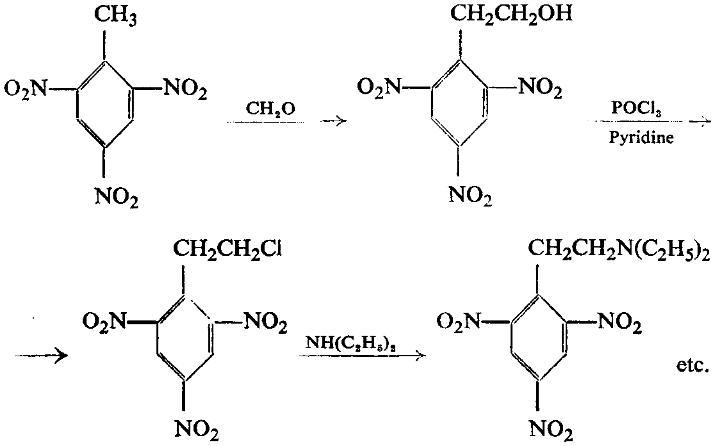
2,4,6-Trinitrostyrene has been prepared by these authors from trinitrotoluene in the following series of reactions:





(6)

Bonecki and T. Urbanski [45] prepared the same substance, also from 2,4,6-trinitrotoluene, but in a different way:



(7)

The next steps were analogous to those mentioned earlier. High purity trinitrostyrene was formed with m. p. 140°C.

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CHAPTER XI

NITRO DERIVATIVES OF NAPHTHALENE

GENERAL INFORMATION

Naphthalene is easier to nitrate than benzene, and one or two nitro groups can be readily introduced into it. The first group enters the α– position, the second takes the α– position on the ring having no substituents. An isomer with a nitro group in position 3 to the first one, on the same ring, is also formed in an insignficant quantity. The introduction of the third nitro group leads to the formation of several isomers.

Armstrong and Wynne [1] have established an empirical rule :

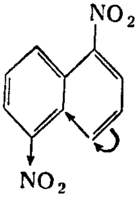
(a) a further group will not enter a position contiguous to a nitro group;

(b) a further group, other factors being equal, will tend to enter the nucleus at a position *peri* to an α– nitro group.

Under drastic conditions of nitration a further nitro group can be introduced into a naphthalene molecule.

By analogy with the rules of substitution in benzene based on the resonance theory and by considering that the quinonoid positions in naphthalene relative to 1 and 2 are 2,4,5,7 and 1,6,8 respectively a less empirical rule of substitution can be established.

Donaldson [2] gives an example. In 1,8-dinitronaphthalene the 3- and 6-positions are the least deactivated and nitration leads to 1,3,6,8-tetranitronaphthalene. Where two positions remain open the α– position shows a greater activity because of the nature of the naphthalene ring. An anomalous and important case is that of 1,5 dinitronaphthalene, in which only positions 3 and 7 are not deactivated. The main product of nitration of 1,5-dinitronaphthalene is 1,4,5-trinitronaphthalene and not 1,3,5- as would be expected. This led Hodgson and Ward [3] to conclude that the predominant hybrid in 1,5-dinitronaphthalene is



It favours electrophilic substitution in position 4. Modern approach to substitution rule consist in molecular orbital calculations [45].

Derivatives with β– nitro groups are more readily nitrated than the others. This Hodgson attributed to a higher electronegativity of β– nitro groups, particularly in the presence of vacant α– positions which are easy to substitute.

Hodgson has summarized the results of the nitration of dinitronaphthalenes (Table 94).

TABLE 94

starting material	Trinitro derivatives	Tetranitro derivatives
1,3-	1,3,8-	1,3,6,8-
1,4-	1,4,5-	1,3,5,8- and 1,4,5,8-
1,5-	1,4,5- and 1,3,5-	1,3,5,8- and 1,4,5,8-
1,6-	1,3,8-	1,3,6,8-
1,8-	1,3,8-	1,3,6,8-
2,6-	none	1,3,5,7-
2,7-	1,3,6-	1,3,6,8-

On reduction, acid reducing agents attack the α– nitro group preferentially, while sodium and ammonium sulphides reduce the β– nitro group.

Until the end of World War I and some years after, nitro derivatives of naphthalene were fairly widely used in mixtures with other explosives, for example with ammonium nitrate (e.g. Schneiderite) or with various other nitro compounds such as picric acid, as well as with potassium chlorate (cheddit) (Vol. III).

During World War II these compositions did not play any significant role. Used mostly in France, they dropped out of use from 1940 onwards.

At present nitronaphthalenes are scarcely used in the manufacture of explosives, mainly because of the shortage of naphthalene. The latter is used in large quantities in the manufacture of phthalic acid and of valuable dye intermediates. The large demand for phthalic acid and the lack of adequate supplies of naphthalene for its production have led to extensive research into the isolation of *o*- xylene and its oxidation to phthalic acid.

Nitronaphthalene is not an explosive. Dinitronaphthalene shows weak explosive properties and only trinitronaphthalene may be regarded as a true explosive. Tetranitronaphthalene is about as powerful an explosive as TNT (Lenze [4]).

Nitro derivatives of naphthalene have the advantage of being only slightly toxic. Although the output of nitro derivatives of naphthalene in Germany was high during World War I, no cases of poisoning were observed. However, eye irritation on exposure to the vapour or on contact with solutions of α– nitronaphthalene have been reported. The irritation is accompanied by eye-sight trouble (Frank [5]; Hanke [6]; Silex [7]; Caspar [8]).

Nitration of naphthalene was first mentioned in description of experiments by Laurent [9] between 1835 and 1842. On boiling naphthalene with nitric acid he obtained a mixture of mono-, di- and tri-nitronaphthalenes.

Later chemical investigations were aimed at establishing the conditions under which individual nitronaphthalenes could be formed. From the numerous investigations on the subject some of the more important work will be mentioned below.

Piria [10], by reacting naphthalene with nitric acid at room temperature for 5-6 days obtained mononitronaphthalene.

Roussin [11] prepared a mixture of mono- and di-nitronaphthalenes which he was able to separate by utilizing the fact that the latter is not soluble in carbon disulphide.

Troost [12] obtained nitro- and dinitro-naphthalenes by successive nitration of naphthalene. Darmstädter and Wichelhaus [13] found that the dinitronaphthalene thus obtained was a mixture of the two isomers.

More detailed studies had been carried out by d'Aguiar [14] who checked the results previously found. He isolated the following naphthalene derivatives :

two dinitronaphthalenes α and β (see p. 427)
three trinitronaphthalenes α,β and so called δ (see p. 431)
and two tetranitronaphthalenes α and β (see p. 434)

Beilstein and Kuhlberg [15] and Beilstein and Kurbatov [16] reinvestigated the methods of preparation and properties of dinitro derivatives of naphthalene and obtained a new product, γ– trinitronaphthalene.

The constitution of α–, γ– and δ– trinitronaphthalenes as well as of β–, δ– and γ– tetranitronaphthalenes has been determined by Will [17]. Friedländer [18] extended these investigations on β– trinitronaphthalene.

However, Dimroth and Ruck [18a] found that some of Will's data required correction: 1,2,5-trinitronaphthalene (δ according to Will's annotation) does not exist and δ– tetranitronaphthalene possesses the structure 1,4,5,8- and not 1,2,5,8,- as Will suggested.

The conditions under which mono-, di-, tri- and tetra-nitronaphthalenes are formed were investigated in detail by Patart [19] in extensive experimental work. By applying similar conditions (temperature and time) for the nitration of naphthalene with various nitrating mixtures, Patart determined the compositions of the products (the number of nitro groups) from the pressures they produced in a manometric bomb. The pressures, produced by pure substances were known, viz. :

nitronaphthalene (MNN) 927 kg/cm^2
dinitronaphthalene (DNN) 2296 kg/cm^2
trinitronaphthalene (TNN) 3280 kg/cm^2
tetranitronaphthalene (TetraNN) 3793 kg/cm^2

Similar experiments were carried out with the products of nitration of dinitronaphthalene.

Later Sapozhnikov [20] used Patart's data [19] for his triangular diagram, representing nitration of naphthalene (Figs. 104). In Fig. 105 and 106 the nitration curves for naphthalene and dinitronaphthalene are shown (Pascal [21]).

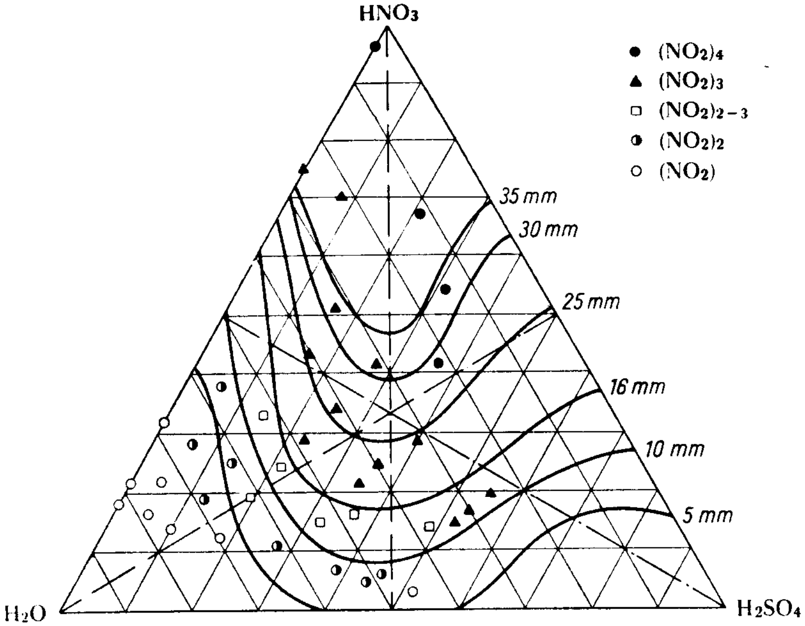


FIG. 104. Sapozhnikov's diagram of the nitration of naphthalene, according to Patart's experiments [21].

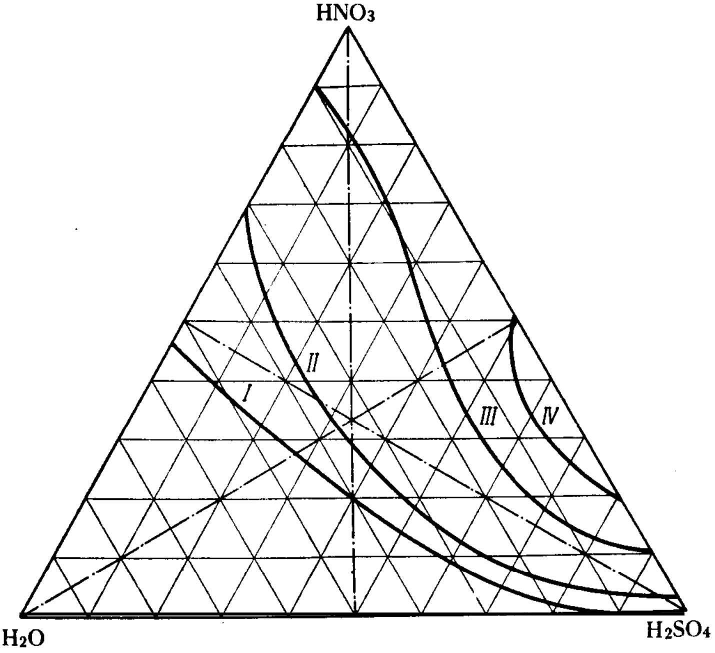


FIG. 105. Pascal's diagram of the nitration naphthalene-limits of formation: I - MNN, II - DNN, III - TNN, IV - TetraNN [20a].

Experiments on the nitration of naphthalene with nitrogen dioxide were carried out by Leeds [22] and more recently by Topchiyev [23]. The latter, in his experiments under various nitration conditions, obtained different products. At room temperature and with an excess of nitrogen dioxide, α– nitronaphthalene was obtained in a yield amounting to 96%; at 60°C, 1,5-dinitronaphthalene was formed (12% yield), along with α– nitronaphthalene (80% yield). At 150°C, in addition to these (in 30% and 36% yields) 1,8-dinitronaphthalene and a certain amount of 1,3,8-trinitronaphthalene were obtained (18% and 2% yields respectively).

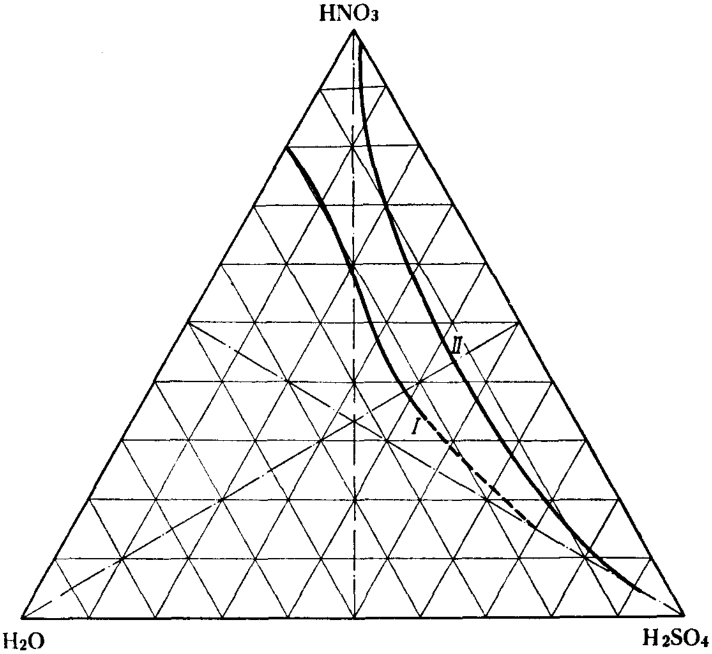
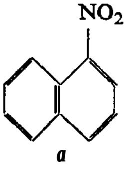


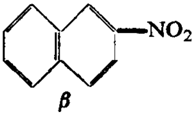
FIG. 106. Pascal's diagram of the nitration dinitronaphthalene-limits of formation: I - TNN, II - TetraNN [20a].

Lantz [23a] has studied the nitration of naphthalene sulphonic acids (mono-, di- and tri-sulphonic acids). He stated that no displacement of the sulphonic groups with nitro groups occurs. By using nitrating concentrated mixtures he was able to introduce nitro groups so that the number of both SO_3H and NO_2 groups reached a maximum of four.

MONONITRO DERIVATIVES OF NAPHTHALENE

Both the mononitro isomers, α and β, are known:





α– Nitronaphthalene (m. p. 60-61°C; b. p. 304°C), MN or MNN, forms pale yellow needles, having the specific smell of a nitro compound. It is insoluble in water, but readily dissolved by most organic solvents.

α– Nitronaphthalene yields molecular compounds with picric acid, trinitrotoluene, nitromannite (described in the chapters dealing with these explosives).

When directly nitrated, naphthalene gives α– nitronaphthalene possibly with some traces of β– nitronaphthalene.

β– Nitronaphthalene (m. p. 79°C) can only be obtained by an indirect route from β– naphthylamine, and hence it has not found any practical use.

According to Patart, α– nitronaphthalene is formed as the result of nitrating naphthalene with a mixture of a composition within the range:

HNO_3	30-50%
H_2SO_4	0-30%
H_2O	40-50%

As Pascal's [20] investigations have shown, α– nitronaphthalene forms with naphthalene a eutectic melting at 36.7°C. The eutectic contains 26.5% of naphthalene. During the first stage of nitration, therefore, when both naphthalene and α– nitronaphthalene are present in the nitrator, a temperature of over 36.7°C should be maintained (e.g. 40-50°C) so as to keep the substance being nitrated in a molten state.

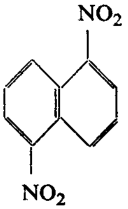
To this end some nitration methods recommend introducing into the nitrator a certain quantity of nitronaphthalene from the previous batch before the process begins.

After most of the naphthalene has been nitrated, the temperature in the nitrator shall be raised to 55-60°C to keep the nitration product molten, which will greatly facilitate the nitration.

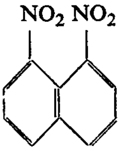
α– Nitronaphthalene is used as a component of explosive mixtures, as for example with picric acid for filling shells, and also in explosives used in mines and in chlorate explosives (Vol. III).

DINITRO DERIVATIVES OF NAPHTHALENE

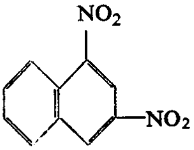
There are three isomeric dinitronaphthalenes, derivatives of α– nitronaphthalene. α– (1,5), β– (1,8), and γ– (1,3)-isomers known:



α
m. p. 215-216°C



β
m. p. 170-172°C



γ
m. p. 144°C

PHYSICAL PROPERTIES

They are fine grey-yellowish (sand-coloured) crystals. The colour of the commercial product frequently depends on its purity. The reddish colour met sometimes is evidence that nitrogen dioxide is present, absorbed by the product.

All the isomers mentioned are sparingly soluble in alcohol and ether. They dissolve more easily in benzene, toluene, acetic acid, acetone and turpentine.

The solubilities of both isomers of dinitronaphthalene, collected from the data of various authors are given in Table 95 (after Orlova [20b].

TABLE 95

SOLUBILITY OF DINITRONAPHTHALENES

Solvent	Temperature °C	Solubility, %	
		1,8-dinitro-napthalene	1,5-dinitro-naphthalene
Ethanol (anhydrous)	22	0.37	0.16
Ethanol 95%	19	0.06	0.06
Acetone	19	6.59	0.59
	boiling point	15.98	2.3
Acetic acid	boiling point	2.01	0.43
Chloroform	19	1.37	2.01
Dichloroethane	19	2.08	0.45
Benzene	50	0.06	0.02
Water	boiling point	0.07	insoluble

The commercial product obtained by the nitration of α– nitronaphthalene is a mixture of the 1,5- and 1,8- isomers, with only a small content of the 1,3-isomer. The melting point of the product ranges from 140-160°C. It is used for the preparation of explosives or for further nitration, without separating the isomers. The

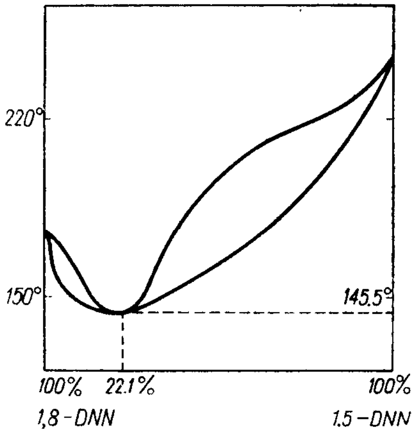


FIG. 107. System of 1,5- and 1,8-dinitronaphthalenes (Pascal [20]).

1,5 and 1,8-isomers are separated only when they are to be used for the manufacture of dyestuffs intermediates. The separation is performed by means of selective solvents, as for example dichloroethane, which dissolves, the l,8-isomer more readily than the 1,5-isomer. Analytically, 1,5-dinitronaphthalene can be separated from the 1,8-isomer by paper chromatography (Franc [24]). The mobile phase consists of ethyl alcohol, water and acetic acid.

According to Pascal [20], both isomers form solid solutions belonging to Rooze boom's system III. When the content of the 1,5-isomer is 22.1%, they have the lowest melting point, which is 145.5°C (Fig. 107). The other systems examined by thermal analysis arc tabulated (Table 96).

TABLE 96

EUTECTICS WITH DINITRONAPHTHALENE :

1,5-DINITRONAPHTHALENE

The other component	% of DNN by weight	m.p. °C	Author
α– Nitronaphthalene	8	54.5	Pascal [21]
Picric acid	10	113.6	T. Urbanski and Kwiatkowski [25]
1,3,5-Trinitronaphthalene	10	101	Pascal [21]
1,3,8-Trinitronaphthalene*	27	165	Pascal [21]
	1,8-DINITRONAPTHALENE		
α– Nitronaphthalene	6	44	Pascal [21]
Picric acid	43	93	T. Urbanski and Kwiatkowski [25]
1,3,5-Trinitronaphthalene	22	88	Pascal [21]
1,3,8-Trinitronaphthalene*	52	135	Pascal [21]

* Minimum of Roozeboom system III.

COMPOSITION OF THE COMMERCIAL PRODUCT

Patart [19] found that commercial grade dinitronaphthalene, being a mixture of isomers, could be obtained by the nitration of naphthalene or α– nitronaphthalene with a mixture of the composition:

HNO_3	8-70%
H_2SO_4	0-76%
H_2O	16-30%

As numerous experiments have shown, the weight ratio of the isomers depends to a large extent on the nitration temperature.

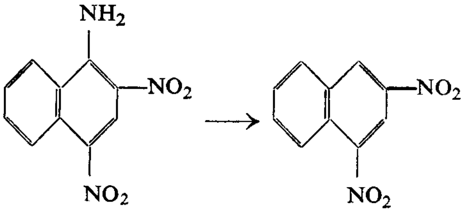
According to Pascal [20], at 70°C a mixture of 60% of the 1,8-isomer and 40% of the 1,5-isomer is formed. Hodgson and Whitehurst [26] have established the 1,5- to 1,8-isomers ratio to be nearly ½, when naphthalene is nitrated at 0-35°C.

Ward and Hawkins [27] nitrated 1-nitronaphthalene with a mixture of nitric (sp. gr. 1.42) and sulphuric (sp. gr. 1.84) acids, at a volume ratio 4:1 at 0°C and obtained a mixture of 1,8- and 1,5-dinitronaphthalenes, their ratio being about 70:30. 2-Nitronaphthalene, nitrated under similar conditions, gave a mixture of 1,6- and 1,7-dinitronaphthalenes along with 1,3,8-trinitronaphthalene, at a ratio of about 42:52:9.

According to Pictet [28] at very low temperatures ranging from -50°C to -60°C, nitration with a mixture of nitric and sulphuric acids resulted in the formation of a large quantity (about 46%) of the 1,3-isomer.

According to German sources (I. G. Ludwigshafen), commercial dinitronaphthalene consists of the 1,5-isomer (20%), 1,8-isomer (53%), the rest (27%) being a resinous substance.

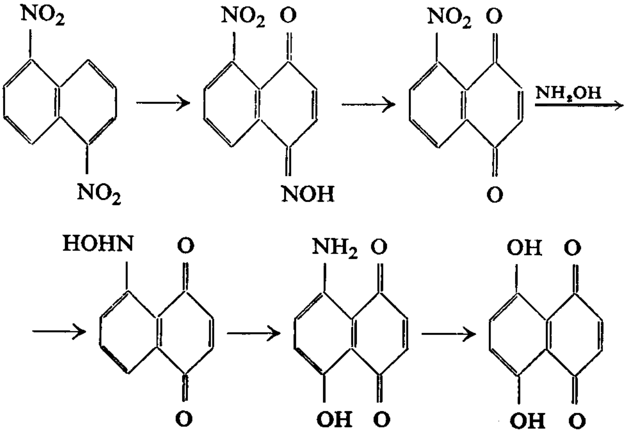
The 1,3-isomer has been obtained from 2,4-dinitro-a-naphthylamine, the amino group being removed by the conventional method, after diazotization (Liebermann [29]):



(1)

CHEMICAL PROPERTIES

It was known for long time that the 1,5- and 1,8-dinitronaphthalenes react under the action of concentrated sulphuric acid to yield naphthazarine - a valuable compound for dyeing [30]. The mechanism of the formation of this compound (based on experiments of Dimroth and Ruck [18a]) probably consists in the transformation of the nitro compounds to quinone-oximes and the reduction of one of the nitro groups by hydroxylamine split off the oxime:



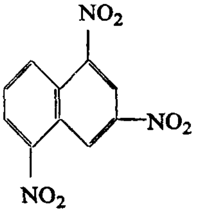
(2)

Gorst and Khlebnikov [31] reported that the colour of the solution of dinitronaphthalene in 84.5% H_2SO_4 did not change appreciably when kept at room temperature. When the concentration of sulphuric acid was 98% the solution darkened after 24 hr. Darkening occurs even more quickly when the sulphuric acid concentration is higher. The darkening is probably due to reactions similar to (2).

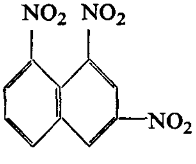
Application. A mixture of the dinitronaphthalene isomers is used in explosive compositions with picric acid and ammonium nitrate for military and mining explosives (Vol. III). The mixture is often referred to as “Dinal”. It is also designated by the symbols DN or DNN. It is an explosive very difficult to detonate. The highest rate of detonation of Dinal, when using a very powerful detonator, is about 5100 m/sec (Calvet [32]).

TRINITRO DERIVATIVES OF NAPHTHALENE

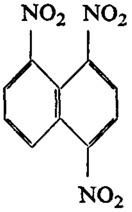
There are three isomers of trinitronaphthalene known, which can be obtained by direct nitration of a-nitronaphthalene, viz. : the α– (1,3,5-), β– (1,3,8-), and γ– (1,4,8-) or 1,4,5-isomers. The δ– isomer (1,2,5-) does not exist, according to Dimroth and Ruck [18a]. It is probably a mixture of the isomers.



α
m. p. 123°C
(119.5°C [18a])



β
m. p. 218°C



γ
m. p. 147°C

They are very fine crystalline, light brownish-grey products, sparingly soluble in organic solvents.

The crude product of the nitration of naphthalene or α– nitro- or commercial dinitro-naphthalene is a mixture of the four isomers. It melts at 115-160°C, the melting point depending on the nitration conditions.

Separation of the isomers can be achieved by taking advantage of their different solubility in alcohol. Thus, the 1,3,5-isomer dissolves in alcohol only with great difficulty. The 1,4,8-isomer does not dissolve in 70% alcohol, while the 1,3,8-isomer dissolves in the hot solution and may be precipitated from the solution either by cooling or by dilution (Pascal and Garnier [33]).

The conversion of dinitro- into trinitro-naphthalene may be achieved by using nitrating mixtures of varying compositions :

HNO_3	15-100%
H_2SO_4	0-70%
H_2O	0-15%

As Pascal [20] found, in the nitration of 1,5-dinitronaphthalene a product of the following percentage of isomers can be obtained:

1,3,5-	24.2%
1,4,8-	8.8%
1,2,5- (?)	47.5%

The rest (19.5%) consists of resinous products difficult to identify, plus unchanged dinitronaphthalene.

Using lower nitration temperatures (e.g. 65°C) results in a decrease of the y-isomer content. The contents of isomers in the product are then:

1,3,5-	34.4%
1,2,5- (?)	58.9%

Resinous substances are present in 6.7%.

According to Pascal, by the nitration of 1,8-dinitroniphthalene two isomers:

1,3,8-	85.1%
1,4,8-	9.6%

may be obtained, along with amorphous products and unconverted dinitronaphthalene.

Pascal also obtained, by nitrating naphthalene to trinitronaphthalene, a mixture of isomers of the composition:

1,3,5-	11-14.7%	1,4,8-	6-10%
1,3,8-	54.3-57.6%	1,2,5- (?)	21.5-25.5x

Patart reports that trinitronaphthalene can be prepared from naphthalene (1 part) using nitration mixtures (30 parts) of the composition:

HNO_3	18-100%
H_2SO_4	0-76%
H_2O	0-6%

When starting from dinitronaphthalene mixtures :

HNO_3	15-100%
H_2SO_4	0- 70%
H_2O	0- 15%

should be used for the preparation of trinitronaphthalene.

CHEMICAL PROPERTIES OF TRINITRONAPHTHALENE ISOMERS

1,3,5- (α)– and 1,3,8- (β)– trinitronaphthalenes form the following molecular compounds $\alpha_3.\beta$, $a.b$, $a.b_3$ (Pascal [20]).

Trinitronaphthalenes can be oxidized relatively easily to form corresponding nitrophthalic acids.

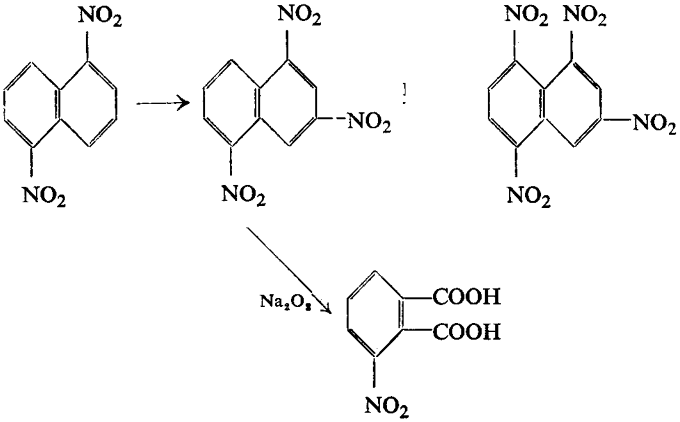
Some of the nitro groups can be relatively readily substituted by a methoxy or ethoxy group when heated with the corresponding sodium alcoholate. The oxidation of such a compound leads in the first place to rupture of the ring with the alkoxy group.

Oxidation reactions have been utilized for determining the constitution of trinitronaphthalene isomers.

STRUCTURE OF α– AND γ– ISOMERS

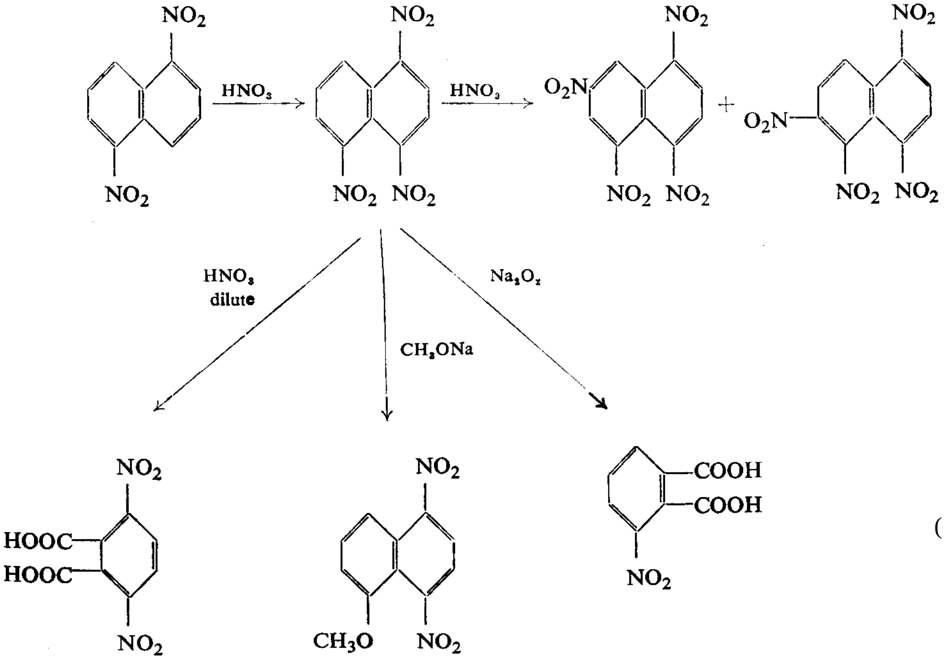
a- Trinitronaphthalene. Will [17] determined the constitution of this compound from the following reactions:

α– Trinitronaphthalene can be formed by the nitration of 1,5-dinitronaphthalene. When oxidized it yields *o*- nitrophthalic acid. Further nitration leads to 1,3,5-tetranitronaphthalene :



(3a)

g- Trinitronaphthalene. The constitution of this isomer has been determined from the reactions:



(4)

EXPLOSIVE PROPERTIES AND APPLICATION OF TRINITRONAPHTHALENE

Trinitronaphthalene is similar to dinitrobenzene as regards its explosive power.

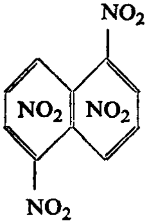
Before and during World War I it was fairly widely used, first in France and later in Germany, for filling shells, mostly in fusible mixtures with TNT.

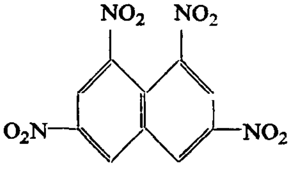
Initially it was known as “Naphtite”, later as “Trinal”. Its other names are TN and TNN.

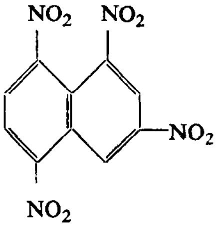
The maximum rate of detonation of trinitronaphthalene is about 5140 m/sec (Calvet [32]).

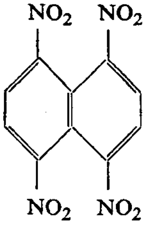
TETRANITRO DERIVATIVES OF NAPHTHALENE

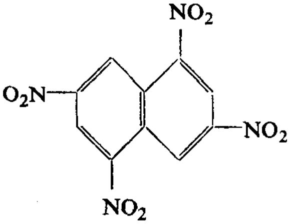
Five isomers of tetranitronaphthalene are known from the literature: the α– isomer, the position of two nitro groups in it being unknown, the β– (or 1,3,6,8-), the γ– (1,3,5,8- or 1,4,6,8-), the δ- (1,4,5,8-) and the 1,3,5,7-isomers:


α
m. p. 259°C


β
m. p. 203°C


γ
m. p, 194-195°C


δ
m. p. 340-345°C


m. p. 260°C
decomposition 263-265°C

The isomer δ was originally thought to be 1,2,5,8-tetranitronaphthalene (Will [17]). This was corrected by Dimroth and Ruck [18a]).

Each of them forms fine sand-coloured crystals, dissolving with difficulty in organic solvents. Some of them (e.g. 1,3,5,8-) are readily soluble in acetone. Concentrated sulphuric and nitric acids are the best solvents for them.

By the nitration of commercial dinitronaphthalene a product is obtained which consists of the 1,3,6,8-, 1,3,5,8- and 1,4,5,8-isomers. The existence of the α– isomer is not quite certain. It was reported by d’Aguiar [14], who obtained it by the prolonged boiling of 1,5-dinitronaphthalene with nitric acid (sp. gr. 1.45). The experiments were repeated by Beilstein and Kuhlberg [15] with a mixture of nitric and sulphuric acids instead of the nitric acid alone. However, Will’s investigations [17] did not confirm the results obtained by the above authors. Under the conditions they described Will obtained a mixture of the 1,3,5,8- and 1,4,5,8-isomers. He separated them by taking advantage of their different solubility in acetone. The 1,3,5,8-isomer is readily soluble even in cold acetone, while the other is insoluble even on boiling.

Lautemann and d'Aguiar [34], by boiling 1,8-dinitronaphthalene with nitric acid for 8 hr, obtained 1,3,6,8-tetranitronaphthalene. This result has been confirmed by Will.

As Patart reports, naphthalene can be nitrated to tetranitronaphthalene with mixtures containing only a small quantity of water:

HNO_3	30-45%
H_2SO_4	50-65%
H_2O	5%

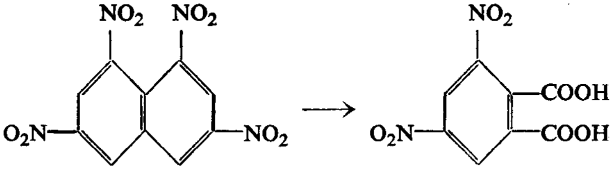
Starting from dinitronaphthalene more dilute nitrating mixtures may be applied :

HNO_3	10-95%
H_2SO_4	5-80%
H_2O	0-10%

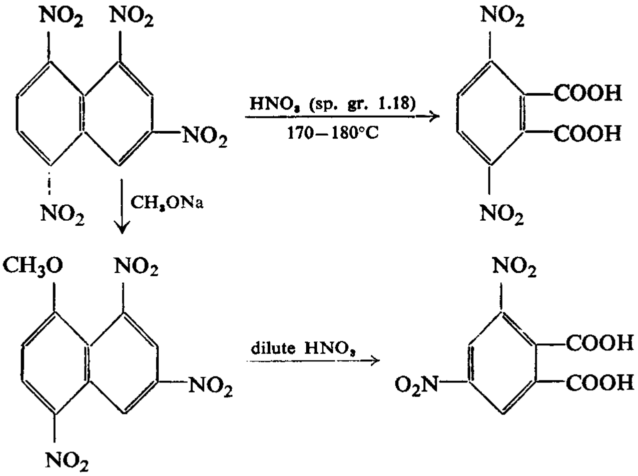
STRUCTURE OF TETRANITRONAPHTHALENES

Will has determined the structure of the 1,3,6,8- and 1,3,5,8-isomers by direct oxidation, or by oxidation of the products formed when reacting the isomers with sodium alcoholate.

Oxidation of 1,3,6,8-tetranitronaphthalene:



Oxidation of 1,3,5,8-tetranitronaphthalene:

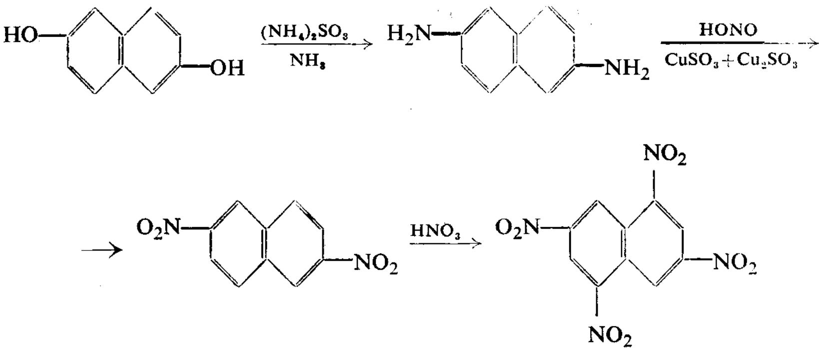


(6)

(7)

Due to difficulties in preparation, tetranitronaphthalenes are not applied as explosives.

1,3,5,7-Tetranitronaphthalene has been prepared (Chatt and Wynne [35]), by an indirect method:



(8)

THERMOCHEMICAL PROPERTIES OF NITRONAPHTHALENES

Rinkenbach [36] determined the heats of formation and heats of nitration from his measurements of heats of combustion of nitronaphthalenes. The heats of combustion of these compounds measured by Badoche [37] are in agreement with the values reported by Rinkenbach (Table 97).

TABLE 97

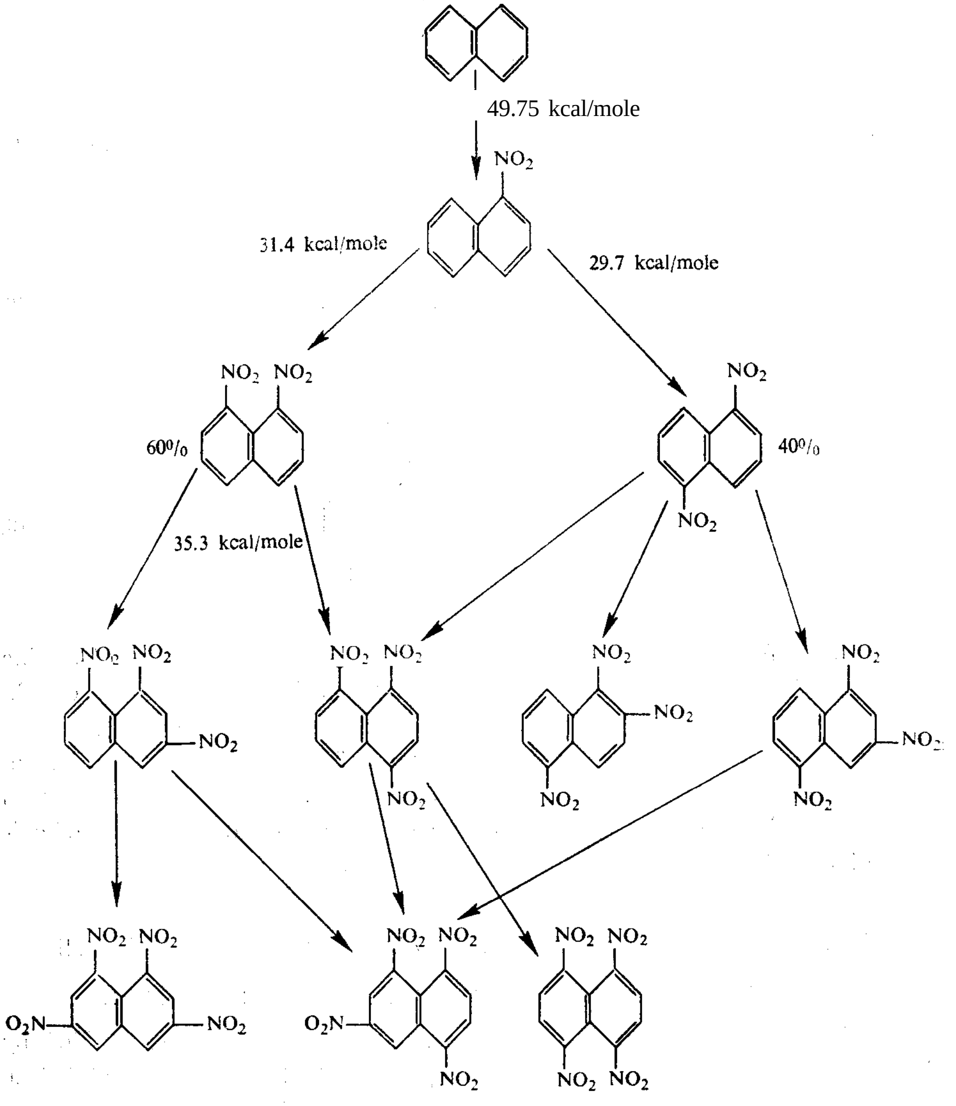
HEATS OF COMBUSTION AND FORMATION OF NITRONAPHTHALENES

Nitro derivative of naphthalene	Heat of combustion (after Badoche) at constant volume kcal/mole	Heat of formation (after Rinkenbach) kcal/mole
α– Nitronaphthalene	1190	-7.15
1,5-Dinitronaphthalene	1152	-5.44
1,8-Dinitronaphthalene	1154	-2.65
1,3,8-Trinitronaphthalene	1118	+5.7
1,4,5-Trinitronaphthalene	1121	-

Hence, the heats of nitration are:

naphthalene to α– nitronaphthalene	49.75 kcal/mole
α– nitronaphthalene to 1,5-dinitronaphthalene	29.67 kcal/mole
α– nitronaphthalene to 1,8-dinitronaphthalene	31.40 kcal/mole
1,8-dinitronaphthalene to 1,3,8-trinitronaphthalene	35.28 kcal/mole

A diagrammatic presentation of the nitration of naphthalene:



SIDE REACTIONS IN THE NITRATION OF NAPHTHALENE

Nitration of naphthalene, and higher stages of the nitration (e.g. trinitration) in particular, are accompanied by oxidation reactions which are manifested by the evolution of large quantities of nitrogen oxides.

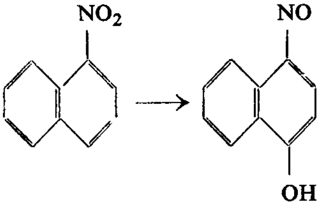
As a result nitrophthalic acids are formed, namely nitro- and dinitro-phthalic:

$$C_6H_3.NO_2(COOH)_2$$
$$C_6H_2(NO_2)_2(COOH)_2$$

Since under the conditions of the above reaction partial decarboxylation may take place, nitrobenzoic acids may also be formed:

$$C_6H_4.NO_2.COOH$$
$$C_6H_3(NO_2)_2COOH$$

In addition nitronaphthols are obtained, which may be formed either by direct oxidation or through isomerization of nitronaphthalenes to nitrosonaphthol or its derivatives :



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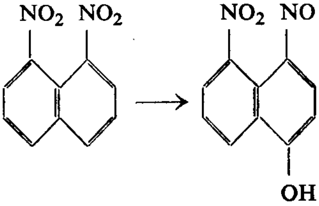


(10)

It has been found that such reactions can occur under the influence of fuming sulphuric acid, at 40-50°C. Nitrosonaphthol may then by oxidized to nitronaphthol. Moreover, picric acid may be formed during the nitration processes.

Resinous amorphous, brown substances are also formed, and found in dinitro- and trinitro-naphthalenes. They are partly soluble in alkalis, hence the suggestion that they are of an acidic or phenolic character and come from products of oxidation of naphthalene.

MANUFACTURE OF NITRO DERIVATIVES OF NAPHTHALENE

NITRATION OF NAPHTHALENE TO MONONITRONAPHTHALENE

Nitration grade naphthalene should be almost chemically pure, purified by sublimation or crystallization (pressed naphthalene). Sublimated naphthalene should not melt below 79.6°C, while the melting point of the pressed product (in lumps, 2-4 cm) should not be lower than 79.0°C.

With concentrated sulphuric acid the naphthalene should not produce a darker shade than a pale reddish pink.

German method

This method has been applied at I. G. Leverkusen. It consists in charging naphthalene into a nitrator, containing a part of the spent acid and nitronaphthalene from the previous batch. To this the nitrating acid is added.

The succession of operations is as follows. A cast iron nitrator of 7 m^3 capacity is charged with 2500 1. of a mixture of spent acid and nitronaphthalene from the previous batch, warmed to 50-55°C. 1100 kg of naphthalene is added during about 15 min, while the nitrator contents are stirred. During this operation the temperature falls to 40-43°C. Then 800 1. of a nitrating mixture of the composition:

HNO_3	33%
H_2SO_4	47.5%
H_2O	19.5%

(sp. gr. 1.625-1.635 at 20°C) is added during 3 hr, the temperature rising by the end of the procedure up to 45°C. Then the rest of the naphthalene and acid are added during about 8 hr, in five lots: four of 200 kg each, alternating with 200 1. batches of the nitrating mixture, then the last of 300 kg of naphthalene, followed by 450 1. of the acid. In all, 2200 kg of naphthalene and 2050 1. (3300 kg) of the nitrating mixture is charged into the nitrator.

The temperature may rise during this period to 55°C. After all the acid has been added, the nitrator contents are stirred for another half an hour at 55°C and a sample is taken.

The nitronaphthalene precipitated by cooling, after washing with water should not melt below 51°C and should not smell of naphthalene. If the test is satisfactory, a part of the mixture in the nitrator is conveyed to a separator and the remaining 2500 1. is left for the next batch. The latter quantity is controlled by the depth of immersion of the pipe that conveys the mixture to the separator. The whole nitration process takes 12 hr.

Separation. Separation of nitronaphthalene from spent acid is effected in a cast iron separator, heated by a steam jacket, which permits the temperature to be maintained at 50-55°C. The separation of the mixture into two layers requires 3 hr. Then the lower layer of the spent acid is drawn off to an intermediate tank of 10 m^3 capacity and is allowed to cool. As a result, unreacted naphthalene collects at the surface as a crystalline mass. It is skimmed off mechanically.

Spent acid of the composition:

H_2SO_4	63%
HNO_3	trace
NO_2	
H_2O	about 37%

is sent to be concentrated.

Granulation and washing. The molten nitronaphthalene in the separator is drained off to a granulator, previously charged with 6000 1. of cold water. During the introduction of nitronaphthalene compressed air is passed through the grantlator to agitate the water. This causes the nitronaphthalene to solidify in the form of granules. The granulation process requires one hour, then the flow of air is stopped and the water is drawn off through a siphon. The siphon pipe inlet is provided with a wire gauze to prevent the nitronaphthalene from being carried away. When the first portion of water has been drained off the nitronaphthalene left is agitated with new portions of water (6000 1. each) until neutrality (Congo red test). Usually 2-3 washings are sufficient. The washing process requires about 6 hr.

Then the vessel is charged with 1000-2000 1. of water and 100 kg of sodium carbonate and the whole is heated with live steam until the nitronaphthalene becomes molten. This requires about 2 hr. The water should remain alkaline towards phenolphthalein. The contents of the vessel are pumped to one of three washing tanks. The tank are made of sheet iron and equipped with a steam heater and with a stirrer (40 r. p. m). After 2 hr of agitation the lower layer (molten nitronaphthalene) is pumped into the next tank charged with a solution of 50 kg of sodium carbonate in 3000 1. of water and heated up to 85-95°C.

The molten nitronaphthalene is pumped to the last tank and is washed there with 3000 1. of water having a temperature of 85-95°C during 2-3 hr. The separation of the nitro compound from water requires 2 hr. The washed, molten nitronaphthalene is transferred to a drying kettle, where after being heated up to 95-105°C it is allowed to remain for 4 hr under reduced pressure (about 200 mm Hg), while constantly stirred (28 r. p. m).

Pure nitronaphthalene is sent, while still molten, for the preparation of $\alpha-$ naphthylamine by reduction.

If $\alpha-$ nitronaphthalene is to be used for preparing explosive compositions, it is poured off from the drying kettle into pans for solidification and then broken up into lumps.

From the quantities of raw materials given above, 2920 kg of nitronaphthalene (m. p. 52-52.5°C) are obtained. This corresponds to a yield of 132.5 kg of nitronaphthalene from 100 kg of naphthalene, i.e. 98% of the theoretical.

French method

The nitration of naphthalene to nitronaphthalene, according to Pascal [20a], is effected in a nitrator of the type shown in Fig. 108. The nitrator (1.16 m in diameter, 1.0 m high) is made of cast iron. The lower, conical part is provided with an outlet 5 cm in diameter, closed by a valve. The sheet iron jacket on the cylindrical part of the nitrator may serve a double purpose: cooling the nitrator contents by water or heating by steam.

The lid is provided with a rectangular opening (1) (35 x 20 cm) for feeding in the naphthalene. After the nitrator has been charged the opening is closed with a sheet iron lid. The nitrator lid is also equipped with pipe (2), connected with a ventilator by means of a stoneware pipe; the ventilator itself is connected with an absorption tower for absorption of nitrogen dioxide in water. In addition the nitrator is equipped with stirrer (3) (85-90 r. p. m) and with two baffles (4) located opposite to each other to increase the stirring effect.

In the nitrator described 300 kg of naphthalene can be nitrated in one batch.

The nitrator is charged with 1100 kg of a nitrating mixture of the composition :

HNO_3	12-14%
H_2SO_4	40-50%
H_2O	36-48%

The mixture is prepared from 600 kg of the spent acid from the dinitronaphthalene manufacture and 550 kg of the spent acid from mononitration, which has been re-used for washing dinitronaphthalene. In consequence the spent acid contains some of the HNO_3 adsorbed by dinitronaphthalene. The composition and the quantity of the mixture should be so calculated as to contain 128 kg of HNO_3, required for complete nitration of 300 kg of naphthalene.

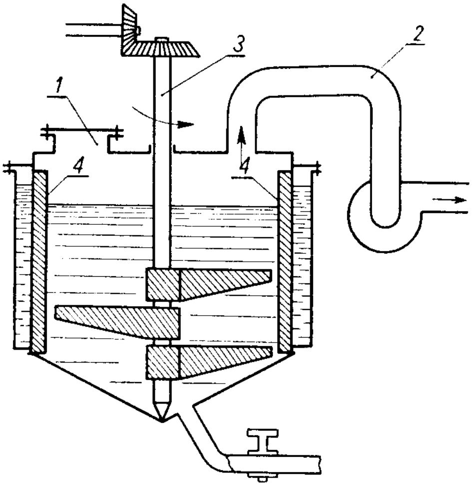


FIG. 108. Diagram of a nitrator for the nitration of naphthalene (Pascal [20a]).

The naphthalene to be nitrated (300 kg) is added to the nitrating mixture during aperiod of 3 hr. Meanwhile the temperature has risen spontaneously up to 50°C. When all the naphthalene has been added, the nitrator contents are heated to 55°C.

After the completion of the nitration process, the mixture in the nitrator is allowed to remain at rest to separate into two layers. Then the lower, acid layer is drawn off into a lead lined tank (I) (Fig. log), 1.5 m high and 1.25 m in diameter. Molten

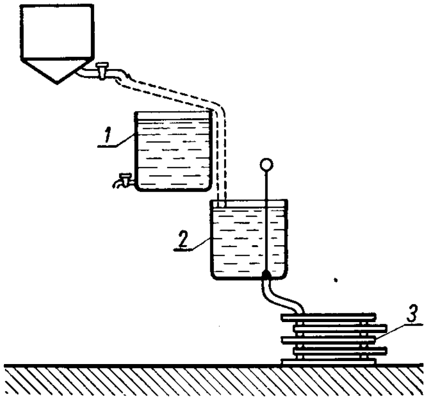


FIG. 109. Flow sheet of the nitration of naphthalene to nitronaphthalene (Pascal [20a]).

nitronaphthalene is drawn off through a lead or aluminium pipe into a similar tank (2), containing water heated by live steam to 70°C and is stirred for half an hour. The lower layer (molten nitronaphthalene) is then drained off into pans (3) arranged in the form of a stack, where it solidifies.

In this way 400 kg of the raw product ready for further nitration are obtained.

NITRATION OF NAPHTHALENE TO DINITRONAPHTHALENE

German method

The direct nitration of naphthalene to dinitronaphthalene by the method applied at I. G. Ludwigshafen is carried out in the following way:

A cast or wrought iron jacketed nitrator (of 3.4 m^3 capacity), equipped with a propeller stirrer (25-26 r. p. m), is charged with the following quantities of acids:

925 kg of 98% H_2SO_4
610 kg of 53% HNO_3
25 kg of 98% HNO_3

a nitrating mixture of the composition:

HNO_3	22.3%
H_2SO_4	58.1%
H_2O	19.6%

being obtained.

As heat is generated during stirring the temperature of the mixture rises to 30°C. Then 295 kg of naphthalene is introduced through a screw metering tank at a rate of 14.75-11.8 kg/hr. The naphthalene is added in the following way:

59	kg	during	the	first	4	hr	at	34-36°C
118	,,	,,	,,	,,	8	,,	,,	36-37°C
59	,,	,,	,,.	,,	4	,,	,,	37-38°C
59	,,	,,	,,	,,	5	,,	,,	38-44°C

After adding all the naphthalene, the temperature is raised during a period of 4 hr up to 80°C and the nitrator contents are kept at this temperature for another hour.

The raising of ihe temperature is necessary for keeping the product of nitration in a molten state, as at this stage it consists of nitro- and dinitro-naphthalenes. The contents of two nitrators are pumped to a lead-lined stirred tank (of 14.9 m^3 capacity) containing 7000 1. of cold water. The temperature in the tank rises to 40-50°C. Due to constant stirring the product is kept in the form of droplets which, after cooling to 30°C, solidify giving sand-coloured granules. The contents of the tank are then conveyed to a vacuum filter of an area of 8 m^2 (6 m^3 capacity).

The spent acid, containing 30% of H_2SO_4 (sp. gr. 1.220) is disposed to a drain. The product on the filter is washed with 6 m^3 of cold, then with 12-14 m^3 of warm water.

French method

The nitration of naphthalene to dinitronaphthalene (after Pascal [20a]) is effected in a nitrator essentially of the same type as that used for the nitration of naphthalene to nitronaphthalene by the French method (Fig. 108, p. 441), the only difference being in the outlet which is wider at the bottom - 8 cm in diameter - since the nitration product is solid.

The nitrator is charged with 1060 kg of a nitrating mixture of the composition:

HNO_3	23-24%
H_2SO_4	54-55%
H_2O	21-21.5%

Then finely ground and sifted naphthalene is added at a rate which at the beginning is about 50 kg/hr, and by the end 35-40 kg/hr. During the addition of naphthalene the temperature is controlled by cooling, so that it does not exceed 55°. By the end of the process the mixture has heated up to 70°C.

After the completion of the reaction, the nitrator contents are discharged into a lead vacuum filter of 1000 1. capacity for separating the product from the spent acid. The spent acid has the composition:

HNO_3	0.5-1.5%
NO_2	1.5-2.5%
H_2SO_4	62-63%
H_2O	33-35%
organic matter	ca. 1.5%

The product is washed as described below (see preparation of dinitronaphthalene from nitronaphthalene).

NITRATION OF NITRONAPHTHALENE TO DINITRONAPHTHALENE

French method

As Pascal [20a] reports, the reaction is carried on in the following way. The nitrator is fed with 1150 kg of a nitrating mixture of the composition:

HNO_3	26.5%
H_2SO_4	51%
H_2O	22.5%

Then during 3-4 hr 400 kg of $\alpha-$ nitronaphthalene is added in lumps obtained by breaking with a hammer the product of mononitration. The temperature is maintained within the range 38-45°C by cooling. A ternary eutectic formed by $\alpha-$ nitronaphthalene and 1,5- and 1,8-dinitronaphthalenes melts within the range 44-54°C, So that at this stage of the process the substance being nitrated is in a molten state, thus facilitating nitration. A stirrer keeps the substance in suspension in the form of drops of l-2 mm in diameter.

After all the nitronaphthalene has been added, the temperature is raised to 55°C within one hour, and then cooled to 40°C. The dinitronaphthalene solidifies in the form of granules.

The nitrator contents are drawn off to the filter tank (1) (Fig. 110). The tank is lead-lined and equipped with a ventilating pipe for conducting away nitrogen oxide. Filtration is most effective with a 20-cm layer of coarse-grained dinitronaphthalene as a filter material, placed between perforated plates of sheet aluminium.

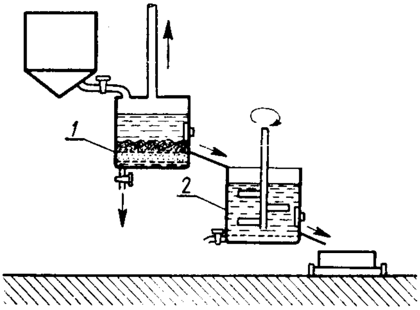


FIG. 110. Flow sheet of the nitration of nitronaphthalene to dinitronaphthalene (Pascal [20a]).

Nearly 60% of the spent acid (600 kg) of composition:

HNO_3	14.5%
H_2SO_4	56.5%
H_2O	29%

flows off from the dinitronaphthalene and is recycled to the nitration of naphthalene to nitronaphthalene. The rest remains in the dinitronaphthalene and can be recovered by washing the latter with the spent acid from mononitration (containing only insignificant quantities of nitric acid and nitrogen oxides). The recovered acid is mixed with the nitrating mixture for the nitration of naphthalene to nitronaphthalene.

The acid-washed dinitronaphthalene is washed six times with water, each time the filter tank being filled with cold water up to the brim. Then dinitronaphthalene is discharged through a side opening into double bottomed wooden vat (2), containing water heated to 60°C. After six washings with hot water, the product is discharged through a side opening and loaded into trucks.

The water content in washed dinitronaphthalene is 25%; the product is dried in dryers, which may be of various construction, until the content of water falls to 0.5%.

The two-stage nitration of naphthalene to dinitronaphthalene requires more complex plant and is more labour consuming: nevertheless it is more economic than single stage nitration, since the product obtained is of higher purity, more easily freed from acid, and the consumption of nitric acid is lower.

The following data given by Pascal illustrate the superiority of two-stage nitration (Table 98).

TABLE 98

MATERIAL CONSUMPTION FOR 1000 kg OF DINITRONAPHTHALENE

Material	One-stage nitration, kg	Two-stage nitration, kg	Calculated theoretical quantity, kg
Naphthalene	625	612	587
HNO_3 (100%)	739	637	579
H_2SO_4 (100%)	732	684	-

The possibility of recovering nitric acid from vapours carried away through the ventilator has not been taken into account.

According to Gorst [31] three grades of DNN are specified in the U.S.S.R. (OST 2940) (Table 99).

TABLE 99

	Grade I	Grade II	Grade III
General appearance	DNN should be a uniform powdery or granular material free from foreign inclusions		
Setting point, °C	150	150	150
Moisture and volatile matters, max.	0.5%	0.5%	0.5%
insoluble in acetone-xylene mixture, max.	0.2%	0.3%	0.5%
Ash total, max.	0.2%	0.2%	0.3%
containing: SiO_2 max.	0.05%	0.05%	0.05%
Pb	-	traces	0.03%
Fe	traces	traces	
Acidity (% H_2SO_4)	0.1%	0.1%	0.2%

NITRATION OF NITRONAPHTHALENE TO TRINITRONAPHTHALENE

French method [31a]

At the St. Chamas plant, the nitrator is of 4 m^3 capacity, equipped with a propeller stirrer (100 r. p. m.) and with a jacket for cooling or heating. There is an outlet 80 mm in diameter at the bottom of the nitrator for discharging the contents.

The nitrator is charged with 800 kg of the spent acid from trinitration and 1330 kg of a mixture:

HNO_3	40%
H_2SO_4	55%
H_2O	5%

This mixture has an exceptionally high content of nitric acid, which is of great importance to obtain the required high degree of nitration.

900 kg of molten nitronaphthalene direct from the nitrator, together with 2600 kg of the above nitrating mixture, is run into the nitrator. The introduction of nitronaphthalene and acid requires about 8 hr. During this procedure a temperature of 57°C is maintained. Then the nitrator contents are stirred for 2 hr at 57°C. After cooling to 40°C during a period of 4 hr the nitrator is discharged at the bottom. During the cooling process the product solidifies to form granules, which can easily be filtered off from the acid on a vacuum filter.

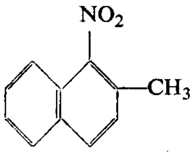
It may happen that trinitronaphthalene becomes lumpy during cooling, thus rendering discharge difficult. If this occurs, the nitrator contents should be reheated to 57°C and then slowly cooled to 45°C prior to being discharged. If this proves ineffective a considerable part of the acid is removed from the nitrator (the acid being the lower layer and trinitronaphthalene the upper), and in its place spent acid from mononitration is introduced. The mixture is then heated to 50-60°C and even to 70°C (the temperature should be the higher the more the mononitration acid has been used) and drawn off into a filter. The filtered nitration product is transferred to a tank containing water. During washing the lumpy material disintegrates, forming granules.

The end product usually contains about 15.6% of nitrogen (the lowest content admissible is 15.1%), while the theoretical content should be 15.97% of N. The melting point of the product ranges from 108°C at the beginning to 124°C by the end of melting.

Although the process is carried out at low temperature it is not quite safe. At the St. Chamas factory an explosion of the nitrator contents occurred in 1940. The accident was caused by a fault in the stirrer. Shortly before the explosion took place an evolution of brown nitrogen oxides had been observed, as well as a local temperature rise up to 77°C, which meant it was 20°C too high. Inflammation of the product in the nitrator then followed.

After the accident additional agitating equipment for mixing with compressed air was installed, as a stand-by for use in the event of a breakdown of the stirrer.

2-METHYL-1-NITRONAPHTHALENE



m. p. 81°C

Since 2-methylnaphthalene has been made available through improvements in coal tar separation methods, considerable interest in the derivatives of this hydrocarbon has been recently shown. Nitration is obviously one of the ways of transforming this raw-material into products of greater commercial application.

As long ago as 1884, Schulze [38] examined the process of nitration of 2-methylnaphthalene with nitric and sulphuric acids and reported 1-nitro-2-methylnaphthalene, a dinitro-product and an oil as the products of nitration. Medinaveitia and de Buruaga [39] also used a mixture of nitric and sulphuric acids and obtained polynitro compounds.

A number of other authors have carried out the nitration of 2-methylnaphthalene, mainly as a step in the preparation of a new intermediate for dyes. Lesser, Glasser and Aczel [40] nitrated 2-methylnaphthalene in the presence of acetic acid and Vessely and Kapp [41] used nitric acid alone at low temperature (5-15°C). They obtained a 58% yield of 1-nitro-2-methylnaphthalene and an oil which contained 4-Nitro-, 6-nitro- and 8-nitro-2-methylnaphthalenes. Vessely and his co-workers [42, 43] identified qualitatively most of the mononitro derivatives of 2-methylnaphthalene and their reduction products.

The most extensive work on the subject so far has been carried out by Brink and Shrieve [44]. The highest yield of 2-methyl-1-nitronaphthalene they obtained was 57% of the theoretical. This was produced by nitrating 2-methylnaphthalene at low temperatures (0-30°C) with a 70% excess of 70% nitric acid. The other isomers appeared as a by-product oil. When using a 15% excess of a nitrating mixture composed of 25% HNO_3, 55% H_2SO_4 and 20% H_2O the yield of l-nitro-2-methylnaphthalene was also 57%. Dinitration took place when acetic anhydride was used. The product was in the form of a solid with m. p. 209-213°C. No determination of the structure of the dinitroproducts was carried out.

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CHAPTER XII

NITRO DERIVATIVES OF HALOGENOBENZENES

APART from a few exceptions nitro derivatives of halogenobenzenes are not used as explosives. Nevertheless they are, or may be, important intermediates in the manufacture of explosives, dyes and drugs.

Derivatives of chlorobenzene are of course the most important, as they are the most readily available. For certain syntheses nitro derivatives of fluoro- or bromobenzene are used. They may be of value sometimes, since the former are less reactive and the latter more reactive than chlorobenzene derivatives. For example, recently 2,4-dinitrofluorobenzene has been widely applied in the elucidation of the structure of peptides (Sanger [1]).

Ingold and Bird [2] investigated the rates of nitration of fluoro-, chloro-, bromo- and iodo-benzenes with acetyl nitrate and found that they could be arranged in the following order: 1: 0.15: 0.033: 0.030: ca. 0.18 (taking the relative rate of nitration of fluorobenzene as unity).

The kind of halogen atom affects the substitution in the ring with the nitro group. Table 100 shows the results of investigations by Sandin and J. R. W. Williams [3]. J. D. Roberts and co-workers [3a] obtained similar results by using isotope dilution analysis.

TABLE **100**

Compound	Halogenonitro compound		
	ortho	*para*	*ortho/para* ratio
C_6H_5F	12.6	87.4	0.14
C_6H_5Cl	30.1	73.1	0.41
C_6H_5Br	37.2	62.5	0.59
C_6H_5I	34.2	65.8	0.52

This trend has been explained in a satisfactory manner by the rule established by Lapworth and Robinson [4]: the increase in relative yield of the ortho-product parallels the decrease in the negative inductive influence of the halogens. The inductive effect which opposes substitution is felt most strongly at the ***ortho*** position.

Ingold [5] summarized his experiments on the rate of substitution. Some rates of nitration which were calculated relative to the total rate for benzene, taken as unity, are given in Table 101.

TABLE 101

Benzene	1	Fluorobenzene	0.15
Toluene	24.5	Chlorobenzene	0.033
Ethyl benzoate	0.00367	Bromobenzene	0.030
Benzyl chloride	0.302	Iodobenzene	0.18

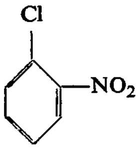
NITRO DERIVATIVES OF CHLOROBENZENE

Chloronitro compounds are nearly always obtained by nitration of the corresponding chlorinated hydrocarbons. Picryl chloride, for example, a trinitro derivative of chlorobenzene, may be prepared by direct nitration. This possibility has in the past aroused some interest in picryl chloride as an explosive. It was indeed manufactured and used in small quantities in Germany during World War I but in the long run did not achieve any importance as a high explosive, mainly because of its high reactivity and its readiness to yield picric acid and, with metals, picrates. Picryl chloride may be a useful starting material in the preparation of several higher nitrated derivatives of diphenyloxide (p. 549) and diphenylamine. Nitro derivatives of *p*- dichlorobenzene (p. 466) were also used during World War I as high explosives.

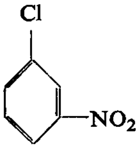
The nitration of chlorobenzene was first mentioned in 1862 by Riche [6]. Later the reaction was studied by Sokolov [7] and Holleman and de Bruyn [8]. Junglleisch [9] was the first to describe the method of preparation of chlorodinitrobenzene from *o*- or *p*- chloronitrobenzene. Laubenheimer [10] investigated the products of the nitration of *m*- chloronitrobenzene, and Ostromyslenskii [11] determined the structure of the products obtained by Jungfleisch, i.e. of 1,2,4- and 1,2,6-chlorodinitrobenzenes. Finally in 1894 the Griesheim factory reported [12] on a method of preparing chlorotrinitrobenzene by direct nitration of chlorobenzene.

MONONITRO DERIVATIVES OF CHLOROBENZENE

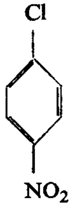
There are three chloronitrobenzene isomers known: *ortho, meta and para:*



m. p. 32.5°C
b. p. 245°C



m. p. 46°C
b. p. 235°C



m. p. 83°C
b. p. 242°C

The *o*- and *p*- isomers can be obtained during the nitration of chlorobenzene. The higher the nitration temperature, the more *o*- isomer is formed.

As Holleman and de Bruyn [8] reported:

At 0°C 30.1% of the *ortho*- and 69.9% of the *para*- isomer is formed, at 30°C 26.9% of the *ortho*-, and 73.1% of the para-isomer is formed. Besides, higher temperatures favour the formation of some small quantities of *m*- chloronitrobenzene. The product is prepared commercially mainly by chlorination of nitrobenzene in the presence of ferric chloride.

According to other authors (McCormack [13]; Dey and co-workers [14]), the *para*- to *ortho*- isomer ratio varies from 66/34 to 64/36, depending on the nitration-conditions.

Bieber and Schuring [15] carried out extensive investigations into the mononitration of chlorobenzene. Mixtures of nitric and sulphuric acids were used and variables included the nitric acid content in the nitrating acid, the ratio of nitric acid to chlorobenzene, the sulphuric acid concentration and the nitration temperature.

In the range of conditions investigated, concentration of nitric acid and the ratio of nitric acid to chlorobenzene had little influence on the final distribution of the chloronitrobenzene isomers. The ratio between *p*- and *o*- isomers varied between 63/37 to 70/30. The temperature effect can be seen from the figures for runs with a final concentration of H_2SO_4 of 80% and 70%:

	80%	70%
at -5°C the ratio was	$\frac{70.5}{29.5}$	-
at 50°C ,, ,,	$\frac{65.6}{34.4}$	$\frac{61.1.}{32.3}$
at 90°C ,, ,, ,,	$\frac{63.4}{36.6}$	$\frac{65.6}{34.4}$

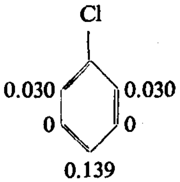
The formation of *p*- chloronitrobenzene could be related to the sulphuric acid concentration and nitration temperature (t) by the equation:

$$\%\ p\text{- ChloroNB} = [0.13 - 0.0027\ S]\ t + 70.6 \qquad (1)$$

where S is % of H_2SO_4.

The content of *m*- chloronitrobenzene varied from 0 to 1.5% apparently increasing with temperature.

According to Ingold and Bird [2] the rate of nitration of each nuclear position can be illustrated by the diagram:



in which unity represents rate of attack on one nuclear position of benzene.

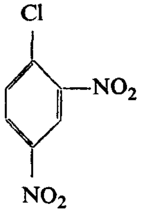
For preparing 1,2,4-chlorodinitrobenzene of high purity, *p*- chloronitrobenzene should be used as starting material since mixtures of *o*- and *p*- chloronitrobenzenes yield mixtures of two dinitro-isomers, namely, 1,2,6- and 1,2,4,-. The corresponding reactions are shown in the diagram on p. 465.

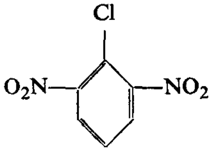
The chloronitrobenzene isomers are highly toxic. Due to their high vapour pressures in summer time or in warm places the atmosphere may contain sufficient chloronitrobenzene to cause poisoning, which may sometimes be fatal. The maximum allowable concentration of chloronitrobenzene in the air is 0.001 mg/l., according to Lazarev [16].

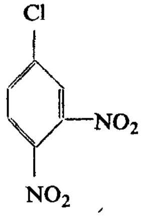
Acute poisoning is characterized by symptoms similar to those appearing in poisoning by nitrobenzene. Lazarev [16] thought nerve paralysis might occur, as well as loss of reflex and tonic spasm. Skin irritation also takes place.

DINITRO DERIVATIVES OF CHLOROBENZENE

Among the six chlorodinitrobenzenes known, the 1,2,4- and 1,2,6-isomers are the most important as they are the principal products of the nitration of chlorobenzene. 1-Chloro-2,4-dinitrobenzene results from the nitration of *o*- and *p*- chloronitrobenzenes and 1-chloro-2,6-dinitrobenzene from the *o*- isomer. Apart from these, the 1,3,4-isomer, which forms in the nitration of *m*- chloronitrobenzene, is of some importance.







All these compounds are known to appear in more than one crystalline forms differing in their melting points. The 1,2,6-isomer can exist in the α– and β– forms (m. p. 92°C and 40°C respectively), and the 1,3,4-isomer in the α–, β–, and γ– forms (m. p. 36.3°C, 37.1°C, 28°C).

1-Chloro-2,4-dinitrobenzene

Physical properties. Three crystalline forms of 1-chloro 2,4-dinitrobenzene are known. A stable α– modification (m. p. 53.4°C) crystallizes from nitric acid (62%) or from alcohol. An unstable, β– modification (m. p. 43°C) can be precipitated, as Ostromyslenskii [11] reports, from a fuming nitric acid solution by treating it with water. It may also be obtained by rapid cooling of the molten substance.

Another unstable modification, γ, melting at 27°C, has also been isolated (Müller [17]).

The solubilities of 1-chloro-2,4-dinitrobenzene in various solvents are given (after Dévergnes [18]) in Table 102.

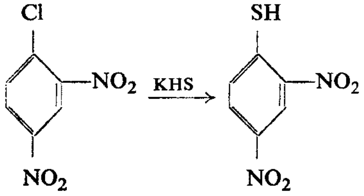
TABLE 102
SOLUBILITY OF 1-CHLORO-2,4-DINITROBENZENE

Solvent	g/100 g of the solvent		
	15°C		100°C
Water	0.0008	at 50°C 0.041	0.159
Methyl alcohol	11.226	at 32°C 32.31	
Ethyl alcohol abs.	8.246	at 32.5°C 18.89	
Ethyl ether	23.517	at 30.5°C 128.13	
Acetone	261.9	at 30°C 581.0	
Ethyl acetate	119.4	at 50°C 287.5	
Chloroform	102.76	at 32°C 210.0	
Carbon tetrachloride	3.851	at 31°C 28.87	
Carbon disulphide	4.212		
Benzene	158.43	at 31°C 359.64	
Toluene	139.89	at 31.5°C 282.55	
Pyridine	2.633	at 20°C 20.85	

In sulphuric acid of concentrations below 80%, 1-chloro-2,4-dinitrobenzene dissolves only with difficulty.

Chemical properties. A chlorine atom *ortho* or *para* to a nitro group is especially reactive and is readily substituted. Numerous examples of such reactions, utilized in the preparation of explosives, are given later in the descriptions of preparation methods for dinitrophenol, dinitroanisole, hexanitrodiphenylamine, hexanitrodiphenyl sulphone, dinitroaniline, tetryl, etc. Chlorodinitrobenzene reacts with sodium sulphide and sulphur to yield sulphur dyes. The action of sodium disulphide results in the formation of tetranitrodiphenyl sulphide (p. 554).

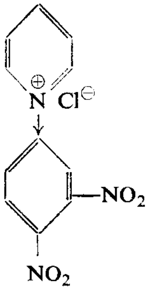
When treated with KHS in alcoholic solution chlorodinitrobenzene yields dinitrothiophenol :



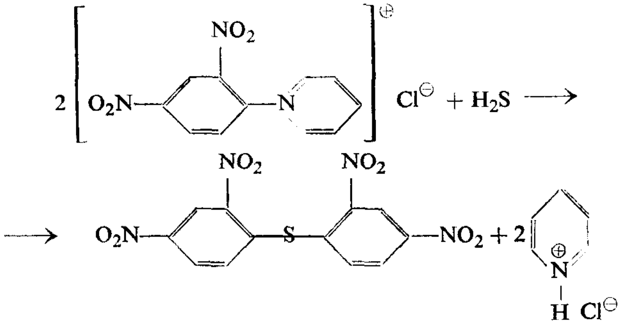
(2)

the reaction being of the nucleophilic substitution type.

Chlorodinitrobenzene reacts with pyridine to form dinitrophenylpyridinium chloride (Vongerichten [19]):

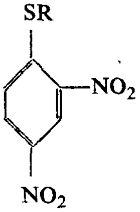


This highly reactive compound may be utilized for various reactions (Zincke [20, 21]). For example, with hydrogen sulphide it forms a tetranitro derivative of diphenyl sulphide (Zincke and Weisspfennig [22]).

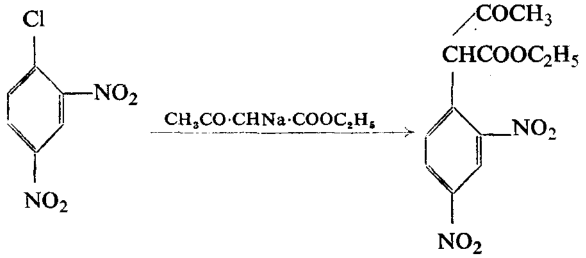


(3)

When reacted with mercaptans or thiophenols of the general formula RSH yields thioethers (Bielig and Reidies [23]):

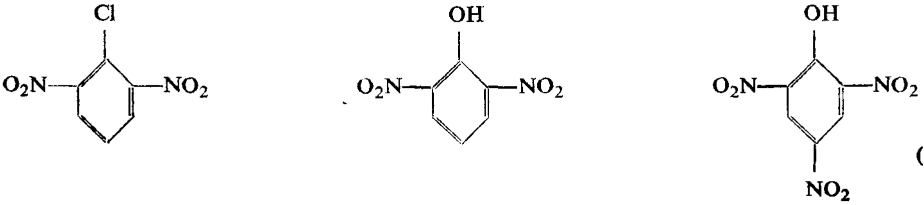


Commercial 1-chloro-2,4-dinitrobenzene prepared by the nitration of a mixture of *o*- and *p*- chloronitrobenzenes usually contains the 1,2,6-isomer. The latter differs from the 1,2,4-isomer in some of its properties. According to Borsche and Rantscheff [24], only the 1,2,4-isomer can react with the sodium salt of acetylacetic ester, the 1,2,6-isomer remaining unchanged.



(4)

The structure of the 1,2,6-isomer has been determined by Ostromyslenskii [11] from the following reactions leading to picric acid:



(5)

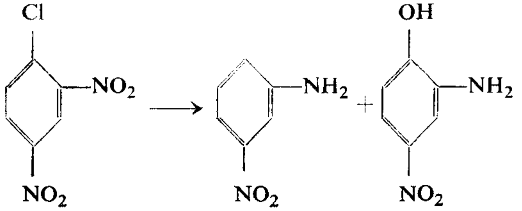
When using chlorodinitrobenzene in the manufacture of explosives, the products obtained from it (e.g. dinitroanisole, dinitrodiphenylamine) are nearly always subjected to further nitration. Both the 1,2,6- and 1,2,4-isomers then yield the same trinitro derivative, 1-chloro-2,4,6-trinitrobenzene. In such cases separation of the isomers and the preparation of highly pure 1,2,4-isomer is not necessary.

There are cases, however, where the presence of the two isomers makes process control difficult, i.e. when the process is controlled by determining the melting point of the product. Then *o*- and *p*- chlorodinitrobenzenes are separated, and only the latter is nitrated, pure l- chloro-2,4-dinitrobenzene being obtained.

Toxicity. The chlorodinitrobenzene isomers are highly toxic. Contact with the skin is especially harmful and provokes eczema. Smiriagin and Shapiro report (see Lazarev [16]) that out of 54 women working with their hands dipped in a liquid containing as little as 0.003% of 1-chloro-2,4-dinitrobenzene, all but 2 suffered from acute eczema after a month of exposure, and were unable to work for 8-23 days or even longer. Grave injuries may also be caused by inhaling the vapours of the hot substance or its dust. The maximum allowable concentration of chlorodinitrobenzene in the air is 0.001 mg/l, according to Lazarev.

Apart from skin injuries the symptoms of poisoning by chlorodinitrobenzene are similar to those produced by dinitrobenzene, namely general bodily weakness, cyanosis, a decrease of the number of red blood cells, disturbances in the functioning of digestive organs and heart failure. Treatment and recovery sometimes prove most difficult especially with regard to the digestive tract and the heart, whereas skin lesions are relatively easier to heal.

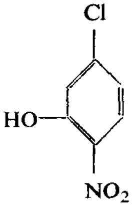
1-Chloro-2,4-dinitrobenzene is converted in the living body into *m*- nitroaniline and nitroaminophenol :



(6)

Both compounds can be determined colorimetrically, by diazotization followed by conjugation with β– naphthol.

The nitration reaction of chlorobenzene is usually accompanied by oxidation reactions, resulting in the formation of phenols, as for example, l-chloro-4-nitro-5-hydroxybenzene (2-nitro-5-chlorophenol) :



in the proportion of about 0.1%.

Other impurities which may be present in chlorodinitrobenzene are: chloronitrobenezenes, as products of an incomplete nitration, *m*- dinitrobenzene formed from benzene present in the chlorobenzene and chloropicrin.

MANUFACTURE OF *o*- AND *p*- CHLORONITROBENZENES

I. G. Griesheim method

At the Griesheim Works the following process was applied for nitrating chlorobenzene to *o*- and *p*- chlorodinitrobenzenes. A cast iron nitrator is charged with 6530 kg of a nitrating mixture of the composition:

HNO_3	30%:
H_2SO_4	56%
H_2O	14%

Then 3500 kg of chlorobenzene from the extraction stage of the process (as described below) is gradually run into the nitrator, with continuous stirring. The chlorobenzene should be of high purity, boiling at 132°C and distilling within a range of 0.5°. Initially a temperature of 40°C should be maintained and allowed to rise to 55°C by the end of the operation. The nitrator contents are then heated to 70-80°C during a period of 2 hr prior to transfer to a separator lined with acid resistant ceramic tiles. After the mixture has settled, the lower acid layer is drawn off to a special tank where it is stirred together with the chlorobenzene to be used for the next nitration. In this way part of the chloronitrobenzene dissolved in the acid, along with the remainder of nitric acid and nitrogen oxides, is extracted by the chlorobenzene.

The oily upper layer of chloronitrobenzene is washed with water, then with a sodium carbonate solution, and again with water, followed by drying under reduced pressure. Drying of the product is necessary to prevent corrosion of the crystallizers. In this way, 4850 kg of crude chloronitrobenzene (m, p. 52°C) are obtained, a yield equivalent to 98% of the theoretical.

I. G. Leverkusen method

4500 kg of chlorobenzene is charged into 2500 kg of waste acid from the previous batch in a nitrator of 10 m^3 capacity. Then 7100 kg of mixed acid containing:

HNO_3	35%
H_2SO_4	52.5%
H_2O	12.5%

is added with stirring and cooling, so that the temperature gradually rises in 9 hr from 20°C to 50°C. The contents are then stirred for 3 hr at 80°C.

A sample is taken to test the washed and dried product (m. p. min. 53°C). The spent acid should possess a density of 1.620 at 15°C; a content of HNO_3 less than 0.4% and of HNO_2 less than 0.4%. Usually the figures are 0.0% and 0.2% respectively.

If the test is satisfactory, the contents of the nitrator are left for 3 hr to settle, then the spent acid is drawn off through a sight glass into an extraction vessel of 10 m^3 capacity. The spent acid after cooling and settling, is transferred to a spent acid vessel of 18 m^3 capacity and from here, after standing, it is finally sent to the acid concentration plant.

The chlorobenzene from the extraction stage is used for the next nitration batch. Chloronitrobenzene is sent to a tile-lined, 10 m^3 washing tank. Here it is agitated three times with 3000 1. of water at 60-70°C by an air stream until neutral to Congo red. Then it is washed with 20 kg of sodium carbonate in 3000 1. of water, and finally with hot water to neutrality. The product is dried at 90-100°C under reduced pressure in a 7 m^3 drying vessel heated by a heating coil. The yield is 98% of the theoretical.

The product has a m. p. of 53-54°C with a dinitro compounds content below 0.1% and is free from nitrophenols. The spent acid contains 70% of H_2SO_4.

Separation of isomers. To separate *o*- and *p*- chloronitrobenzenes the Leverkusen Works crystallize large quantities (14,000-15,000 1. batches) of crude chloronitrobenzene in crystallizers of 15 m^3 capacity, equipped with two cooling coils (cooling area of 600 m2). The two coils are separated from each other by a horizontal, perforated plate. The crystallizer is charged with hot (80-100°C) crude chloronitrobenzene. The product is cooled down to 20°C during 25 hr, then the liquid eutectic mixture (6000-7000 1.) is drawn off through the tap at the bottom of the crystallizer, which takes about 8 hr. The crystalline residue in the crystallizer is washed three times with methyl alcohol (2000-4000 1. each time). The alcohol used for the first washing has already served twice for the same purpose. The second washing is done with alcohol which was used only once, while for the third one freshly distilled methyl alcohol is used. After being used three times the methyl alcohol is sent to a distillation unit, where it is re-distilled and then returned to the washing operation. The residue left after the alcohol is distilled off is added to the liquid eutectic.

The washed product left in the crystallizer is pure commercial *p*- chloronitrobenzene and should have a freezing point of 82-82.5% If not, an additional wash should be given.

The liquid eutectic goes to a distillation column where it is separated into fractions at a pressure in the receiver of about 10 mm Hg and at 180°C at the bottom of the column; the temperature in the dephlegmator is 100-120°C. The first fraction. I, is a mixture of chlorobenzene and chloronitrobenzene isomers (mainly *m*- chloronitrobenzene). The second, II, is rich in *p*- chloronitrobenzene. Finally the main fraction is distilled off, melting initially at 35°C and towards the end of distillation at 28°C. The last, III, is *o*- chloronitrobenzene of 90% purity.

From fraction I a mixture containing 72% of *m*- chloronitrobenzene and 28% of *p*- chloronitrobenzene is drawn off by distillation.

By treating this mixture with sodium hydroxide solution the *p*- isomer is converted to *p*- nitrophenol, while the ***m*-** isomer remains unchanged.

Fraction II is recrystallized. From fraction III *o*- chloronitrobenzene is isolated by crystallization, effected by slow cooling to 15-18°C for about 80 hr.

The resultant crystals are not washed with methyl alcohol. The product melts at about 32°C. The crystallization liquor is added to that from the first crystallization.

At the Griesheim Works the isomers are separated in a similar way but using chlorobenzene for washing instead of methyl alcohol.

NITRATION OF *p*- CHLORONITROBENZENE TO 1-CHLORO-2,4-DINITROBENZENE

According to the Griesheim method of nitration of *p*- chloronitrobenzene to 1-chloro-2,4-dinitrobenzene, 4500 kg of molten *p*- chloronitrobenzene (m. p. 82.4°C) is introduced into a nitrator, followed by 5700 kg of a nitrating mixture,

HNO_3	35%
H_2SO_4	65%

with simultaneous stirring and cooling.

The cast iron nitrator of 8 m^3 capacity is equipped with a jacket and a lead coil.

Nitration starts at 95°C the temperature then being lowered to 45-55°C. After all the acid has been added the mixture is stirred for 2 hr at 65°C. Nitration is considered to be complete when a sample of the dry product solidifies at 49.6°C.

The mixture in the nitrator is then cooled to 55-60°C diluted. with 1000 kg of water, stirred and allowed to settle. Then the lower spent acid layer is drained off and mixed with chlorobenzene to recover nitrogen oxides and nitro compounds present in the acid. The chlorobenzene is then nitrated to chloronitrobenzene (as described above), while the spent acid goes to the concentration plant to obtain concentrated sulphuric acid.

The nitro compound layer is washed with warm water, then with a warm dilute solution of sodium carbonate and again with warm water. The washed nitro compound is dried by heating under reduced pressure. From 100 kg of *p*- chloronitrobenzene 128.5 kg of 1-chloro-2,4-dinitrobenzene is obtained, which is 98.5% of the theoretical yields.

NITRATION OF CHLOROBENZENE TO CHLORODINITROBENZENE (GRIESHEIM METHOD)

The nitration of chlorobenzene to chlorodinitrobenzene without separating the isomers of chloronitrobenzene is accomplished in two successive stages in the same nitrator.

Mononitration. 3000 kg of chlorobenzene, boiling within a range of 0.8°C, is mixed with the spent acid from dinitration, containing 78% of H_2SO_4. Then 1850 kg of a nitrating mixture of the compositions :

HNO_3	87-88%
H_2SO_4	11%

is added to the solution at 40-55°C, while stirring and cooling. The whole is heated to 70°C and stirred at this temperature for 2 hr. When nitration has been completed the stirrer is stopped and the mixture is allowed to remain at rest. After it has separated into two layers, the lower one - spent acid containing 70% of H_2SO_4 - is transferred to a tank of 13 m^3 capacity lined with acid resistant bricks, where it is agitated with chlorobenzene. The chlorobenzene, now containing chloronitrobenzne extracted from the spent acid, is used for nitration, while the acid freed from the nitro compound is concentrated.

Dinitration. 5100 kg of a nitrating mixture of the composition:

HNO_3	35%
H_2SO_4	65%

is run into the nitrator containing the chloronitrobenzene, a temperature of 50-55°C being maintained by cooling.

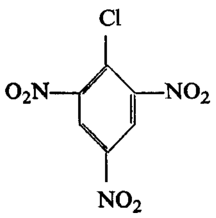
The whole is heated to 70°C and stirred for 2 hr at 70-80°C. Nitration is complete if a sample of the product has a melting point of 47.6°C, and, when steam distilled after being brought to alkalinity, the distillate does not smell of *o*- nitrophenol. After nitration has been completed, the whole is cooled to 50°C diluted at this temperature with 390 kg of water and allowed to remain at rest for separation. The lower spent acid layer, containing 78% of H_2SO_4 is used for mononitration.

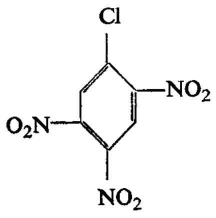
Chlorodinitrobenzene forming the upper layer is washed with warm water. then with a warm dilute solution of sodium carbonate and again with warm water, until entirely free from acid. Then it is dried by heating under reduced pressure in a 20 m^3 tank.

From 100 parts of chlorobenzene 175 parts of chlorodinitrobenzene with a melting point of 47.6°C is obtained, which corresponds to 97.5% of the theoretical yield.

TRINITRO DERIVATIVES OF CHLOROBENZENE

Of the trimtro derivatives of chlorobenzene, l-chloro-2,4,6-nitrobenzene (m. p. 81.5-83°C), known also as picryl chloride, is the most important. Next in importance is 1-chloro-2,4,5-trinitrobenzene (m. p. 116°C):





picryl chloride

l-Chloro-2,4,6-trinitrobenzene (picryl chloride) was obtained by Pisani in 1854, in the reaction of phosphorus pentachloride with picric acid. Similarly Ullmann [25] prepared picryl chloride when treating picric acid with toluene-p-sulphonchloride.

Both methods are merely of theoretical interest. A method reported by R. Boyer. Spencer and Wright [26] is of greater practical importance. It is based on the reaction of pyridine picrate with phosgene in which picryl chloride forms in theoretical yield. The pyridine in the aqueous solution left after picryl chloride has been separated is regenerated as picrate by treating the solution with picric acid. The picrate is returned to the process. According to T. Urbanski, Kuboszek and Dworak [26a] phosgene can be replaced by thionyl chloride. For industrial practice a method was developed at Griesheim [12] consisting in the nitration of l-chloro-2,4-dinitrobenzene. It was applied in Germany during World War I.

As Desvergnes [18] reports, nitration by this method was effected in the following way: 100 parts of chlorodinitrobenzene were dissolved in 200 parts of 40% oleum. A mixture of 400 parts of anhydrous sulphuric acid and 300 parts of 94% nitric acid was added to the solution. The whole was heated to 150°C with stirring, this temperature being maintained for 3 hr longer. After cooling the mixture was left for crystallization, filtered and the product was washed with cold water.

According to Desvergnes [18] and Frankland and F. H. Garner [24], chlorodinitrobenzene can be nitrated with a mixture containing less nitric acid and more sulphuric acid. The resultant product is of higher purity and the yield is also higher.

Desvergnes suggests a mixture of 560 parts of sulphuric acid (100%) and 150 parts of nitric acid (93%) for the nitration of 100 parts of chlorodinitrobenzene dissolved in 200 parts of 40% oleum at 150°C.

Frankland and Garner dissolved 100 parts of chlorodinitrobenzene in 750 parts of sulphuric acid (100%) and added 125 parts of nitric acid (93%) to the solution.

As Desvergnes pointed out in a comparison of the three methods the third one looks the best as can be seen from the following figures (Table 103):

TABLE 103

Method	Theoretical yield %	Melting point of the product °C
Griesheim	55	65
Desvergnes	82.5	75.8
Frankland and F. H. Garner	85	76

Physical properties. Picryl chloride is only sparingly soluble in water: at 15°C 0.0178 parts and at 100°C 0.346 parts dissolve in 100 parts of water.

On dissolution in hot water picryl chloride undergoes partial hydrolysis, picric acid being formed. Solubility data for picryl chloride in organic solvents are given in Table 104.

Kast [28] reports the specific gravity of molten and then solidified picryl chloride to be 1.76.

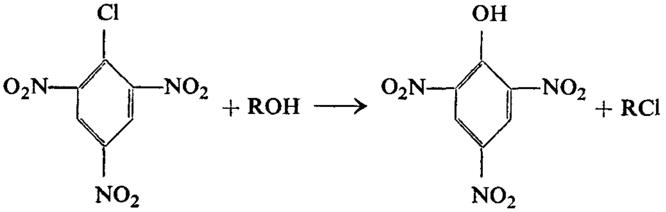
TABLE 104

SOLUBILITY OF PICRYL CHLORIDE IN ORGANIC SOLVENTS (g/100 g OF SOLVENT)

Solvent	at 17°C	at 50°C
Methyl alcohol	10.24	34.8
Ethyl alcohol (absolute)	4.48	15.1
Ether	7.23	10.6*
Ethyl acetate	91.5	238.35
Acetone	212.0	546.4
Chloroform	12.36	233.4
Carbon tetrachloride	0.56	2.45
Benzene	36.39	428.1
Toluene	89.44	321.1

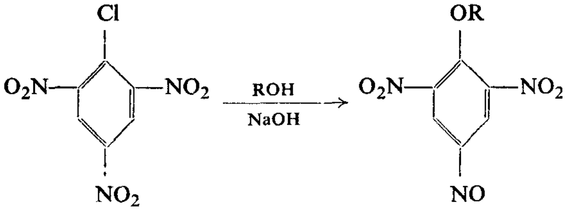
* At 31°C.

Chemical properties. The chlorine atom in a picryl chloride molecule is exceptionally reactive. Besides hydrolysis to picric acid when heated with water, as mentioned above, picryl chloride can yield picric acid when boiled with alcohols, according to the equation:



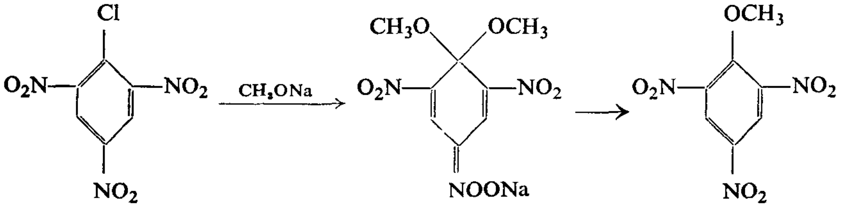
(7)

If the reaction proceeds in the presence of sodium, potassium or calcium hydroxides, the corresponding picric acid ethers are formed:



(8)

The same compounds can be obtained by the action of the corresponding alcoholates, through the formation of intermediate addition products:



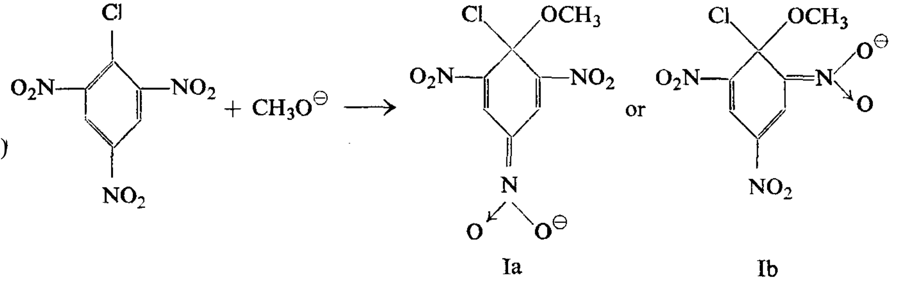
(9)

The interaction of equimolar proportions of picryl chloride gives a number of reactions, according to a recent investigation by Farmer [29]. There are two stages of the reaction. The first is very rapid and gives an intense colour. This is followed by a phase in which the red colour fades gradually. After some days the solution becomes pale yellow and yields methyl picrate (trinitroanisole). Part of the methyl picrate is formed in the first stage (ca. 40%) and the remainder in the second stage.

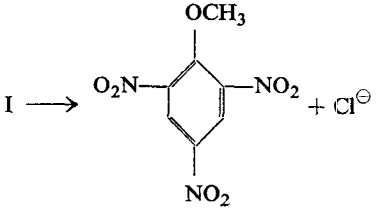
Farmer suggests the following mechanism for the reactions:

Stage I (very rapid at room temperature):

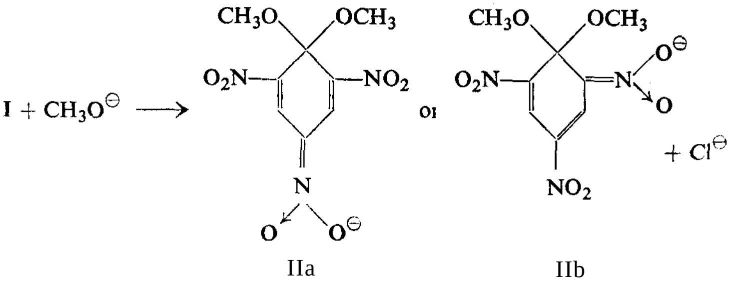
(A)



(B₁)

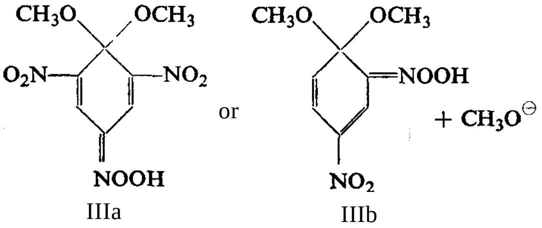


(B₂)

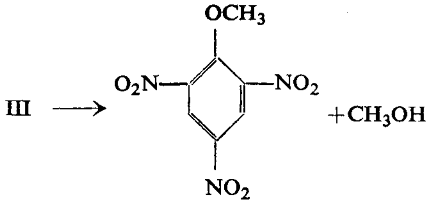


Stage II - gradual conversion of the product II into methyl picrate:

(C) II + CH_3OH <->

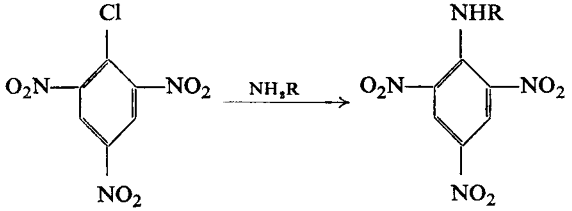


(D$_1$)



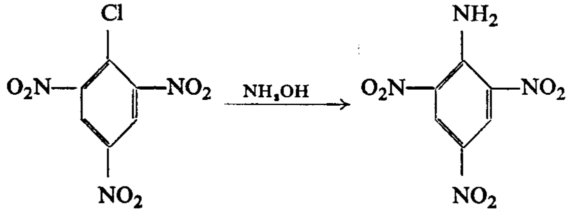
(D$_2$) Action of CH_3O- at very low concentration on residual picryl chloride.

With ammonia or amines picryl chloride yields picramide or its derivatives:



(10)

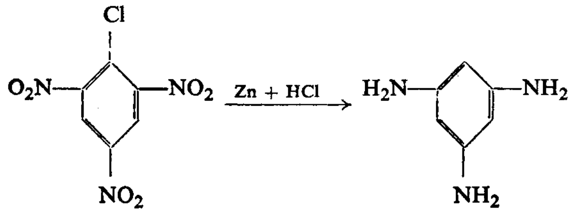
The reaction of picryl chloride with hydroxylamine hydrochloride is worth mentioning. As Borsche [24] observed, instead of the expected phenylhydroxylamine derivative, picramide was formed :



(11)

When reacted with hydroxylamine in the presence of sodium acetate, picryl chloride was found to form dinitrodinitrosobenzene (Nietzki and Dietschy [30]) (p. 258).

Picryl chloride may be used as the starting material for the preparation of trinitrobenzene (p. 255). With strong reducing agents, picryl chloride yields triaminobenzene (Fleisch [31]) :



(12)

Picryl chloride is toxic. It acts in much the same way as chlorodinitrobenzene, but is slightly less poisonous.

With aromatic hydrocarbons such as naphthalene, anthracene, acenaphthene, fluorene, phenanthrene, retene, picryl chloride forms addition compounds with the mol. ratio 1:1.

Here are a few data related to these compounds given by Jefremov [32] (Table 105).

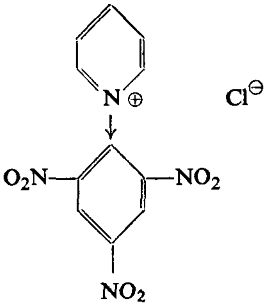
TABLE 105

Picryl chloride and the second component	m. p., °C
Acenaphthene	113.2
Anthracene	decomp.
Fluorene	64.6
Naphthalene	91.2
Phenanthrene	82.4
Retene	53.5

According to the same author (Jefremov and Frolova [32]), with l-chloro-2,4-dinitrobenzene picryl chloride forms an addition compound (mol. ratio 1:1) m. p. 31.2°C. Formerly Frankland and P. H. Garner [27] and Desvergnes [18] reported only the formation of a simple eutectic containing 44-45% picryl chloride with m. p. 25.0-25.6°C.

Recently T. Urbanski, Semenczuk and Górski [32a] confirmed the statement of Jefremov and Frolova.

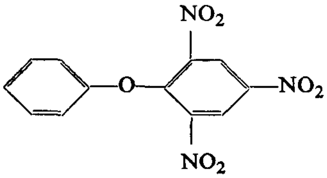
Picryl chloride reacts with pyridine to form picrylpyridinium chloride (IV)

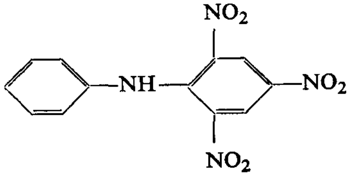


IV (m. p. 113-115°C)

This compound, first prepared by Wedekind [33], is even more reactive than dinitrophenylpyridinium chloride (p. 454). Bielig and Reidies [23] described a reaction after Zincke and Weisspfennig's work [22] which resulted in the formation of hexanitrodiphenyl sulphide (picryl sulphide) (p. 553).

Okon [34] in a number of investigations found that when picrylpyridinium chloride reacts with phenols or aromatic amines, derivatives of trinitrodiphenyl oxide or trinitrodiphenylamine are obtained :



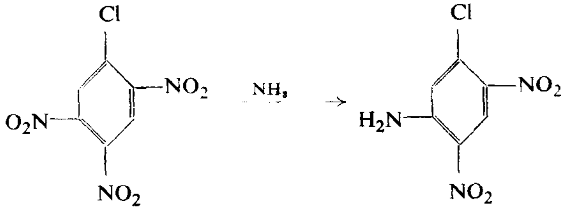


On treating picrylpyridinium chloride with alcohol Hodges [35] obtained picrylpyridinium picrate. The same salt was obtained by Okon when subjecting picrylpyridinium chloride to hydrolysis by means of an aqueous solution of pyridine.

1-Chloro-2,4,5-trinitrobenzene

By the nitration of 1-chloro-3,4-dinitrobenzene with nitric acid in the presence of 40% oleum, at a temperature of 140-150°C a picryl chloride isomer, 1-chloro-2,4,5-trinitrobenzene, is formed.

A nitro group in the position ortho and para to other nitro groups exhibits higher reactivity than a chlorine atom. That is why by the action of, for example, ammonia, chlorodinitroaniline can be formed:

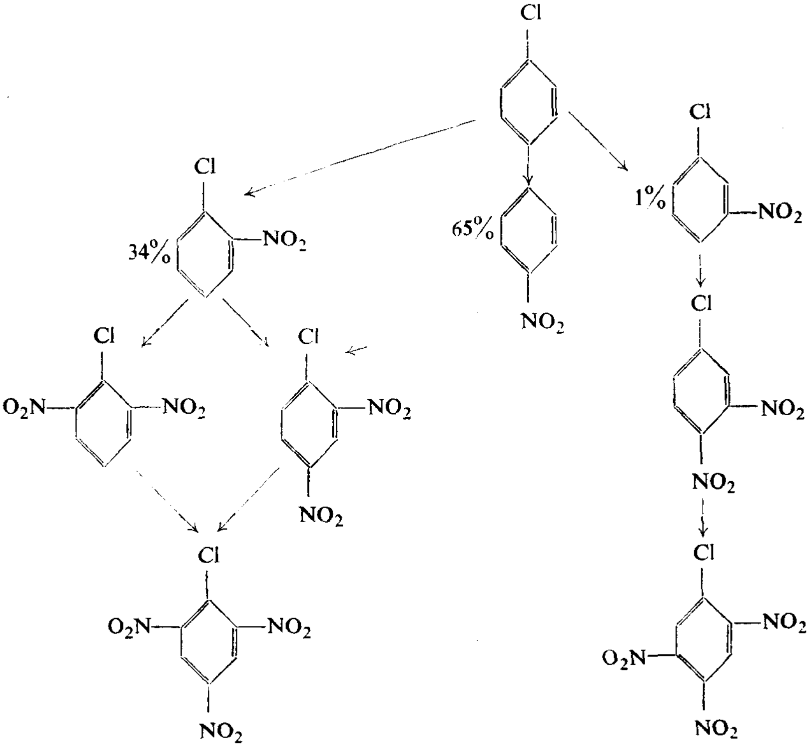


(13)

The chlorine atom in 1-chloro-2,4,5-trinitrobenzene becomes reactive only at higher temperatures.

Diagram of the nitration of chlorobenzene

The following diagram represents the complete process of nitration of chlorobenzene to trinitro derivatives :



THERMOCHEMICAL AND EXPLOSIVE PROPERTIES OF CHLORONITROBENZENES

Desvergnes has tested the explosive properties of 1-chloro-2,4-dinitrobenzene in a manometric bomb. At a density of 0.25, on comparison with other dinitro compounds, he obtained pressures:

for chlorodinitrobenzene	2016	kg/cm^2
for chlorodinitrophenol	2084	,,
for dinitrobenzene	2194	,,

It can be seen from the above that the explosive properties of chlorodinitrobenzene are slightly inferior to those of dinitrobenzene.

Experiments with chlorodinitrobenzene in mixture with picric acid for filling shells have given no satisfactory results.

NITRO DERIVATIVES OF *p*- DICHLOROBENZENE

In the explosives industry only the nitro derivatives of p-dichlorobenzene and 1,3,5-trichlorobenzene have gained any importance.

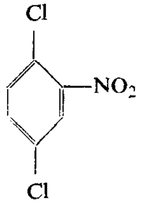
p- Dichlorobenzene is the most important of the dichlorobenzene isomers, being the principal product in the chlorination of benzene. Other isomers are formed in smaller quantities.

Mono- and di-nitro derivatives were first obtained by Jungfleisch [9] in 1868. Kijrner [36] demonstrated that the product of dinitration of *p*- dichlorobenzene consists of the α– and β– isomers. Morgan and Norman [37] isolated yet another one, the γ– isomer. The preparation and properties of all these isomers were investigated by Holleman [38].

Towards the end of World War I *p*- dichlorodinitrobenzene was used in the U.S.A for shell filling under the name of “Parazol”. When brought to explosion it produced an irritating gas, because of the large quantity of chlorine in the molecule. This was probably the reason why it was used as an explosive, as its power was relatively poor.

Mononitro derivatives of *p*- dichlorobenzene

1,4-Dichloro-2-nitrobenzene (m. p. 55°C; b. p. 267°C) was obtained by Jungfleisch by the nitration of *p*- dichlorobenzene.

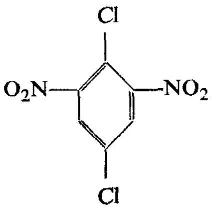


A product of higher purity was isolated by Beilstein and Kurbatov [39] from the products of chlorination of nitrobenzene in the presence of antimonium chloride

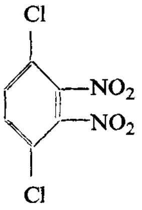
(*o*- and *m*- chloronitrobenzenes were also obtained in the reaction). The crude product contains traces of chloropicrin as an impurity.

Dinitro derivatives of *p*- dichlorobenzene

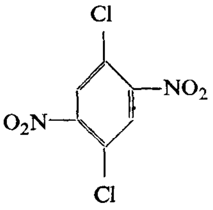
Three isomeric *p*- dichlorodinitrobenzenes α (m. p. 106°C), β (m. p. 101°C; b. p. 318°C) and γ (m, p. 119°C) are known, with the nitro groups in the positions 2,6- (3,5-), 2,3- and 2,5- (3,6-) respectively.



α



β



γ

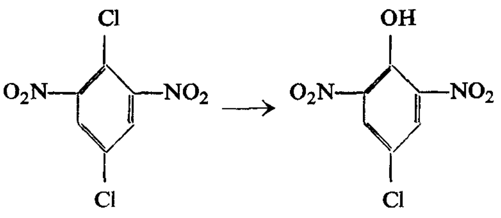
The 2,6-isomer is the principal product of nitration of *p*- dichlorobenzene, the 2,3-isomer being formed in a smaller quantity, and the 2,5-isomer to a still smaller extent.

The melting point of the crude nitration product ranges between 60°C and 80°C. Traces of chloropicrin can be detected in the product.

MacLeod, Pfund and Kilpatrick [40] believed that the 2,6- and 2,5-isomers formed an addition compound (in a 3:2 ratio), melting at 81°C. The isomers are very poisonous (Voegtlin [41]).

1,4-Dichloro-2,6-dinitrobenzene is difficult to dissolve in water and cold alcohol, though it dissolves readily in hot alcohol and in most organic solvents.

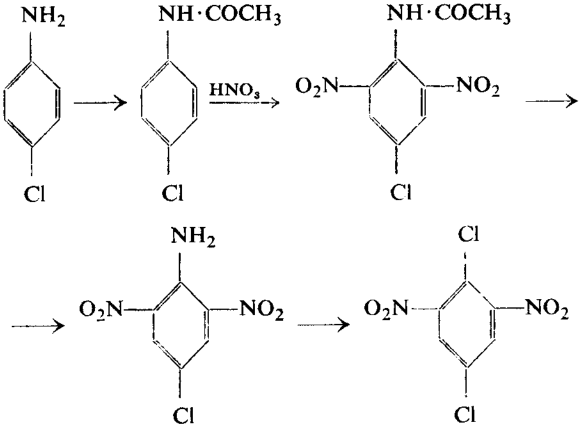
One of the chlorine atoms (adjacent to the nitro groups) is very reactive and can easily be substituted by some other group. In consequence, on boiling the compound with, for example, an aqueous solution of sodium carbonate, chlorodinitrophenol can be obtained:



(14)

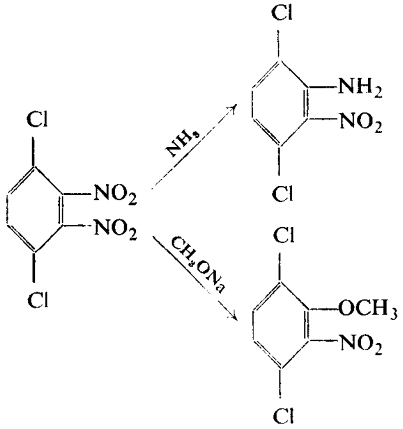
With ammonia or amines it yields the corresponding amines, the reactions being characteristic of such chloronitro compounds.

Holleman [38] obtained very pure 1,4-dichloro-2,6-dinitrobenzene in the following way:

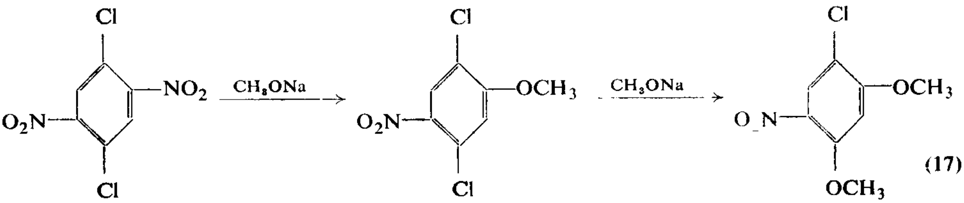

(15)

The reactivity of the nitro groups in 1,4-dichloro-2,3-dinitrobenzene and 1,4-dichloro-2,5-dinitrobenzene is exceptionally high, exceeding that of the chlorine atom.

Thus, Körner [36] observed that when treated with ammonia the dinitro-isomer having the NO_2 groups in the 2,3-positions is converted to dichloronitroanilinc. Holleman found that with sodium alcoholate the compound yielded dichloronitro-anisole :

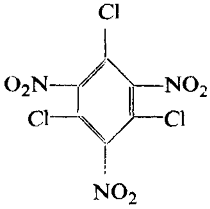

(16)

Holleman believed the 2,5-isomer behaved in the same way at the first stage of the reaction. Only by prolonged treatment with an alcoholate can a chlorine atom be substituted, a resorcinol derivative being formed:


(17)

2,4,6-TRINITRO DERIVATIVE OF 1,3,5-TRICHLOROBENZENE

1,3,5-Trichloro-2,4,6-trinitrobenzene (m. p. 187°C) can be prepared by the nitration of 1,3,5-trichlorobenzene with anhydrous nitric acid and oleum (Jackson and Wing [42]). However, according to van Ryn [43] the yield is poor.



Alone, the compound is of no interest as an explosive, for 1,3,5-trichlorobenzene is too expensive as a starting material. It is prepared by the chlorination of aniline followed by diazotization and reduction with alcohol. Nevertheless it may be used for the preparation of explosives with certain specially valuable properties, for example, an initiating substance - trinitrotriazidobenzene - (Vol. III) or for the very powerful high explosive - trinitrotrimethylnitroaminobenzene (Vol. III). It was used in Germany as an insecticide.

Manufacture of 1,3,5-trichloro-2,4,6trinitrobenzene. The I. G. Griesheim Works applied the following process for the manufacture of the above product.

The reactor is charged with 980 kg of 30% oleum to which 100 kg of solid trichlorobenzene is added during the course of one hour. The whole is heated to 100°C for another hour and kept at this temperature for 2-3 hr longer with constant stirring. Towards the end of this operation sulphonation takes place. The reaction may be considered complete when a sample of the mixture taken from the nitrator dissolves completely in water.

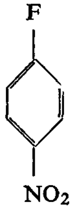
After cooling the reactor contents to 50°C 300 kg of 99% nitric acid are added during about 4 hr. While this is being done the temperature rises to 100°C. After all the nitric acid has been added, the mixture is stirred for another 10-14 hr, then during the course of a further 8 hr the temperature is gradually raised to 140-145°C. As too rapid a rise of temperature would involve the risk of decomposition, if this occurs the nitrator contents should be drained off into a safety tank. After a temperature of 140-145°C has been attained, the mixture in the nitrator is stirred at this temperature for further 45 hr. At this stage of the process the product of the reaction crystallizes. Then the nitrator contents are cooled down to 20°C and transferred by compressed air to the filter. The filtered product is transferred to a washing tank, where it is washed by mixing with cold water, followed by decantation, several times until free from acid (Congo paper test).

The spent acid contains 13% of HNO_3 and H_2SO_4 + SO_3 equivalent to 90% H_2SO_4.

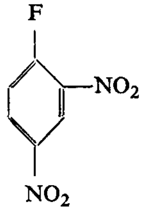
The washed, acid-free product is filtered off on a vacuum filter and dried under reduced pressure at 100°C. In this way 125 kg of the product melting at 189 -190°C are obtained, which corresponds to 72% of the theoretical yield.

NITRO DERIVATIVES OF FLUOROBENZENE

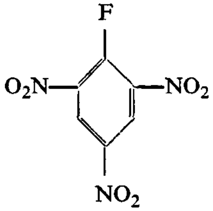
The most important nitro derivatives of fluorobenzene are:



m. p. 27°C



m. p. 25.8°C



m. p. 35°C

The nitration of fluorobenzene was studied by a number of authors. Most of the earlier work was devoted to mononitration (Wallach [44], Hollernan [45], Swarts [46]).

Dinitration to obtain 1,2,4-fluorodinitrobenzene was described by Holleman and Beekman [47] who nitrated *p*- fluoronitrobenzene. Zahn and A. Würz [48] prepared the same dinitrocompound by nitrating fluorobenzene. 1,2,4,6-Fluorotrinitrobenzene (picryl fluoride) was prepared by Olah, Pavlath, J. Kuhn and Varsanyi [49] by acting on 1,2,4-fluorodinitrobenzene with a nitrating mixture composed of fuming nitric acid and 60% oleum. The yield was 36% of theoretical.

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CHAPTER XIII

NITRO DERIVATIVES OF PHENOL

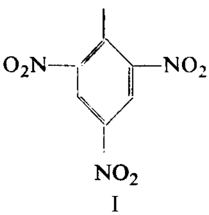
GENERAL INFORMATION

AMONG nitrophenols 2,4,6-trinitrophenol - picric acid - is of the greatest importance. The fact that this compound was first obtained as long ago as the mid-eighteenth century can be explained by the exceptional ease with which nitro groups can be introduced into the aromatic ring, due to the presence of the phenol group.

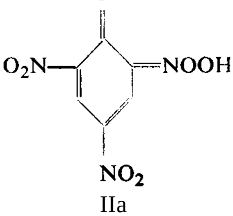
Three nitro groups can be introduced by nitrating with nitric acid of a relatively low concentration, while concentrated acid enables four and even five nitro groups to be introduced.

The presence of nitro groups enhances the acidic properties of the phenol group. This is why the trinitro derivatives are also called acids, e.g. trinitrophenol is known as picric acid and trinitroresorcinol as styphnic acid. These compounds readily form salts with metals or bases. Polynitro derivatives of phenols also form addition compounds with hydrocarbons, e.g. naphthalene.

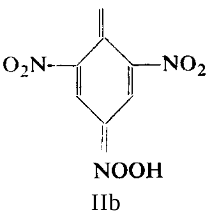
According to Hantzsch, nitrophenols exist in two forms: a phenolic, colourless form (I) and a quinonoid coloured one (IIa and IIb). This occurs with picric acid:



I



IIa



IIb

Due to the presence of a phenolic group nitrophenols are soluble in water and their acidic character enables them to dissolve in aqueous solutions of bases with the formation of the corresponding salts. Solutions of the salts are usually brightly coloured due to the presence of form II. Strong acids precipitate nitrophenols from their solutions as colourless products.

The ability of nitrophenols to appear in the coloured quinoid form has been utilized in acidimetry, where some of them are used as indicators, e.g. *m*- and *p*- nitrophenols, 2,4-, 2,6- and 2,5-dinitrophenols, nitrohydroquinone etc.

Of all the nitrophenols, picric acid has been known the longest. The first mention of it can be found in alchemical writings of 1742, in which Glauber's experiments are described. He acted with nitric acid on wool or horn and isolated picric acid in the form of its lead or potassium salt. A more detailed description was given by Woulfe [l] in 1771, who prepared picric acid from indigo by treating it with nitric acid and found that the new substance had dyeing properties ("indigo yellow"). while Haussmann [2], in 1788, proved that it behaved like an acid. Later, many workers obtained the same product by acting with nitric acid on various organic substances, such as silk, natural resins etc. (Welter [3]; Braconnot [4]). Chevreul [5] was the first to express the opinion that picric acid contained certain constituents of nitric acid and this was later confirmed by Dumas [6] and Marchand [7]. The latter gave $C_{12}H_6N_6O_{14}$ as the empirical formula of picric acid which is exactly double the correct formula.

Some of the authors had drawn attention to the explosive character of picric acid salts, but it was not until 1830 that Welter [3] suggested the possibility of applying picrates as explosives. At that time picric acid was obtained solely by acting with nitric acid on indigo. Marchand [7] expressed the view, which proved to be true. that it was aniline, formed as an intermediate product in the process of decomposition of indigo, silk and other organic matter, which yielded picric acid under the influence of nitric acid.

The constitution of picric acid was determined by Laurent [8] in 1841. He prepared it by reacting phenol with nitric acid. He was also able to isolate dinitrophenol formed in an intermediate stage of the nitration. A further improvement in the method of preparation of picric acid from phenol was its sulphonation prior to nitration (Schmidt and Glutz [9]).

In the second half of the nineteenth century, picric acid was very widely used as a fast dye for silk and wool. The first definite suggestions as to the application of picric acid for the manufacture of explosives go back to the early second half of the nineteenth century. They referred to the application of picric acid salts as by then the explosive properties of picrates were already well known. Thus, for example, Designolle [10] suggested potassium picrate, and Brugere [11] ammonium picrate as propellants (Vol. III), while in 1871 Abel [12] proposed ammonium picrate as a high explosive. At that time potassium picrate was already being used in Great Britain and in the U.S.A. for filling shells.

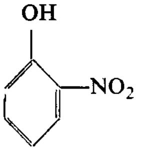
The view then prevailed, supported by such an authority as Abel, that picric acid itself is not an explosive but only its salts are. Nevertheless in 1873 Sprengel [13] proved that picric acid could be brought to explosion by a detonator and Turpin [14] proposed applying this property of picric acid by utilizing it for filling shells. In Russia methods of preparation of picric acid and using it as a shell filling were worked out near 1894 by Panpushko [15]. Eventually picric acid was accepted all over the world as the basic high explosive for military uses.

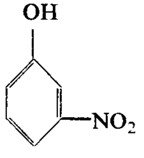
Since picric acid melts at high temperature, shells are loaded by pouring it in. mixed with various nitro compounds: dinitrophenol, mono- and di-nitronaphthalenes, TNT, TNX etc. (Vol. III).

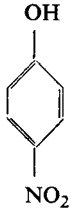
However, after the useful properties of TNT as a material for filling shells had been established (early twentieth century), the importance of picric acid decreased somewhat. Nevertheless it was still widely used mainly because of its very simple method of preparation. In the course of time, however, as themethods of manufacture of TNT continuously improved and new sources of toluene (for example petrochemical synthetic toluene) became available, the importance of the latter went on increasing. The acidic character of picric acid and its corrosive action on metals resulting in the formation of salts sensitive to impact and friction led to a decline in the importance of picric acid, and there is a trend to eliminate it from armaments altogether. Because of its relatively high sensitiveness to impact, picric acid alone was unsuitable For filling certain special purpose ammunition, for example For armour piercing shells (p. 322).

MONONITRO DERIVATIVES OF PHENOL

Three isomeric mononitrophenols are known: *ortho* (m. p. 44-45°C; b.p. 214-216°C with decomposition); *meta* (m. p. 96°C) and *para* (m. p. 114°C):







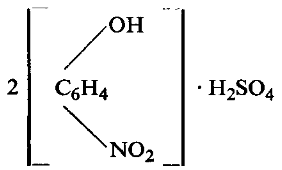
The *o*- and *p*- isomers are always formed when phenol is nitrated with dilute (e.g. 30%) nitric acid, the proportion of the *o*- isomer increasing with nitration temperature.

Separation of the two isomers may be accomplished by steam distillation: the volatile *o*- nitrophenol passes over, while the *p*- isomer remains in the residue.

Since apart from the nitrophenols some dark coloured, often resinous by-products are formed, *o*- and *p*- nitrophenols are Frequently prepared on an industrial scale From the corresponding chloronitrobenzene derivatives.

Pure *p*- nitrophenol may also be prepared by nitrosation of phenol, followed by oxidation of *p*- nitrosophenol with dilute nitric acid. The *m*- isomer is usually prepared by diazotization of *m*- nitroaniline.

The *m*- and *p*- isomers combine with sulphuric acid to Form molecular compounds, melting at 83°C and 90°C respectively:

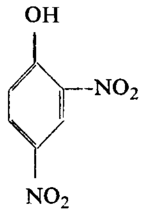


$$2\left[C_6H_4\begin{matrix}OH\\NO_2\end{matrix}\right]\cdot H_2SO_4$$

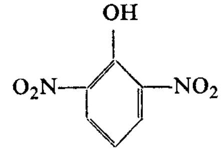
while *o*- nitrophenol does not yield such a compound (Kendall and Carpenter [16]).

DINITRO DERIVATIVES OF PHENOL

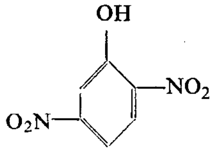
There are six isomers of dinitrophenol: α or 2,4- (m. p. 113-114°C), β or 2,6- (m. p. 62-63°C), γ or 2,5- (m. p. 104-108°C), δ or 3,4- (m. p. 134°C), ε or 2,3- (m. p. 114°C) and ϑ or 3,5- (m. p. 122°C).



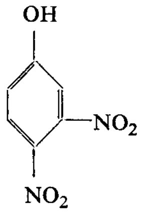
α



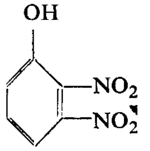
β



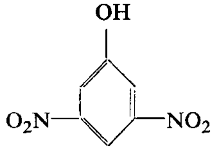
γ



δ



ε



ϑ

Of these only the 2,4-isomer is used in explosive compositions or as a starting material for the preparation of picric acid by one of the methods described later. The 2,6-isomer on nitration also gives picric acid but it is not used for this purpose on a commercial scale. Both these isomers may be obtained by the nitration of phenol with nitric acid. All the other isomers are prepared by indirect methods.

Laurent [8] was the first to obtain dinitrophenol by nitrating phenol. Investigations that followed revealed that Laurent's dinitrophenol was not a chemical individual, but a mixture of the 2,4- and 2,6-isomers. Kiirner [17] obtained pure 2,4-dinitrophenol by the nitration of *p*- nitrophenol and Armstrong [18] prepared 2,6-dinitrophenol along with some 2,4-isomer, starting from *o*- nitrophenol. Clemm [19] determined the constitution of 2,4-dinitrophenol, which was later confirmed by Salkowski [20].

Finally Hübner and W. Schneider [21] defined the conditions under which the formation of the two isomeric dinitrophenols must proceed and pointed out the difference in their structures. They proved the *p*- nitrophenol was nitrated to 2,4-dinitrophenol when using 54% nitric acid. *o*- Nitrophenol is slightly more difficult to nitrate and yields a mixture of 2,6- and 2,4-dinitrophenols. The two isomers may be separated by steam distillation, since the 2,4- is more volatile than the 2,6-isomer. In consequence the residue in the retort becomes enriched in the 2,6-isomer which can finally be obtained in a pure form. Another method of separation is based on taking advantage of the difference in solubility of the barium salts of the two isomers, the 2,4-isomer salt being readily soluble in water, while the salt of the 2,6-isomer dissolves only with difficulty.

TABLE 108

CHARACTERISTICS OF 2,4-DINITROPHENATES

Salt	Number of molecules of water of crystallization	Dehydration temperature °C	Initiation temperature °C	Inflammability from flame
NH_4	1	50*	-	
Na	1	180	380	readily inflammable
Mg	12, 9, 1	180	-	
K	1,½	160	400	
Ca		180	-	
Mn	5	50* (monohydrate)	340	
Ni	8	100*	-	
Cu	-	-	340	
Zn	-	50*	355	
Sr	3	150	-	
Ba	6, 5, 4	160-180	-	
Hg	-	50	355	highly inflammable
Pb	6	15**	345	

* At 38 mm Hg.
** At 10 mm Hg.

In 1930 Desvergnes [25] gave the following values for the solubility of the barium salt in water and alcohol:

in 100 ml of water at 25°C	1.5 g
75°C	7.2 ,,
in 100 ml of alcohol it 22°C	0.3 ,,
,, ,, ,, ,, ,, ,, 78°C	3.5 ,,

Apart from this barium dinitrophenate dissolves easily in acetone, whereas it is insoluble in chloroform and ether.

TOXICITY OF DINITROPHENOLS

Dinitrophenols are highly toxic. According to Mayer [30], 2,4-dinitrophenol is toxic not only when ingested but also when its dust is inhaled or absorbed through the skin. Fatal cases are known which were caused by inhalation of dust in a concentration of 0.004 mg/l. A dose of 0.01 g/kg of body weight is considered toxic. Other authors report 0.2 g/kg as the fatal dose, pointing out that dinitrophenol vapours in a concentration corresponding to volatility at room temperature are not poisonous.

Dinitrophenol enhances metabolism and has been applied as an agent For the treatment of obesity. Chronic dinitrophenol poisoning may cause liver and kidney damage. According to Lazarev [31], poisoning by dinitrophenol is characterized by the following symptoms: general weakness, lack of appetite, rush of blood to the head, accelerated pulse (100-130), and respiration, a rise in temperature to 39-40°C, and moreover, in severe cases, blue mucous membranes, and spasms. Death, as *post mortem* examinations have indicated, is usually caused by pneumonia and meningitis. In many cases chronic poisoning may manifest itself by cataracts of the eye lenses, and eczema in people with sensitive skin. Inflammation of the lymphatic glands and degeneration of nails can often be observed.

Martin [32] found that dinitrophenol undergoes in the body a partial reduction either to 2-amino-4-nitrophenol or to 4-amino-2-nitrophenol and 2,4-diaminophenol. Part of the compound is excreted unchanged in the urine.

During the 1914-1918 war, in France, where dinitrophenol was manufactured in large quantities for explosive compositions, cases of poisoning among the workers, including fatal cases, were frequent, e.g. within 3 months 277 fatal cases occurred in a factory with a relatively large scale of production. Experience has shown that most of the cases are caused by impure dinitrophenol. The reason for this is, however, not clear since the impurities commonly present in the product are less poisonous than 2,4-dinitrophenol itself.

Workers in the dinitrophenol plant should be protected in the usual way (i.e. gloves, respirators, change of clothes, bath, etc.). Selection of workers handling dinitrophenol is also recommended since it has been shown that a great many people are resistant to its toxic effects, Selection is based on 15 days' medical observation of each new worker in the dinitrophenol plant, in particular in the analysis of the urine every other day. A test for the presence of aminonitrophenols is particularly importance. Usually Derrien's reaction [33] is used. According to Lazarev [31], the reaction comprises acidification of the urine with 10% sulphuric acid and diazotization with sodium nitrite, followed by shaking up the prepared solution with an ammoniacal solution of β– naphthol. If a red colour appears it indicates the presence of 4-amino-2-nitrophenol in the urine, while a violet shade is evidence for the presence of 2-amino-4-nitrophenol.

If Derrien's test is positive, the worker should be examined every day. If after 5-6 days the reaction is still positive, the worker must be barred from handling dinitrophenol. If the test is negative for 15 days or becomes negative by the end of this period, the worker may carry on with his job. Medical examination should be repeated from time to time.

In the U.S.S.R. industrial hygiene in dinitrophenol plants is determined by NKT regulation No. 211, dated 16. June 1930 and also by the U.S.S.R. Ministry of Health, Instruction No. 443, dated 17. June 1949. The regulations apply chiefly to the safe handling of dinitrophenol when used as a material for impregnating railway sleepers.

PRINCIPLES OF PREPARATION OF NITROPHENOLS

There are several methods of nitrophenol preparation:

(1) nitration of phenols;
(2) hydrolysis of chloronitro derivatives of aromatic compounds;

(3) oxidation of nitrosophenols;

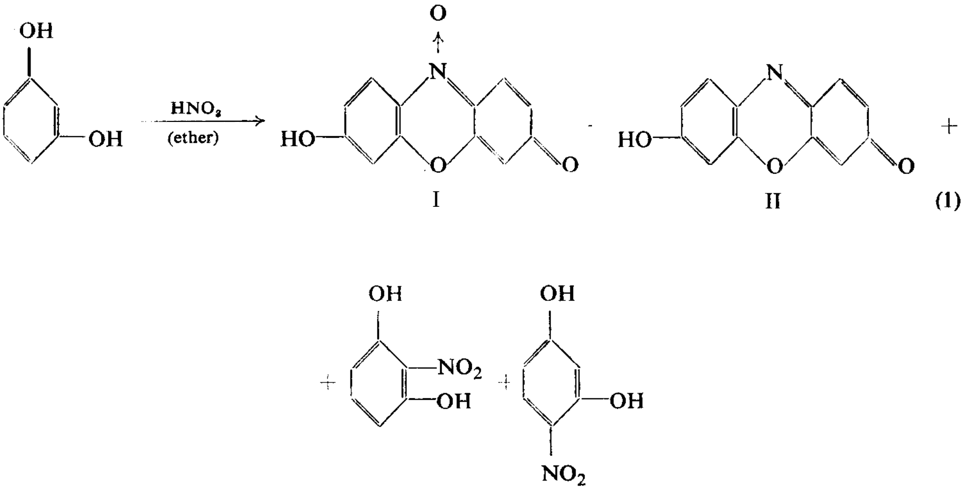
(4) nitration of benzene or other aromatic hydrocarbons with nitric acid in the presence of mercury salts (Wolffenstein and Bötters's [23] method, pp. 110, 520)

In industrial practice methods (1) to (3) are applied, the choice depending on the product which is to be prepared, on economic considerations, etc.

Nitration of phenol. The process is effected in two stages. The first is the sulphonation of the phenol, followed by acting with nitric acid on a solution of phenolsulphonic acid in sulphuric acid. In the latter process the sulpho groups are replaced by nitro groups (p. 501). This indirect procedure has to be adopted because the direct action of nitric acid on phenol yields undesirable by-products, sometimes brightly coloured, which contaminate the principal product.

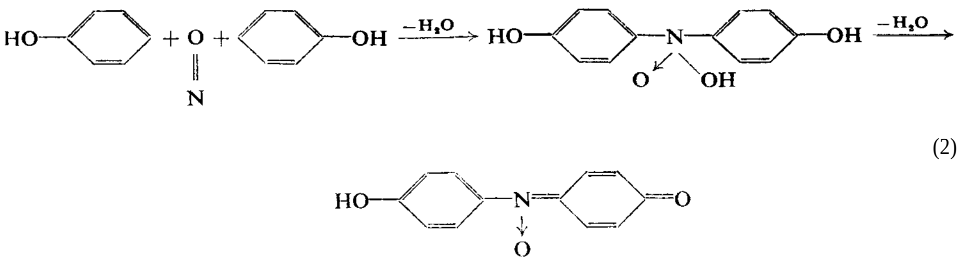
The reaction of substitution of the sulpho groups by nitro groups should be absolutely complete. If not, the nitrophenolsulphonic acids which, due to the presence of one or more sulpho groups, are water soluble, will remainin the spent acid and in the washings from nitrophenol purification.

The direct action of nitric acid on phenol has been the subject of investigation by a number of workers. Thus, Wesselsky [34] succeeded in isolating a dark coloured substance by treating resorcinol in ether solution with fuming nitric acid. Brunner and Kramer [35] assumed that the following products, having a phenoxazine ring, were formed: resazurin (I) and resorufin (II) along with nitro derivatives of resorcinol :



I II (1)

The reaction of nitric acid with phenols (including resorcinol) has been fully investigated by K. H. Meyer and Elbers [36]. They isolated a reddish-brown product to which they assigned the indophenol N-oxide structure (III). The compound can be, formed directly from phenol and nitric acid, according to the scheme:

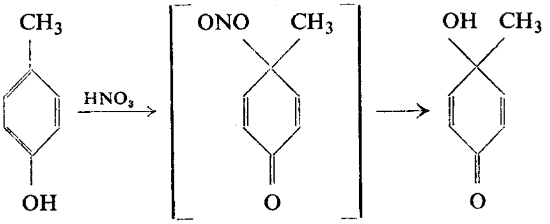


(2)

III

The direct formation of styphnic acid from resorcinol and nitric acid may also be explained by this series of reactions.

Earlier, Auwers [37] expressed the opinion that phenols when reacted with nitric acid, could yield dark coloured quinols, e.g.:



"Nitroketone"

(3)

Hydrolysis of chloronitro compounds. The chlorine atom in chlorobenzene and in its homologues becomes reactive after one or more nitro groups have been introduced into the ring. This is used widely in the preparation of nitrophenols and their ethers. The preparation of dinitrophenol, dinitroanisole and dinitrophenetole may serve as a classical example (see Chapter XVI).

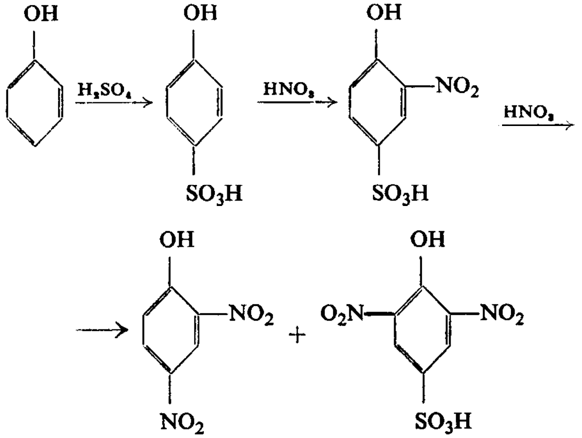
Oxidation of nitrosophenols. This method is applied when fewer nitro groups are to be introduced on the ring than those obtained by way of nitration. It is also applied when a pure product, free from its isomers, is to be prepared, e.g. *p*- nitrophenol from phenol. Direct nitration of phenol yields a mixture of the *o*- and *p*- isomers, dinitrophenol being readily formed as a by-product. Similarly dinitroresorcinol may be obtained by oxidation of dinitrosoresorcinol (p. 537).

MANUFACTURE OF DINITROPHENOL BY DIRECT NITRATION

Reverdin and de la Harpe's method [22]

This method consists in the sulphonation of phenol to phenolsulphonic acid which, on heating with nitric acid, is converted into dinitrophenol. In addition some 2,6-dinitrophenolsulphonic acid is also formed. As the latter remains in solution the yield of dinitrophenol is lower than the calculated one.

According to Marqueyrol and Lorriette [38], the reaction proceeds as follows:



(4)

100 parts of phenol are added to 400 parts of sulphuric acid (sp. gr. 1.84) heated to 110°C, then the whole is heated for 3 hr to bring it to a temperature of 130-140°C. The solution is then cooled to room temperature and 1375 parts of nitric acid (sp. gr. 1.20) are added gradually, the temperature being maintained at 45-50°C.

The mixture is left at room temperature for 24 hr, then heated gradually to about 90°C. After cooling, 2,4-dinitrophenol is filtered off, dinitrophenolsulphonic and picric acids remaining in the filtrate.

Seyewetz's method [38a]

Two modifications of this method are known. In one of them, applied at the St. Fons Factory in France, between 1915-1918, sodium nitrate is used for the nitration of phenol, and the other method utilizes dilute nitric acid.

Nitration with sodium nitrate is effected as follows. To a stoneware vessel, sodium nitrate (195 kg), water (300 kg) and sulphuric acid of sp. gr. 1.84 (240 kg) are added successively. The temperature rise brought about by mixing the sulphuric acid with water results in the complete dissolution of sodium nitrate. After all the reactants have been introduced, the temperature of the solution is about 53°C. This is the temperature required for the initiation of the nitration reaction. If the temperature is lower, it should be raised to 53°C by introducing live steam.

A solution of 25 kg of phenol in 40 kg of water heated to 26°C is poured in which takes about 4 min. During this period the temperature should not be allowed to exceed 80°C. If it does some cold water should be added. For the first 15-20 min the reaction proceeds rather violently. It is accompanied by the evolution of large quantities of nitrogen oxides.

After 60-75 min, when nitration has come to an end, water should be added to bring the temperature down to 70°C and to reduce the solubility of dinitrophenol in the spent acid.

The dinitrophenol rises to the surface of the liquid and may be skimmed off by means of a small aluminium sieve. It is then washed in wooden vats and separated on a vacuum filter.

From 100 kg of phenol 140 kg of the dark red product is obtained, which is 76% of the theoretical yield. The crude product melts at 102-103°C.

Another modification of the Seyewetz method (applied also at St. Forts 1915-18) is to use dilute nitric acid for the nitration, the process being carried out as follows. A vessel of acid resistant bricks (2 m^3 capacity) is charged with 1500 kg of 26% nitric acid (6 moles) heated to 20-30°C. An emulsion of 100 kg of phenol and 50 kg of water heated to 55-60°C is then introduced into the acid, which takes about 8-10 min.

While this is being done and during the next operations the nitrator contents are agitated by compressed air which enters through 4 pipes. During the mixing of the reactants the temperature rises to 60°C and, after 15 min from the beginning of the reaction, to 80°C. Should it rise higher than this, cold water must be added and the flow of compressed air stopped until the temperature falls again to 80°C. When it has stopped rising, i.e. when nitration has been completed, which usually requires 45 min, air is blown through the reaction mixture until the temperature goes down to 40°C. This takes about 12 hr. The dinitrophenol formed is either skimmed off from the surface of the mixture by means of a sieve or filtered off on a vacuum filter.

100 kg of phenol yields 155 kg of yellowish-orange coloured dinitrophenol, which equals 80% of the theoretical yield. The melting point of the product ranges between 101.5° and 105°C.

Nitration by this method has also been carried out in nitrators of smaller capacity for batches of 18 kg of phenol and 155 kg of 26% nitric acid. Here the temperature may be allowed to rise to 90-92°C. The yield and the purity of the product obtained are as in the above processes.

The spent acid separated from dinitrophenol contains:

HNO_3	11-12%
HNO_2	0.02-0.03%
oxalic acid	1.5%
dinitrophenol	0.4-0.5%

It is used as a spray in towers for the recovery of the nitrogen oxides evolving during the nitration of phenol to dinitrophenol. As a result of this operation the HNO_3 content in the acid rises to 19-20%.

A part of this acid is mixed with concentrated nitric acid (sp. gr. 1.40-1.50) to obtain the 26% acid to be used for nitration again. The rest is transferred to a distillation unit for concentration.

Purification of dinitrophenol

The product prepared by the above methods usually contains:

2,4-dinitiophenol	88-89%
2,6-dinitrophenol	3 4%
p- nitrophenol	0-4%
picric acid	3-5%

Since liquid impurities may produce exudates in explosive compositions, to avoid this the crude product should be purified. For a preliminary washing, a dilute (2%) solution of sodium carbonate may be used. Picric acid reacts with the carbonate which then goes into solutions as sodium picrate. Instead of sodium carbonate milk of lime or calcium hydrogen carbonate may be used.

Desvergnes describes the purification process used in various plants as follows. A wooden double-bottomed vat of 650 1. capacity is charged with 350 kg of dinitrophenol, which is stirred with 200 1. of a 3% solution of calcium hydrogen carbonate at a temperature of 70°C. The contents of the vat are allowed to remain at rest for 1 hr, then the aqueous solution is decanted and the operation is repeated with a fresh solution of calcium hydrogen carbonate. Then the purified product is washed with cold water. The melting point of dinitrophenol obtained is about 105.5%

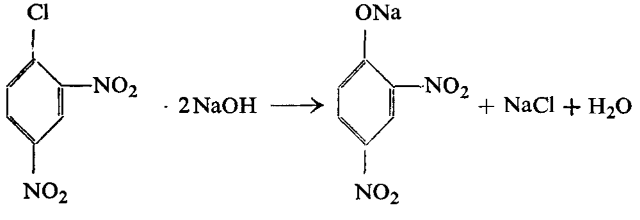
A product of still higher purity may be prepared by washing with sulphuric acid. 100 parts of dinitrophenol and 120 parts of sulphuric acid (sp. gr. 1.84) are agitated for 12 hr at room temperature. Then the sulphuric acid is filtered off and the dinitrophenol is washed with a small quantity of fresh sulphuric acid and finally several times with water. In this way the melting point of the product can be raised to 108.5°C.

The compounds dissolved both in the spent calcium hydrogen carbonate solutions and in the sulphuric acid, such as mononitrophenols, dinitrophenols and picric acid, may be recovered by precipitation: from the calcium hydrogen carbonate solution by acidification, and from sulphuric acid solution by dilution with water.

The product thus obtained may be blended with dinitrophenol for the preparation of picric acid.

MANUFACTURE OF DINITROPHENOL BY CHLORODINITROBENZENE HYDROLYSIS

In industrial practice, hydrolysis of chlorodinitrobenzene is now the main method of producing dinitrophenol. The reaction proceeds as follows:



(5)

From the resulting dinitrophenate, dinitrophenol is obtained by acidification.

Russian method

The following method (after Lebedev [39]) was applied in Russia (1915-1916) and later in the U.S.S.R.

The hydrolysis process is effected in a wrought iron reactor of 4 m^3 capacity, equipped with a cooling jacket, a heating coil and a stirrer. The reactor is charged with water heated to 70°C then a 42% solution of NaOH is run in from a measuring tank in such a quantity as to obtain 2130 1. of a 7% NaOH solution (5% in excess of the calculated quantity). Then 360 kg of molten chlorodinitrobenzene at a temperature of 70-75°C is added over a period of 10 min. The temperature rises to 100°C. When the vigorous stage of the reaction has subsided the mixture is heated to 100-110°C for 1 hr.

Towards the end of this operation a sample should be taken and diluted with water to test whether hydrolysis is complete. A completely hydrolysed product will go into solution. Otherwise chlorodinitrobenzene will collect as an oil.

According to Lebedev, the hydrolysis process requires 2 hr 20 min, including the following schedule of operations:

charging with water	15 min
charging with sodium hydroxide solution	10
analysis of the solution	10
introducing chlorodinitrobenzene	10
heating at 100-110°C	60
analysis	10
pumping out the reactor contents	15
blowing out the pipes	10
Total	2hr20min

As a result of the hydrolysis process a sodium dinitrophenate solution is formed. To obtain'dinitrophenol this solution is transferred to a wooden vat containing 30% sulphuric acid in a quantity exceeding the calculated amount by 5%. Spent acid from the nitration, diluted with water to the required concentration, may be used.

After testing the suspension for complete acidification (with Congo red test paper), it is transferred by compressed air, while still hot (70°C), to a cloth-lined vacuum filter. The dinitrophenol is washed on the filter 3-4 times with water until the acid content in the washings is reduced to 0.01%. Then it is centrifuged in copper centrifuges to a moisture content of 12-15%.

According to Lebedev, the time required for the conversion of dinitrophenate to dinitrophenol is 60 min individual operations requiring:

charging the reactor with acid	10 min
introducing the dinitrophenate	15
stirring	15
analysis	10
draining off on the filter	10
Total	60 min

The product is then dried to reduce the moisture content to 1-2%.

From 100 kg of chlorodinitrobenzene roughly 82 kg of dinitrophenol is obtained, the yield being 91% of the theoretical.

German method.

The German process of hydrolysis (applied at Griesheim) comprises the following operations :

1300 kg of chlorodinitrobenzene and 7500 1. of water (90°C) are charged into the reactor. To this mixture, 1500 kg of a 35% solution of NaOH is introduced with stirring over a period of 4 hr, the temperature being maintained within 95-100°C. If a test for a complete hydrolysis is satisfactory, the solution is introduced with stirring to about 780 l. of hydrochloric acid (30%). The mixture is then cooled to 30°C and the separated dinitrophenol is filtered off on a vacuum filter, washed with cold water, dried and ground.

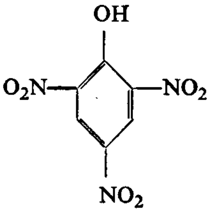
Dry dinitrophenol prepared by hydrolysis of chlorodinitrobenzene usually melts at 110-111°C. Its impurities come from the chlorodinitrobenzene, which may contain unhydrolysed admixtures (such as *m*- chloronitrobenzene, dichlorodinitrobenzene isomers, *m*- dinitrobenzene).

Dinitrophenol from chlorodinitrobenzene, to be used for the preparation of picric acid, should satisfy the following specifications (Lebedev [39])

melting point (determined as setting point)	not below 109°C
inorganic matter (ash)	max. 0.2%
iron content in ash	trace
lead content in ash	none
dinitrophenates and picrates	none
acid content (calculated on H_2SO_4)	no more than 0.1%
metal chlorides	no more than 0.5%
chlorodinitrobenzene	no more than 0.5%
dinitrophenol	not less than 96%

PICRIC ACID

Picric acid is the most important of the trinitro derivatives of phenol. The commercial product for military purposes is 2,4,6-trinitrophenol of high purity:



As an explosive it is known under various names: Ekrasit (Austria), Mélinite (France), Granatfiillung 1888-abbrev. Grf 88 (for shells), Sprengkörper 88 (for field engineer cartridges) (Germany), Pertite (Italy), Shimoza (Japan), TNF (Poland), Picrinit (Spain), Lyddit (United Kingdom), Melinit (U.S.S.R.).

PHYSICAL PROPERTIES

Picric acid crystallizes in colourless or yellowish needles or lamellae of the orthorhombic-bipyramidal system. The melting point of picric acid is 122.5°C and its setting point 121.3°C Kast [40]). When heated to a temperature above its melting point it begins to sublime.

Specifications for commercial picric acid differ in various countries but the setting point should never be lower than 120°C.

Solubilty. Doliriski [41] gave the following figures for the solubility of picric acid in water at various temperatures (Table 109) (see also Findlay [41a]).

TABLE 109

SOLUBILITY OF PICRIC ACID IN WATER

Temperature °C	Content of picric acid, g	
	in 100 g of the solution	in 100 g of the solvent
0	0.67	0.68
10	0.80	0.81
20	1.10	1.11
30	1.38	1.40
40	1.75	1.78
50	2.15	2.19
60	2.77	2.81
70	3.35	3.47
80	4.22	4.41
90	5.44	5.72
100	6.75	7.24

The solubility of picric acid in sulphuric acid varies with the concentration of the latter. It is highest for concentrated acid and lowest in 18-20% acid. This can be seen from Table 110 [41b].

TABLE 110

SOLUBILITY OF PICRIC ACID IN H_2SO_4

H_2SO_4 CONCENTRATION %	PICRIC ACID CONTENT IN 100 G OF THE SOLUTION		
	18°C	50°C	80°C
0	1.184	2.399	4.541
2.3	0.230	0.692	1.940
4.7	0.142	0.368	1.251
10.0	0.091	0.265	0.727
18.0	0.079	0.214	0.561
25.5	0.092	0.230	0.587
50.5	0.429	0.645	1.104
69.7	0.928	1.424	2.203
87.9	2.461	5.826	7.610
97.4	7.531	12.785	24.020
100.0	10.180	16.230	25.860

In Table 111 data for the solubility of picric acid in dilute nitric acid at 25°C are given.

TABLE 111

SOLUBILITY OF PICRIC ACID IN NITRIC ACID (DRUCKER [42])

HNO_3 concentration mole/l.	Picric acid concentration mole/l.
0.00000	0.05327
0.00635	0.05095
0.02564	0.04281
0.05166	0.03493
0.0872	0.02604

In organic solvents picric acid dissolves more readily than in water as Table 112 shows.

TABLE 112

SOLUBILITY OF PICRIC ACID IN ORGANIC SOLVENTS

Solvent	Temperature °C	Amount of the solvent	Amount of picric acid
Ethyl alcohol	25	100 parts	7.452 parts
Ethyl ether	13	100 ,,	1.08 ,,
Ethyl ether (water saturated)	13	100 ,,	4.00 ,,
Benzene	6	100 ,,	3.50 ,,
Benzene	15	100	5.9 ,,
Toluene	20	100 ml solution	12.0 g
Amyl alcohol	20	100 ,, ,,	1.755 g

The solubility of picric acid in aqueous solutions of methyl-, ethyl-, isopropyl- and n-propyl alcohols, as well as of acetone has also been determined (Duff and Bills [43]), Table 113.

TABLE 113

SOLUBILITY OF PICRIC ACID IN AQUEOUS SOLUTIONS OF ORGANIC SOLVENTS

Percentage of the organic component of the solution	Grammes of picric acid per 100 g of the solvent at 25°C		
	Methyl alcohol	Ethyl alcohol	Acetone
0	1.3	1.3	1.3
30	2.4	3.1	9.5
60	7.1	10.5	46.7
80	-	13.8	87.8
81		13.8	-
85	-	13.2	
90	16.0	12.3	
100	21.1	8.0	43

In Table 114 partition coefficient of picric acid between two liquid phases arc tabulated for water-toluene and water-ether (Sisley [44]).

TABLE 114

PARTITION COEFFICIENTS OF PICRIC ACID BETWEEN TWO LIQUID PHASES

Concentration of picric acid g/l. of the solution	Solution volumes water-toluene	Grammes of picric acid in 100 ml of the solution		Partition coefficient
		water	toluene	
10g	100 : 100	0.275	0.725	1 : 2.63
3		0.125	0.175	1 : 1.24
1		0.062	0.038	1 : 0.63
0.1		0.010	-	-
-	water-ether	water	ether	-
10g	106 : 96	0.374 -	0.670	1 : 1.79
1		0.085	0.011	1 : 0.129
0.1		0.0105	0.00011	1 : 0.010
0.01		0.000952	-	-

Similar values have been obtained by Sisley for amyl alcohol and water.

Mindowicz [45] has also studied the partition coefficient (k) of picric acid between water and various organic solvents. Table 115 summarizes his results expressed in terms of the Nemst [46] and Shilov [47] equation

$$k = \frac{C_1^n}{C_2}$$

where n is an exponent independent on the temperature, C_1 and C_2 are concentrations.

TABLE 115

Temperature °C	Benzene-water N = 1.727 $k \times 10^2$	Temperature °C	Toluene-water n = 1.667 $k \times 10^2$	Chlorobenzene-water n = 1.674 $k \times 10^2$
10	1.563	20	1.875	2.421
30	1.892	40	2.323	2.965
50	2.275	60	2.884	3.548
70	2.673	80	3.532	4.416

As may be seen from the above data, from concentrated solutions picric acid can be extracted by an organic solvent, while in the case of dilute solutions it remains in the aqueous phase.

Hygroscopicity. Picric acid is only slightly hygroscopic. Marsh [48] found that picric acid, in contact with water-saturated air at 32°C for 48 hr absorbed 0.37% of water. If, however, the picric acid contained 0.05% of SO_3, as sulphates or sulphuric acid, it absorbed 1.9% of water under the same conditions, while at 0.16% SO_3, ca. 5% of water was taken up.

Density. The specific gravity of picric acid is 1.813, and that of molten product 1.589 at 124°C and 1.513 at 170°C. The apparent weight of the crystalline substance is 0.9-l .0.

The density of pressed picric acid depends on the pressure applied (Dautriche [49]).

Pressure, kg/cm^2	Average density, g/cm^3
275	1.315
685	1.480
1375	1.614
2060	1.672
2750	1.714
3435	1.731
4125	1.740

Kast found the density at 4000 kg/cm^2 to be 1.63 g/cm^3 and at 4500 kg/cm^2 1.74 g/cm^3. In practice, on account of the risk involved, pressures higher than 2000 kg/cm^2 are seldom applied.

Molten picric acid solidifies, when cooled slowly, to a substance of an average density of 1.66 g/cm^3. On rapid cooling a density of 1.70 g/cm^3 may be attained (Kast [40]).

THERMOCHEMICAL PROPERTIES

The specific heat of picric acid, as measured by C. A. Taylor and Rinkenbach [50], is:

Temperature, °C	Specific heat, Cal/g
0	0.234
20	0.250
40	0.266
60	0.282
80	0.300
100	0.318
120	0.337

The heat of solidification of picric acid is, according to Gamer and Abemethy [51], 4.30 Cal/mole. Rinkenbach [52] reported it to be 4.66 Cal/mole.

Heat of combustion and heat of formation of picric acid and of other nitrophenols. The heat of combustion of picric acid at constant volume (corrected for the nitric acid formed) is 621.2 kcal/mole and the heat of formation is 63.3 kcal/mole or 276.4 kcal/kg (Gamer and Abemethy [51]).

According to other authors, the heat of formation of picric acid ranges from 46.8-50.9 kcal/mole.

Garner and Abemethy have given the following values for heats of formation of other nitrophenols:

o- nitrophenol	+63.4 kcal/mole
p- nitrophenol	+66.3 kcal/mole
2,4-dinitrophenol	+69.9 kcal/mole

Heat of nitration. The heat of conversion of phenol into picric acid has been calculated on the basis of the above data (see diagram on. p. 261):

phenol - *o*- and *p*- nitrophenol	+35.0 kcal/mole
o- and *p*- nitrophenol - 2,4-dinitrophenol	+24.5 keel/mole
2,4-dinitrophenol - picric acid	+ 12.9 keel /mole
	+72.4 kcal/mole

Heat of explosion - see below, under explosive properties.

CHEMICAL PROPERTIES

An outstanding feature of picric acid is its acidic character. It readily forms picrates (they are dealt with in a special chapter, p. 525) and esters, which are phenol ethers, e.g. trinitroanisole (p. 545), trinitrophinetole (p. 548).

Like other polynitroaromatic compounds, picric acid readily forms addition products with aromatic hydrocarbons. This behaviour is especially pronounced in picric acid. Addition compounds with phenols, aromatic ketones, acids and even with nitro compounds are also known.

Here are some of the addition compounds formed by picric acid combined with other substances in molecular proportion of 1: 1:

Second component	Melting points, °C
Anthracene	ca. 141 (non uniform melting)
Benzene	84
Fluorene	a4
Naphthalene	150
Phenol	85
Resorcinol	100
Pyrocatechol	124
Guaiacol	88.6
o- Cresol	89.8
p -Cresol	ca. 65.6 (non uniform melting)
Thymol	96.8
β -Naphthol	145.8
Triphenylcarbinol	138.5
Acetophenone	ca. 50 (non uniform melting)
Benzophenone	27 (readily dissociates)
Cinnamic acid	106.5

With *m*- cresol, picric acid forms a compound (m. p. 61.6°C) containing the two constituents in the mol. proportions of 1: 2. With salicylic aldehyde it forms two non-uniformly melting compounds in the proportions of 1: 1 (m. p. - 55°C) and 1: 2 (m. p. - 35°C). With *m*- hydroxybenzoic aldehyde, picric acid forms a series of compounds containing the constituents in proportions from 1: 1 to 1: 5, dissociating at 90°C on melting.

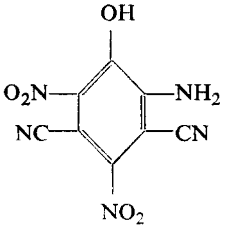
Jefremov [53] was able to identify the following compounds in molecular proportion 1: 1 by means of thermal analysis:

Constituents	M. p., °C
Picric acid with α– benzylnaphthalene	97.0
α– chloronaphthalene	125.7
α– bromonaphthalene	35.0
α– nitronaphthalene	about 55 (non uniform melting)
β– chloronaphthalene	81.5
acenaphthene	160.8
phenanthrene	132.8
retene	120.9

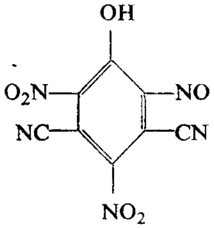
With amines, picric acid yields picrates. Some of them such as quinine or quinoline picrates, are very difficult to dissolve in water and this may be utilized for quantitative determination of picric acid or these bases.

The composition of various practically applied eutectics given by picric acid is discussed in the chapter on fusible explosive compositions in Vol. III.

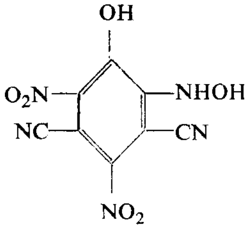
For the qualitative determination of picric acid a characteristic reaction with potassium cyanide may be utilized. When an aqueous solution of the two compounds is boiled a red-coloured potassium salt of "isopurpuric acid" is formed. Formula I was assigned to this compound by Nietzki and Petri [54], while Borsche and Böcker [55] suggested the formulae IIa or IIb.



I



IIa



IIb

However, Lobry de Bruyn [56] demonstrated that "isopurpuric acid" is a mixture of compounds in which one of the nitro groups has been reduced to an azoxy-, azo-, or nitroso group, while the cyano groups have entered the ring, replacing a hydrogen atom or a nitro group.

Picric acid is not resistant to strong oxidizing agents. It is oxidized by boiling nitric acid to yield oxalic acid. Boiling with ammonium persulphate results in a complete oxidation, according to the equation:

$$C_6H_2(NO_2)_3OH \xrightarrow{(NH_4)_2S_2O_8} CO_2 + HNO_3 + HCN \qquad (6)$$

When mildly reduced, for example with sodium sulphide or hydrosulphite or with ferrous sulphate, picric acid is converted into picramic acid, a very useful intermediate in the dyestuffs industry and a starting material for the preparation of dinitrodiazophenol, a primary explosive (Vol. III). Stronger reduction may lead to the formation of triaminophenol.

Violent boiling of picric acid with a concentrated solution of sodium hydroxide may bring about decomposition of the former:

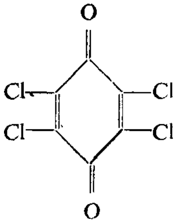
$$C_6H_2(NO_2)_3OH \xrightarrow{NaOH} NH_3 + HCN + HNO_2 \qquad (7)$$

Hypochlorites decompose picric acid, which undergoes chlorination to form chloropicrin. The reaction is carried out with calcium hypochlorite. The calcium hydroxide formed in the reaction neutralizes the hydrochloric acid formed. This is a commercial method of preparation of chloropicrin.

$$C_6H_2(NO_2)_3OH + 11HOCl \xrightarrow{85°C} 3\ CCl_3.NO_2 + 3CO_2 + 6H_2O + 2HCl \qquad (8)$$

When reacted with chlorine, aqua regia or potassium chlorate in the presence of hydrochloric acid, picric acid yields chloranil along with chloropicrin:

$$C_6H_2(NO_2)_3OH \xrightarrow{Cl_2} CCl_3.NO_2 +$$



(9)

If the reaction is stopped just when the formation of chloropicrin starts. the presence of 6-chloro-2,4- and 4-chloro-2,6-dinitrophenols can be also detected along with it.

When heated to a temperature above its melting point, picric acid can react with sulphur. Addition of sulphur lowers the ignition temperature of picric acid (see below).

Action of heat. According to Kast [40], picric acid, when heated to 160°C begins to decompose slightly and an insignificant evolution of gases occurs. At 200-210°C the evolution of gases is stronger and heating at 260°C for half an hour results in explosion. The explosion may not occur below temperatures of 300-310°C when a small quantity of the acid is heated more rapidly.

Micewicz and Majkowski [54] reported that the initiation temperature of picric acid is 243-288°C on slow heating, while it rises to 337-346°C on rapid heating.

T. Urbanski and Pillich [58] found that picric acid with a 5% addition of sulphur exploded at 251°C and with 10% at 247°C whereas pure picric acid exploded at 330°C.

Picric acid melts prior to burning giving a sooty flame. The heat of fusion lowers the temperature of the layer adjacent to the burning one, so the substance may either stop burning or continue to burn only gently. In large quantities, burning of picric acid may proceed slowly, especially when it is spread over a larger area. If, however, the product is concentrated on a small area or when it is in a confined space, explosion may occur. Burning the product containing metal picrates may result in explosion. Similarly a potential danger exists when burning picric acid is in contact with metals, since in the molten state it forms picrates which may initiate explosion. This depends largely on the metal: lead, iron, copper should be considered as particularly dangerous.

It was unexpected to find that picric acid does not decompose when exposed to sunlight. Ciamician and Silber [59] found that an alcoholic solution of picric acid when exposed to sun rays for many months does not show any change in its properties. The fact that picric acid turns slightly yellowish when exposed to light may be ascribed, according to Stepanov [60], to the formation of traces of ammonium picrate on the irradiated area.

EXPLOSIVE PROPERTIES

Picric acid decomposes according to the equation (Kast [40]):

$$16C_6H_3O(NO_2)_3 = 32CO_2 + 40CO + 4CH_4 + 2H_2O + 3C_2H_2 + 3HCN + \\ + 4.5H_2 + 21.5N_2 + 2NH_4HCO_3 + 9C \qquad (10)$$

Its heat of explosion is 1000 kcal/kg, the volume of gases produced Ve = 675 l./kg and temperature t = 3230°C.

Schmidt [61] has derived a number of equations for the decomposition of picric acid at various densities. For example, at $\Delta = 1.39$ the equation derived for 1000 g (i.e. 4.36 moles) of the substance is:

$$4.36C_6H_3O(NO_2)_3 = 6.14CO_2 + 14.37CO + 3.94H_2O + 1.33H_2O + 0.16CH_4 + \\ - 0.07C_mH_n + 0.15HCN + 0.54NH_3 + 6.12N_2 + 5.1C \qquad (11)$$

The heat of explosion = 960 kcal/kg, the volume of gases V_0 = 737 l./kg, t = 3530°C.

R. Robertson and Garner [62] found the heat of explosion to be 910-935 kcal/kg, and the volume of gases V. = 725 l./kg.

The impact sensitivity of picric acid is higher than that of TNT. In many countries the value of 100 has been taken for the sensitiveness of picric acid, sensitiveness of other explosives being expressed in terms of that of picric acid. Thus the value for tetryl will be 70 and that for TNT - 115-275, according to various authors.

The sensitiveness of picric acid to friction is low, but slightly higher than that of TNT.

The expansion produced in the lead block, as reported by various authors is 250-350 ml. Taking the value for TNT as 100, that for picric acid will be 102-120.

In the mortar test picric acid gives a value of 110-120, and in the sand test 104, relative to TNT = 100.

The rate of detonation of picric acid, as measured by various workers, is given in round numbers in Table 116.

TABLE 116

RATE OF DETONATION OF PICRIC ACID (m/sec)

Density	According to Kast* [70]	According to Friedrich**[63]	According to Roth***[64]
0.7		4020	
0.9		4635	-
1.1		-	4560
1.23	-	-	5430
1.30	5980	6190	-
1.32	-	-	-
1.41	6465	-	6940
1.47	-	-	-
1.49	6885	-	--
1.50	7110	-	
1.54		6930	-
1.56	-	-	7504

* For unconfined charges of 21 mm diameter and a 1 g detonator.

** In a metal pipe 10-15 mm in diameter.

*** In a bakelite pipe 4.5-8.2 mm in diameter.

Cybulski [65] found the rate to be 7260 m/sec at a density of 1.7g/cm^3. As the highest rate of detonation values from 7100 to 7500 m/sec are accepted.

TOXICITY

In the unanimous opinion of a number of authors picric acid is more toxic than the nitro derivatives of toluene, xylene or naphthalene. It is, however, much less toxic than nitro derivatives of benzene.

According to Lazarev [31], the single lethal dose for a cat is 0.5 g per kg of its weight. A daily dose of 0.05-0.2 g per kg causes death after 9 days.

Saladini [66] pointed out that small doses of picric acid cause no ill-effects in man.

Koelsch [67], from observation of 1200 workers engaged in handling picric acid, described the symptoms of poisoning as follows: a yellow colouration of unprotected parts of the skin and hair, irritation of the mucous membranes and of the upper parts of the respiratory tract and the digestive tract. In addition, a constant bitter taste and a lack of appetite appear. Cases of acute or chronic poisonings were not observed.

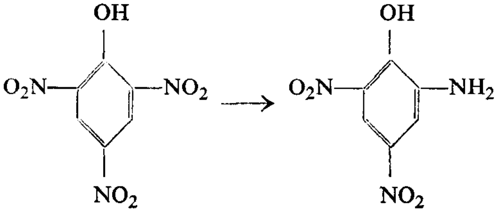
Similar results of observations carried out at the Institute of Occupational Diseases in Leningrad were reported by Matussevich [68]. He also mentioned the nails turning yellow.

Lebedev [39] described the signs of mild poisoning by picric acid as follows: yellow coloration of the skin, the teeth, the saliva and nasal mucus, bitter taste, lack of appetite, occasionally nausea and vomiting. A decrease in the acidity of the gastric juice is also possible, as well as conjunctivities, irritation of the upper respiratory tract and of the middle ear. Instances of perforation of the nasal wall are also known. In more severe cases an intense headache appears, as well as abnormally high temperature, dizziness, spasms, disturbances of the digestive organs, anaemia and more rarely kidney trouble. In women menstrual disturbances may occur. More or less severe eczema may also appear.

According to Nawrocki and his co-workers [69], a concentration of picric acid in air amounting to 1-17.5 mg/m^3 may cause severe poisoning after six hours' exposure.

Koelsch [67] suggested the following protective measures when working with picric acid. Adequate ventilation to prevent the accumulation of picric acid dust, protective clothing including gloves and head coverings to cover as large an area of the skin as possible and washing the face and the hands and rinsing the mouth before meals. Taking meals in working quarters should be forbidden. Workers should be subjected to medical inspection at regular intervals.

Karplus [70] found that in man or in animals picric acid undergoes partial conversion into the more toxic picramic acid:



(12)

According to Ishiwara [71], after a 30 min action a 0.04% aqueous solution of picric acid exhibits bactericidal activity against typhoid bacteria, staphylococci, streptococci and gonococci.

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CHAPTER XIV

MANUFACTURE OF PICRIC ACID

PRINCIPLES OF MANUFACTURE

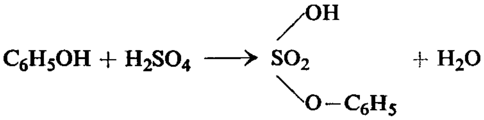
PICRIC acid is produced either by nitrating phenol or by nitrating dinitrophenol prepared by hydrolysis of chlorodinitrobenzene.

NITRATION OF PHENOL

The process is effected in two stages. Phenol is first sulphonated and then the sulphonation product is nitrated with nitric acid (p. 126).

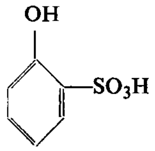
Two features of the process may justify its use. First of all, direct nitration of phenol with a nitrating mixture may lead to the formation of various by-products resulting from oxidation, condensation, resinification etc. (p. 480) which will contaminate the product and lower its yield. In addition, when two separate stages are used - sulphonation and nitration - it is possible to carry out the nitration without any excess of acids, so that the spent acids left after separation of the product may be discharged into the drainage system without further treatment which would increase production costs. This is of great importance, principally because the acids are not suitable for concentration as they contain picric acid. Picric acid is known to be rather volatile and may escape from sulphuric acid solutions if in the concentration process the H_2SO_4, content becomes higher than 72.5%. Picric acid vapours, after being condensed on metal parts of the equipment, may form picrates, for example, with lead or iron, which explode readily.

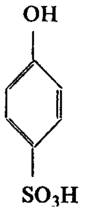
For the first stage of the process, i.e. sulphonation of phenol, sulphuric acid is used in some excess (4-4.5 moles of sulphuric acid per 1 mole of phenol). Initially a sulphuric acid ester is formed:



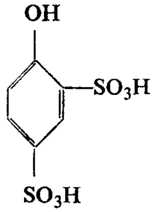
$$C_6H_5OH + H_2SO_4 \longrightarrow SO_2\begin{matrix}\diagup OH \\ \\ \diagdown O-C_6H_5\end{matrix} + H_2O \qquad (1)$$

which is later converted into a mixture of *o*- and *p*- phenolsulphonic acids:





At room temperature the conversion proceeds slowly, whereas it occurs rapidly on heating. The higher the temperature, the more *p*- isomers are formed. At 90-100°C phenoldisulphonic acid is also formed:



Its presence is advisable, as later it will facilitate the nitration process.

Marqueyrol and Loriette [1] investigated the process of phenol sulphonation with varying sulphuric acid concentration, time and temperature of sulphonation. Their results are presented below (Table 117).

TABLE 117

SULPHONATION OF PHENOL UNDER VARIOUS CONDITIONS

H_2SO_4 concentration, %		Per cent of phenol converted into disulphonic acid
92		62
93		66
94		71
96		82
97		91
100		100
Time of sulphonation with 93% H_2SO_4 at 100°C, min		
15		48
30		65
60		66
120		68
240		68.5
Sulphonation with 93% H_2SO_4, temperature °C	Sulphonation time, min	
75	30	51
75	60	59
150	15	50
150	30	66
150	60	66.5

Phenoltrisulphonic acid is formed only when using an excess of 20% oleum.

The second stage in the preparation of picric acid is the nitration of the phenolsulphonic acid obtained in the first stage of the process.

"Sulphophenol", which is the name of the starting material for the second stage, is a mixture of 1,4-phenolsulphonic and 1,2,4-phenoldisulphonic acids.

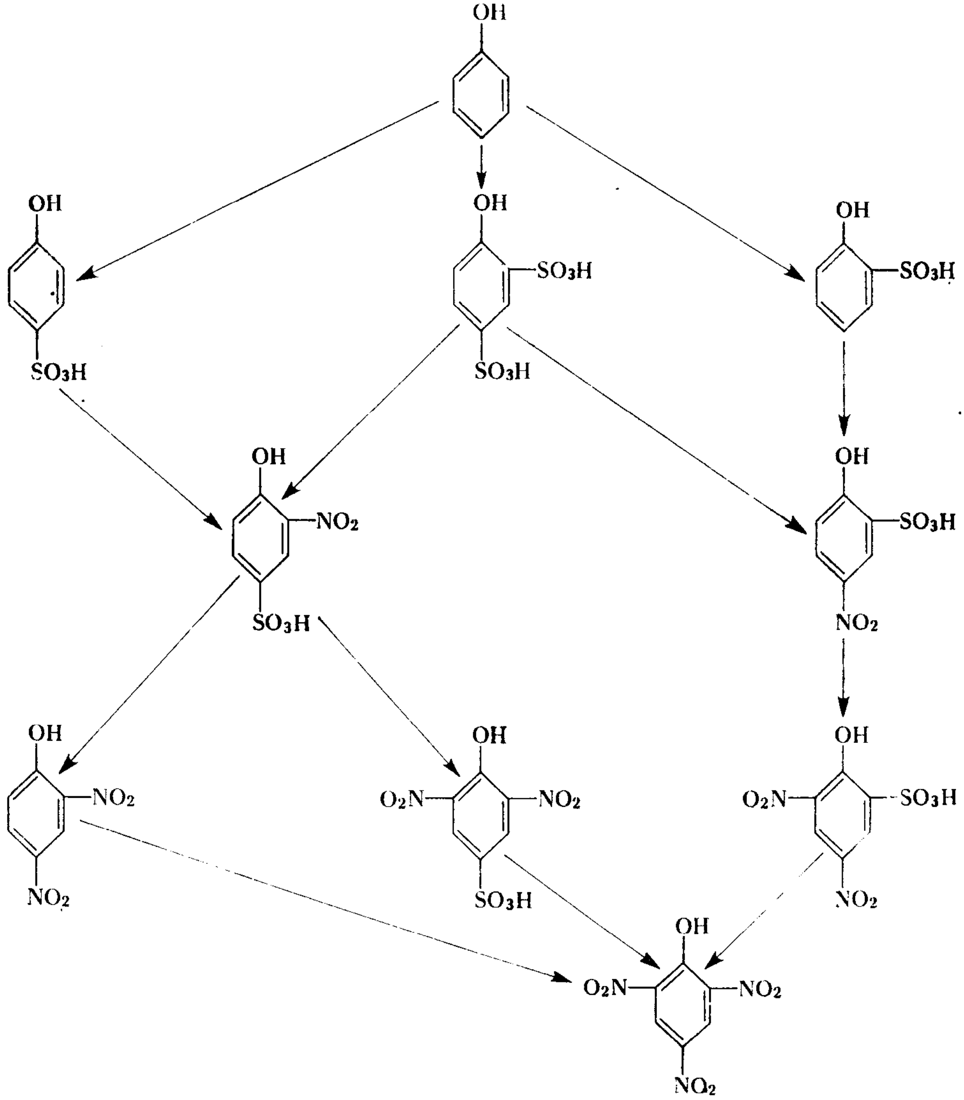
For the nitration the following nitrating agents may be used:

(a) dilute (44-65%) nitric acid;

(b) mixture of dilute nitric acid and sodium nitrate;

(c) concentrated nitric acid.

A schematic presentation of the reactions occurring in the process of preparation of picric acid acid via sulphonic acid is given below (Pascal [2]):



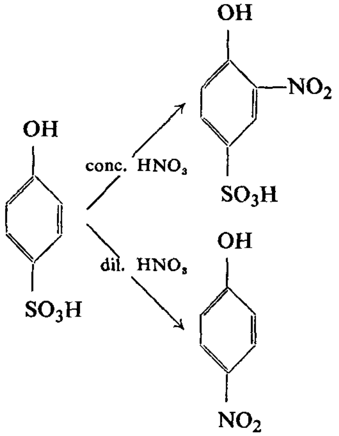
As this scheme indicates, phenolsulphonic acid is first nitrated to 2-nitro-4-sulphonic and 4-nitro-2-sulphonic acids. The former yields 2,4-dinitrophenol and 2,6-dinitro-4-sulphonic acid, and the latter 2,4-dinitro-6-sulphonic acid. All these dinitro compounds are finally converted into picric acid.

The introduction of nitro groups proceeds the more rapidly the more sulpho groups "sulphophenol" contains. The nitration of disulphonic acid is faster than the nitration of monosulphonic acid, but not so fast as the nitration of trisulphonic acid.

Thus, when heating 1-hydroxy-2,4,6-trisulphonic acid with 61% nitric acid at 110°C, picric acid is produced in a yield amounting to 90% of the theoretical (220 parts of picric acid per 100 parts of phenol), whereas from 1,2,4-phenoldisulphonic acid under analogous conditions, the yield of picric acid is 86% of the theoretical (208-210 parts of picric acid per 100 parts of phenol).

Moreover, it has been proved by Marqueyrol and Loriette [1] that the rate of formation of picric acid from 2,6-dinitro-4-sulphonic acid is higher than that from 2,4-dinitro-6-sulphonic acid. Since for the formation of both *p*- phenolsulphonic and 2,4-disulphonic acids high sulphonation temperatures are favourable, it is evident that efforts should be made to attain sulphonation temperature as high as possible. This is especially important if dilute nitric acid is to be used.

King [3] has shown that phenolsulphonic acid can be nitrated by the action of concentrated nitric acid to yield nitrophenolsulphonic acid. On the contrary, reaction with dilute nitric acid leads to the exchange of the sulphonic group by the nitro group:

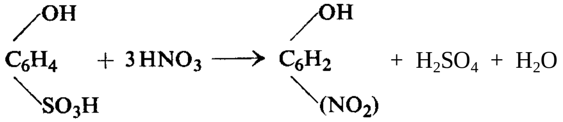


(2)

If sulphonation is carried out at a low temperature, nitric acid of higher concentration should be used or a higher temperature should be maintained during the nitration. The latter must, however, be kept within safety limits. Apart from this, higher temperatures naturally favour undesirable side reactions (e.g. oxidation).

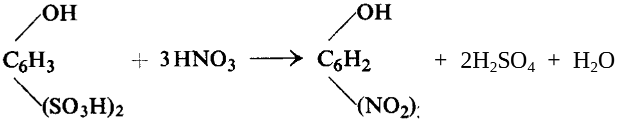
The reactions occurring in nitration with sodium nitrate are as follows:

$$NaNO_3 + H_2SO_4 \rightarrow NaHSO_4 + HNO_3 \qquad (3)$$



$$C_6H_4(OH)(SO_3H) + 3HNO_3 \longrightarrow C_6H_2(OH)(NO_2) + H_2SO_4 + H_2O \qquad (4)$$

Or



$$C_6H_3(OH)(SO_3H)_2 + 3HNO_3 \longrightarrow C_6H_2(OH)(NO_2)_3 + 2H_2SO_4 + H_2O \qquad (5)$$

The sulphuric acid formed in reactions (4) and (5) decomposes new portions of sodium nitrate in accordance with reaction (3).

The spent acid from the nitration of phenol by the methods described contains several by-products, among them : 2,4-dinitrophenol-6-sulphonic acid in the proportions of 22 parts per 100 parts of phenol used for the process, which corresponds to a 8% loss of the phenol, and oxalic acid in the proportion of 5-6 parts per 100 parts of phenol. These are the principal by-products that lower the yield of picric acid.

A certain amount of picric acid may be converted into its salts - undesirable products - which may be formed by the contact of picric acid either with metal parts ofthe plant or with certain salts (e.g. dissolved in the water used for washing the picric acid).

The theoretical yield of picric acid amounts to 243 parts of picric acid from 100 parts of phenol. Because of by-products formation, however, the actual yield hardly exceeds 200-205 parts (82-85%) of the theoretical. During World War I in France a yield of 175 parts of picric acid (72% of the theoretical) was reported.

It should, however, be remembered that commercial picric acid prepared by this method contains lower nitrated phenols. To obtain a chemically pure product, commercial picric acid should be subjected to additional nitration (Arundal, Davies and ICI Ltd. [4]).

NITRATION OF DINITROPHENOL

This is the most modern industrial method for the preparation of picric acid from chlorobenzene via chlorodinitrobenzene (for preparation of dinitrophenol from chlorodinitrobenzene, see p. 484). The nitration of dinitrophenol to picric acid is carried out by conventional methods, using nitrating mixtures containing some 0-5% of water.

The following three grades of purity of picric acid are specified in the U.S.S.R. standard, OST 3515 (Table 118).

TABLE 118

	Grades		
	I	II	III
General appearance	crystalline powder free from foreign matter		
Colour	light yellow		
Setting point, not less than, °C	119.5	119.5	119
Moisture and volatile matters, max.	0.5%	0.5%	0.5%
Insoluble in benzene, max.	0.2%	0.3%	1.0%
this includes :			
picrates	not present	trace	max. 0.03%
SiO_2, max.	0.05%	0.05%	0.1%
Sulphuric acid, max.	0.1%	0.2%	0.3%
Halogen	trace	trace	trace

Picric acid should be transported in wooden cases or barrels with thick walls 1.5 cm.

METHODS BASED ON PHENOL NITRATION

Raw materials. A high grade phenol should be used. The U.S.S.R. specifications of 1931, for example, require for nitration top grade phenol with a setting point not below 39°C. A small amount of moisture present, resulting in lowering the setting point to 37°C, does not prove harmful to the nitration process. The purity of the product should be tested by determining the setting point of a dry sample, which should lie within the above mentioned limits.

Nitration grade phenol should be completely soluble in water, giving a clear solution. Not more than 0.1% of non-volatile residue left after the evaporation of phenol, when heated on a steam bath, is permissible.

Acids used for the nitration of phenols should be free from any detectable quantity of lead.

NITRATION METHODS USING DILUTE NITRIC ACID OR MIXTURES OF NITRIC ACID AND SODIUM NITRATE

These are primitive methods (applied during 1914-1918 in Russia, France, Italy and Great Britain), which gained considerable popularity, solely because they enabled large scale production to be achieved rapidly by the hitherto unprepared allied powers.

The main part of the operation consisted in nitrating sulphonated phenol with materials readily available in those days - dilute nitric acid and sodium nitrate. To prevent any corrosion of the nitrators and to prevent any possible formation of metal picrates, the nitrators were built of stone-ware.

Sulphonation of phenol

The first stage of the production process - the preparation of phenolsulphonic acid - may be effected in various ways.

Pascal [2] describes it as follows. Phenol, which is supplied in iron drums, is melted by placing the drums, after removing their lids and bottoms, into steam heated cylinders (I) (Fig. 111). Molten hot (80°C) phenol is collected in the heated tank (2) which also acts as a proportioner. Adjacent to it, is a tank (3) for 92% sulphuric acid.

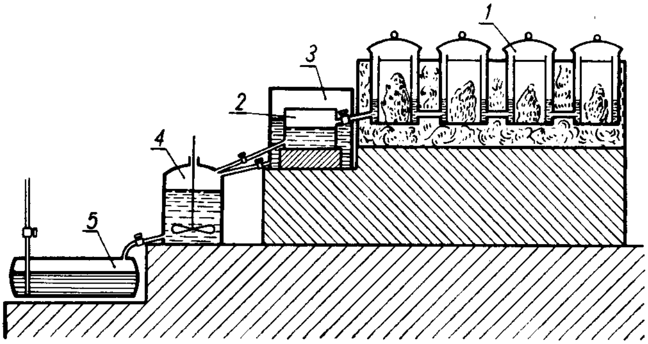


FIG. 111. Diagram of lay-out for sulphonation of phenol (Pascal [2]).

Both liquids flow down to the sulphonator (4), designed for 150-250 kg of phenol. For 100 parts of phenol 500 parts of sulphuric acid is used. The phenol in the sulphonator being hot, the sulphonation reaction starts spontaneously, resulting in a temperature rise to 100°C. After some 10-20 min, sulphonation may be regarded as completed and hot “sulphophenol” is transferred by means of a pressure-egg (5), to the nitrator. The pipeline for conveying the product should be heated, otherwise the phenolsulphonic acids are likely to crystallize.

According to the Lebedev’s description [5], phenol is sulphonated with 98% sulphuric acid taken in the proportion of 400-500 parts of acid for 100 parts of phenol. The sulphonation temperature is maintained within 70-80°C or 100-110°C. The reaction time is 4 hr. A temperature of 125-130°C may also be maintained, in which case the reaction time may be reduced to 2 hr. Cast iron sulphonators are used, 2 m in diameter and 1.8 m high. The required temperature may be maintained in the sulphonator by heating with a steel heating coil or with a heating jacket.

A schematic design of a sulphonator used in Great Britain is presented in Fig. 112. The reaction temperature is regulated by adjusting the flow of hot phenol. The propeller stirrer (1) is placed in cylinder (2) to get a better circulation of the reaction mixture. Flat blades (3), mounted above the stirrer, break up the stream of liquid raised by the propeller.

The lid of the sulphonator has an exit for the exhaust pipe, two inlets for introducing the reactants, a manhole, an inlet and outlet for steam passed through the coil and a thermometer hole. In addition to this, the lid is equipped with a sight glass and four handles to open the sulphonator. The heating coil is not shown. This vessel is discharged at the bottom.

If concentrated (98%) sulphuric acid has been used for the sulphonation, the sulphophenol should be diluted with water prior to nitration, otherwise the nitration reaction may proceed too violently. Besides some dilution is advantageous to precipitate any salts present, such as lead or ferric sulphates.

Lebedev [5] advises using wash water from the purification of picric acid, as this effects some economy in nitrating and picric acids.

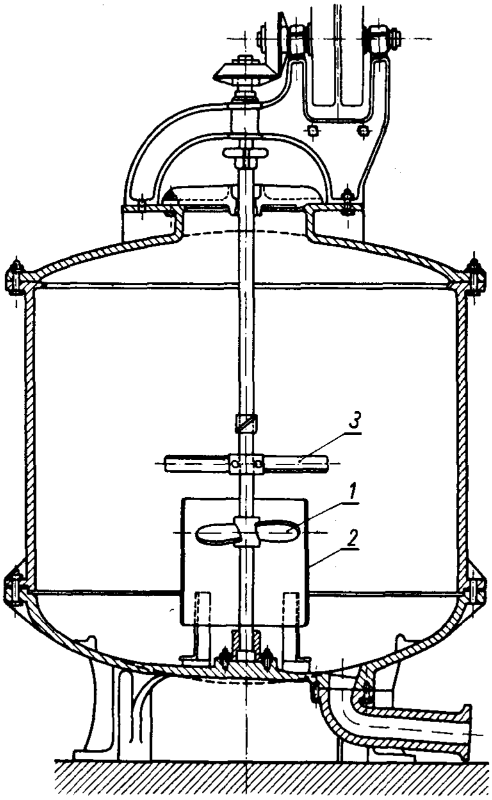


FIG. 112. Sulphonator for phenol (according to Lebedev [5]).

The dilution of sulphophenol is effected in special stoneware vessels. For 95 kg of sulphophenol 72l. of wash water is added. The specific gravity of the sulphophenol after dilution should be 1.35. The diluted sulphophenol is left to settle and then filtered through a sand filter. The temperature of the sulphophenol which is to be nitrated should not be lower than 50°C which is necessary for initiating the nitration reaction.

Nitration of phenolsulphonic acid in movable vessels

The second stage in the manufacture of picric acid is the nitration of the phenolsulphonic acid (sulphophenol) obtained. The simplest reactors used for this process are stoneware jars, "tourills", which may be of various size (e.g. 85 cm diameter in the widest part, 1.35 m in height). The lids of the jars are equipped with two wide entry holes, 15 cm in diameter (Fig. 113), one for feeding the nitrator with acid and sodium nitrate, the other for connecting the nitrator with the ventilating system. In addition to this, three smaller holes in the lid serve for introducing sulphophenol, inserting a compressed air line that reached down to the bottom of the jar and for inserting a thermometer. Naturally, various modifications of the nitrator construction are possible. These jar-nitrators have the disadvantage of not being equipped with heating or cooling devices: the heat is supplied by the reaction itself and the required temperature is maintained by adjusting the flow of the reactants.

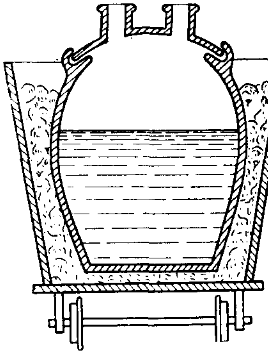


FIG. 113. Jar for the nitration of sulphophenol (Pascal [2]).

To facilitate working and increase output the nitrators are transported in wooden carts from the nitration section to a separate place, where the nitrator contents are allowed to cool prior to their transport to the purification section, where picric acid is separated from the spent acid and washed with water.

Usually the nitrator is tightly enclosed in the cart by a cement layer. This is necessary to isolate and to prevent the nitrator from any damage. Should the jar-nitrator crack because of too high a temperature, the cement layer prevents the reaction mixture from flowing off; sometimes it can even be recovered.

In France nitration was effected in the following way (Pascal [2]).

The jar-nitrator is charged with 275 kg of 44% nitric acid or with the mixture:

nitric acid (44%)	120 kg
sodium nitrate	90 kg

To this 180 kg of warm 50-70°C sulphophenol (corresponding to 30 kg of phenol) is gradually added. At the same time compressed air is passed through the nitrator to mix the reactants well. The rate of addition of sulphophenol should be so adjusted as to prevent the temperature from rising too rapidly at the beginning of the reaction. Hence the sulphophenol should be added carefully at first, although its flow must be rapid enough to attain a temperature of 100°C, at which the main portion of the product nitrates. If the process is operated properly, 95-100°C is attained within 20 min from the beginning of the process (initial temperature 25-30°C).

After one hour a temperature of 115-120°C is attained. All the sulphophenol should be added within one and a quarter hours. By this time the temperature falls to 90-100°C. Then, to remove nitrogen oxides, air is blown through the nitrator for 10-20 min and the nitrator is disconnected from the ventilating pipe and transported to the cooling section.

The nitrator contents are stirred repeatedly with a wooden pole while cooling to prevent picric acid from forming lumps which might retain impurities. After cooling for 34 hr at a temperature of about 60°C, 50-100 1. of water is added, thus preventing the precipitation of sodium bisulphate or, if it has already been precipitated, causing it to go into solution. The diluted acid contains some 45% of H_2SO_4, the concentration at which the solubility of picric acid is lowest. After it has cooled to ambient temperature 12-24 hr, the spent acid is drawn off by a siphon and the picric acid is transported to another section, where it is washed with water. Since the spent acid usually does not contain more than 1% of HNO_3, its recovery is pointless.

As Pascal describes it, a nitrating section is usually designed for 8 nitrators mounted on carts. Every 20 minutes nitration starts (and ends) in a successive nitrator, the whole cycle averaging 2-2.5 hr to complete. Thus during 24 hr, in a battery of 8 nitrators 72 nitrations can be effected. Since each nitrator produces 52 kg per batch, 3744 kg of picric acid will be obtained in 24 hr.

In Russia, as Lebedev reported, the French method gave satisfactory results in summer time only, whereas for the most part of the year (autumn, winter) on account of high heat losses, nitration was never complete and the picric acid yield was low (150-160 parts per 100 parts of phenol). Moreover, the product contained high proportions of mono- and di-nitrophenols.

In this connection various modifications of the process have been developed, consisting first of all in using more nitric acid and less phenol.

The jar-nitrator is charged with 141 kg of 44% nitric acid and 91 kg of $NaNO_3$. Then 172 kg of sulphophenol (which corresponds to 31 kg of phenol) is run into it over a period of nearly 1 hr 40 min. During the last 10-15 min a temperature of 115°C is maintained. Sulphophenol is added in seven equal portions after the following temperatures have been attained:

	Temperature, °C
I	26-30
11	62-70
III	88-89
IV	96-97
V	106-107
VI	111-113
VII	113-115

Since in winter time the cold compressed air used for mixing might cool the reactants, the sulphophenol should be passed into the nitrator in a weaker stream (or the air should be warmed), otherwise it would be difficult to attain the required temperature. On the other hand, insufficient mixing may cause the formation of undesired lumps of picric acid. Further operations do not differ from those in the process described above.

Nitrogen oxides, as well as nitric acid vapours, generated in the reaction, flow via the ventilating pipe to a system of jars, coolers and absorption towers, where they are absorbed.

There are also other methods in which the procedure consists in first introducing “sulphophenol” to the nitrator and adding the nitric acid afterwards.

Washing picric acid

The contents of 4-5 nitrators (200-300 kg of picric acid) are transferred by means of wooden ladles to a wooden washing vat (Fig. 114), where picric acid is washed several (mostly five) times with 150-200 1. portions of water. For 100 kg of picric acid 400 1. of water is used. The product is tested for purity by determining the SO_4^{2+} ions in a solution of the picric acid in distilled water. After washing, picric acid is separated from water in a centrifuge usually made of copper, the water content being brought to 5-7%.

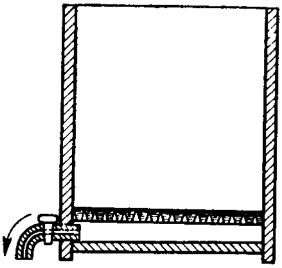


FIG. 114. Wooden vat for washing picric acid (Lebedev [5]).

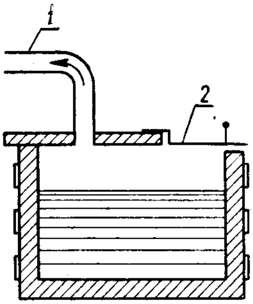


FIG. 115. Nitration tank for the nitration of sulphophenol to picric acid (Pascal [2]).

Washings are collected in special wooden tanks for settling. The spent acid is also added to the washings so as to bring the H_2SO_4 content to 10-30% as in such an “acid water” the solubility of picric acid is at its lowest. The water is decanted from time to time and disposed off into the river, after being neutralized, while the settled picric acid is collected from the bottom of the tank.

The recovered picric acid usually contains large quantities of mineral matter (determined as ash - 0.2%, compared with the permissible limit of 0.03%, as well as H_2SO_4 (0.1% instead of 0.02%). Such a product cannot be used for military purposes without further purification by crystallization from water.

Nitration of phenolsulphonic acid in stationary reactors

The stationary nitrators used in France have the dimensions 2 x 1.8 x 1.0 m (Fig. 115). They are constructed of acid-resistant bricks, joined by an acid-resistant cement and are reinforced from outside by tarred sheet iron tightened by hoops. The top of the nitrator is partly covered by a Volvic plate equipped with a pipe connected with the ventilating duct (1). An aluminium plate (2) covers the rest of the nitrator top.

In the nitrator described batches of 100-150 kg of phenol may be nitrated: The whole nitration unit is shown in Fig. 116. Nitrators (1) are connected with proportioning tanks for sulphophenol and nitrating acid. Vapours evolving during the nitration flow to jars (3), (4) and (5), passing on their way through the cooling coil (6). Here nitric and nitrous acids are condensed. Non-condensed nitrogen oxides pass to the absorption tower (7), sprayed with water and supplied with air for oxidation. Here the oxides are converted into nitric acid.

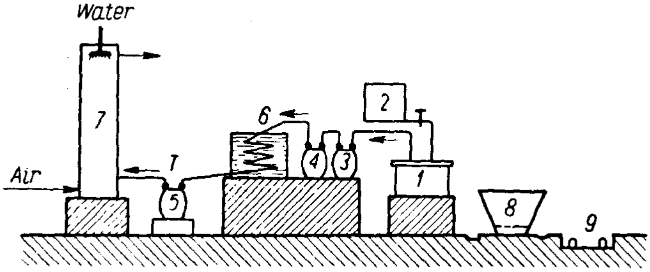


FIG. 116. Flow sheet of the nitration of sulphophenol to picric acid (Pascal [2]).

Next to the nitrator is a wooden double-bottomed tank (8) (the diameter of its upper parts is 1.15 m, height 1.0 m) for separating picric acid from spent acid and for washing the product with water. A narrow gauge railway (9) operates for two lines of nitrators located symmetrically on both its sides.

Similar cylindrical nitrators were in use in Great Britain (Fig. 117).

According to British data, the consumption of raw material for 1 ton of picric acid is:

	British method	French method
Phenol	540 kg	538 kg
$NaNO_3$	1990 kg*	1870 kg
H_2SO_4	2930 kg	2620 kg

* The nitric acid recovered in absorbers from nitrogen dioxide generated in the nitration process, has not been taken into account here. Usually 160 kg of HNO_3 (100%) per 1 ton of picric acid em be recovered.

United States method

During World War I a method of manufacture of picric acid was established in the United States.

Olsen and Goldstein [6] described the method as follows.

302.2 kg of phenol are sulphonated with 605 kg 93% sulphuric atid at 95-98°C during 6 hr. The product is composed of 80% phenol-4-sulphonic acid and 20% phenol-2,4-disulphonic acid.

FIG. 117. General view of nitrators for the production of picric acid [8].

The mixture of phenolsulphonic acids is diluted with 737.5 1. of water. Usually wash-waters are used for this purpose. The concentration of phenolsulphonic acid in the resulting solution is 18.4% calculated on phenol.

Nitration is carried out in two stages. In the first stage the nitrator is filled with a nitrating mixture composed of 70% HNO_3, 10% H_2SO_4 and 20% H_2O. The quantity of the mixture corresponds to that calculated for the introduction of one nitro group. Phenolsulphonic acid is added to the nitrating mixture at 30°C at the beginning and at 52°C at the end. During the first stage mononitro derivatives are formed.

After the first stage the temperature in the nitrator is raised to 60°C and the second stage begins. It consists in adding the same nitrating mixture. During the first hour of mixing the temperature increases to 110-115°C. Altogether 1250 kg of nitrating mixture are added (i.e. 2.75 kg of HNO_3 for 1 kg of phenol).

This method is not accompanied by the evolution of large quantity of nitrogen oxides. The nitration is ended when the content of the nitrator changes colour from red (the colour of phenolsulphonic acids) to yellow (the colour of picric acid).

The yield is 667.6 kg of picric acid, i. e. 220% by weight (theoretical yield 243%).

The spent acid contains 1.0% and 1.5% of picric and oxalic acid respectively. It is diluted with double its weight of water; water from washing picric acid is being used. The solution is brought to boiling for 5 hr to transform the remaining nitrophenolsulphonic acids into picric acid. After cooling, a second crop of picric acid is obtained in quantity 15% by weight of phenol, i.e. the total yield is 235% by weight. The losses of picric acid in the wash waters correspond to 1% of phenol.

Also Reed [7] described a method of nitrating phenolsulphonic acids in a large pot nitrator of 5500 1. capacity made of acid-proof bricks. Picric acid was settled in a wooden, lead-lined slurry tank and eventually separated in a centrifuge.

CONTINUOUS NITRATION OF PHENOLSULPHONIC ACID

During World War I Brookes [8] introduced in England a continuous method of phenol nitration based on the following principle.

The nitration is performed in a long tank, built of acid resistant bricks joined by a mixture of asbestos and sodium silicate (Fig. 118). The tank is 25 m long, 0.6 m wide, 0.5 m deep inside and with walls 0.2 m thick. At one end of the tank, an area two meters long is separated from the rest of the tank by an inside wall, lower than the walls of the tank. This is a chamber for mixing the reactants. The main part of the tank, 22 m long, is fitted with stoneware covers, equipped with a number of steam pipes (1) for heating up the nitrator content and pipes (2) for conducting away volatile products evolving during the nitration. The reaction mixture flows out continuously through outlet (4) at the other end of the nitrator. A general view of the installation is shown in Fig. 119.

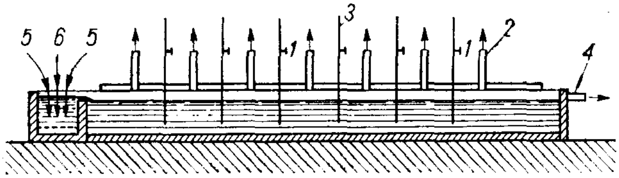


FIG. 118. Diagram of continuous production of picric acid (Pascal [2]).

The continuous nitration runs as follows. Phenolsulphonic acid, prepared by reacting 2 moles of H_2SO_4 with 1 mole of phenol, is diluted with water to a sp. gr. of 1.36 and introduced into the mixing chamber by pipe (5). Into it 65% nitric acid and the spent acid from nitration containing about 60% of H_2SO_4 and traces (up to 1%) of HNO_3 are introduced by a set (some 20) of aluminium pipes (6). The total amount of H_2SO_4 introduced is 6 moles per 1 mole of phenol, out of which only 2 moles come from fresh acid. The outlets of all the pipes are arranged below the surface of the liquid. Then the temperature is raised to 102°C by passing steam through the pipes (1). Additional heat may also be supplied by a steam coil, located in this space.

Some picric acid precipitates at the end of the tank and is carried away with the spent acid through the overflow. To facilitate the outflow of picric acid crystals, the reaction mixture coming up to the outlet is agitated now and then by a wooden pole.

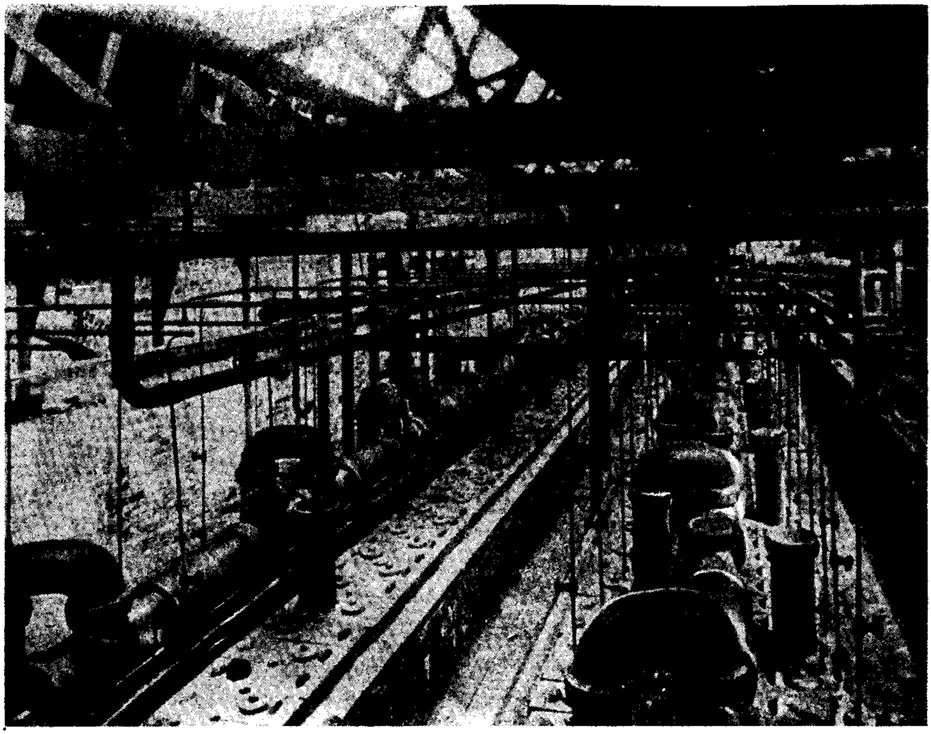


FIG. 119. General view of continuous production of picric acid [8].

The liquid, together with the crystals, is run into a crystallizer equipped with a lead cooling coil and a stirrer rotating at a low speed. Here the rest of the picric acid is precipitated and then separated from the spent acid on a vacuum filter.

Generally the use of lead as a material for construction of a picric acid plant is avoided, except in Great Britain and in the U.S.A. where it is used for the parts of installation which are also in contact with inorganic acids. The latter, being strong acids, are assumed to inhibit the formation of lead picrate.

The spent acid, containing 40-55% of H_2SO_4, is heated to 120°C in an acid-resistant brick tank equipped with an internal lead heating coil. Here the completion of the nitration (conversion of nitrosulphonic acids to picric acid) takes place along with the concentration of the acid. The acid is subsequently transferred to a cooler: crystallizer, similar to that described above, and from there to a vacuum filter for separating picric acid. The spent acid, now containing 60% of H_2SO_4, is returned to the nitration.

By the continuous process 190 parts of picric acid are obtained from 100 parts of phenol. The consumption of acids for the output of 1 ton of picric acid is:

HNO_3 (100%)	1270 kg
H_2SO_4 (100%)	2000 kg

NITRATION WITH CONCENTRATED ACID

The low yield of the nitration with the dilute nitric acid is the principal disadvantage of the above methods. Attempts have been made to use more concentrated acids both for sulphonation and nitration, to increase yield. It has been shown, however, that primitive stoneware installations for nitration, without provision for rapid heating or cooling, or for vigorous stirring, are not suitable for concentrated acids. The classical nitration plant, in which the nitrator is equipped with a heating or cooling jacket as well as with a mechanical stirrer, has proved necessary. Nowadays this is the method of nitration generally used.

Nitration with concentrated acid by the Griesheim method is effected in the following way.

To 400 parts of 30% oleum 94 parts (1 mole) of phenol is added with stirring, the temperature being maintained below 90°C. The mixture is heated to 90-100°C during a period of 5 hr. As a result phenoldisulphonic acid is formed.

The oleum solution is then diluted with 200 parts of sulphuric acid (sp. gr. 1.84). The whole is cooled down to 50°C and 80 parts of 80% nitric acid is added. After the temperature has gone up to 60-80°C, a new portion of 80 parts of nitric acid is added. Finally, when the temperature has exceeded 80°C a further 100 parts of nitric acid is added. Altogether, for 94 parts of phenol 260 parts of 80% nitric acid is used, the excess being 16% over the theoretical amount.

The phenoldisulphonic acid thus prepared is then nitrated in conventional iron nitrators with a jacket and a stirrer. 1000-2000 kg of sulphophenol may be nitrated at a time. From 100 parts of phenol 205 parts of picric acid can be obtained.

A flow diagram of picric acid manufacture by a method applied in the U.S.S.R is presented in Fig. 120 (after Lebedev [5]).

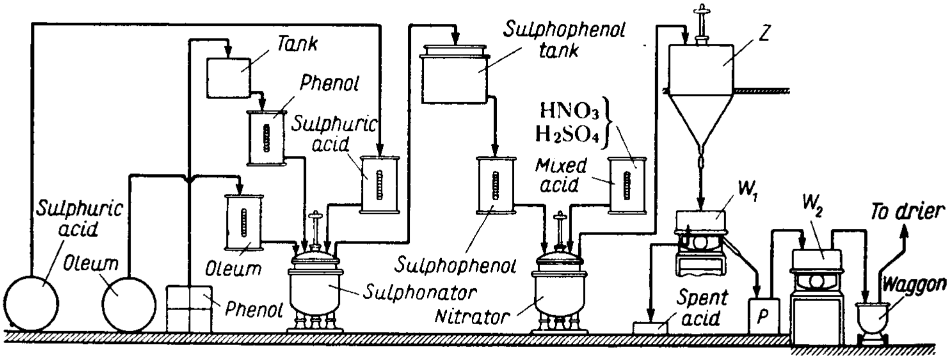


FIG. 120. Flow sheet of the nitration of phenol with concentrated nitrating mixture (Lebedev [5]).

Sulphonation

The first step of the process - sulphonation of phenol - is effected in an iron sulphonator, equipped with a jacket, a heating coil and a stirrer. The construction of the sulphonator is in principle similar to that applied in Great Britain, as described above (Fig. 112, p. 506).

Molten phenol having a temperature of 80°C is transferred to a heated proportioner and from there to the sulphonator, where a quantity of 1750 kg phenol may be sulphonated at a time, this quantity being sufficient for 3-5 nitrations.

After the phenol has been introduced 7800 kg of 20% oleum is fed into the sulphonator. During this operation cold water is passed through the jacket and the coil, the cooling and the flow of oleum being so regulated as to allow the temperature to attain 90°C towards the end of the introduction. Then the cooling is stopped, while the sulphonator content is heated by steam to 100°C and kept at this temperature for 3 hr, before being cooled down again. Then the product is diluted with 3725 kg of sulphuric acid (sp. gr. 1.84). Spent acid may also be used for dilution. This operation should be carried out directly in the nitrator to utilize nitric acid and nitrogen oxides present in the spent acid.

The diluted sulphophenol is cooled down to 35°C before being transferred by compressed air to a sulphophenol tank, heated by a heating coil. The pipe line through which it passes should also be heated up.

The sulphonation takes about 7.5 hr, namely:

Charging with phenol	15 min
Feeding with oleum	21hr
Steam heating	9 min
Main reaction	3 hr
Cooling	36 min
Dilution	1 hr
Conveying to the tank	36 min
Total	7hr 36 min

The second stage of picric acid manufacture - sulphophenol nitration - is carried out with a mixture of the following composition:

HNO_3	70%
H_2SO_4	20%
H_2O	10%

For easy control the nitration process is divided into 3 stages: (1) mononitration, (2) dinitration and (3) trinitration. All are effected in one nitrator. The acid required is therefore added in three portions, their weights being in the ratio of 80: 80: 100.

Sulphophenol is subjected to nitration, diluted either with fresh sulphuric acid or with spent acid. The dilution with spent acid usually takes place in the nitrator itself just before the nitration process begins.

For this purpose a portion of 1906 kg of concentrated sulphophenol is run into the nitrator and cooled down to 35°C, then during cooling and stirring, 938 kg of spent acid of the composition:

H_2SO_4	76%
HNO_3	0.3-1.5%
HNO_2	2.54%
oxalic acid	2-3%

picric acid	1-2%
total acidity (as H2SO4)	83-84%
SP. gr.	1.775

is added. Before starting the nitration the diluted sulphophenol should be cooled down to 40°C.

The separate nitration stages are effected as follows.

Mononitration

To the nitrator containing diluted sulphophenol the first portion of 377.5 kg of the nitrating mixture is run in. During this operation the temperature rises from 40° to 60°C. The addition of the nitrating mixture usually takes 45-60 min (the temperature rises at a mean rate of about 2° per 5 min). At the beginning of the process especially vigorous cooling should be applied to the nitrator contents. Then, as the process goes on, the cooling may be less intense.

Dinitration

In the second nitration stage, another portion of 377.5 kg of the nitrating atid is added. The initial temperature of 60°C rises to 80°C towards the end of the process. The addition of acid takes 45 min. At this stage the nitration proceeds most smoothly and the temperature rises slowly, no cooling being required. If the temperature rises too slowly (less than 2° per 5 min), steam may be passed through the heating coil for a while (not longer than for 1 min) to attain the required temperature by the end of the nitration. If nitration is carried out properly at this stage of the process, it helps the third stage nitration run smoothly. Frothing, which may occur there, may be due to incomplete nitration at the second stage.

Trinitration

At this stage a portion of 470 kg of the nitrating acid is run into the nitrator. The initial temperature is 80°C and towards the end it is 100°C. All the nitrating acid should be added within a period of one hour. The nitrator contents are then kept at 100-110°C for one hour longer. During the addition of the acid the nitrator contents should be cooled. If a rapid rise in temperature occurs the acid flow should be stopped for l-2 min. After all the acid has been added, the nitrator contents should be heated to prevent the temperature falling below 100°C. On the other hand care should be taken to prevent it rising above 112°C. Higher temperatures should be considered dangerous, although British operating conditions for a similar method permit 115°C as the upper limit. A temperature higher than 100°C and close to 110°C favours the formation of larger crystals on cooling.

Nitration completed, the nitrator contents are cooled down to 35°C to precipitate picric acid. The mixture is then transferred by means of compressed air (4 atm) to a higher mounted tank Z (Fig. 120) and from there to the centrifuge W_1 for separating picric acid from spent acid. For each tank a separate centrifuge is provided.

The sulphophenol nitration takes ca. 64 hr, including:

Charging the nitrator with sulphophenol	30 min
Mononitration	l hr
Dinitration	45 mill
Trinitration	l hr
Heating	1 hr
Cooling	l hr 20 min
Discharging	30 min
Total	6 hr 15 min

Separation and washing picric acid

Picric acid is separated from spent acid by centrifuging. The centrifuge W_1 shown in Fig. 120 is made of V4A stainless steel. It can work at both low and high speeds. As the picric acid suspension in spent acid is drawn off from tank Z_1 the centrifuge is rotated at a low speed (some 200 r. p. m.), then at full speed. Since the crystals of picric acid may be quite minute the centrifuge basket should be lined with stainless steel gauze.

Picric acid is washed with a small quantity of cold water when still in the centrifuge. Thissash water is then added to the spent acid. The product is discharged at the bottom and transferred to a wooden or aluminium washing tank P, equipped with a mechanical stirrer or with a bubbler. Here, after mixing with water, the stirrer is stopped and, after settling the water, is drawn off by a siphon. After 5-6 washings, the remaining water is removed in centrifuges, W_2, made of tinned copper.

The average charge of the washing tank consists of 350 kg picric acid (the quantity produced in one batch) and 1000 1. of water. The washing operation, comprising charging, mixing, decanting, etc., takes 40-46 min. If the product has formed lumps, it should be crushed in a roll crusher before washing.

Counter-current washing processes also are applied. In a system described by Lebedev [5], acid washings containing some 0.007% of H_2SO_4 coming from centrifuge W_2 which is fed with fresh water, are mixed with acid washings from the picric acid washing tank P containing 1.1% of H_2SO_4. In this way acid water containing 0.85% of H_2SO_4 is obtained. This water is used for washing picric acid in centrifuge W_1. The water flowing out of it contains 3.2% of H_2SO_4. A part of this water is introduced into the washing tank P together with fresh water, in such a quantity as to achieve a content of H_2SO_4 in the washings from the tank P equal to 1.1%, as mentioned above.

Centrifuge W_2 is fed initially with the acid water from washer P, finally with fresh water.

Such a system requires 3 m^3 of fresh water per 1000 kg of picric acid, whereas conventional methods require 10 m^3 of water for the same quantity of picric acid.

After washing, picric acid is centrifuged in centrifuge W_2 so as to reduce its moisture content to 5-6%.

The spent acid flowing out of the centrifuge has a composition as given on p. 515. Its specific gravity 1.775, is similar to that of picric acid (1.813). This is why the picric acid which has passed through the centrifuge gauze and has precipitated on cooling, does not settle at the bottom but mostly remains suspended in the spent acid. The latter may subsequently be used for dilution of sulphophenol (p. 515).

The spent acid may also be utilized in a different way, namely by diluting with water to a total acidity of 72-75%, further precipitation of picric acid from the solution may be brought about. After a few days standing, the picric acid is separated from the solution on a vacuum filter, as grade II product. The spent acid thus diluted, after being fortified by adding nitric acid and oleum, may be used for the nitration again.

Drying and screening

The construction of picric acid driers presents certain difficulties because of the ready formation of picrates. Having this in mind, wood is mostly used as the construction material for driers, and any metal parts (screws, nails) should be made either of metals that form picrates with difficulty such as copper or aluminium, or of tinned metals or stainless steel. Floors should be made of wood covered with linoleum or concrete coated with asphalt. At the beginning of World War I when concrete floors were commonly in use, picric acid would with time form picrates with cationic constituents of the concrete: calcium, magnesium, sodium and iron. Washing the floor created conditions favourable for the penetration of picric acid into the concrete, and after several months a thick layer of picrates used to form. Any friction, as for example, by moving a bench around or any sort of blow, initiated an explosion of picrates all over the floor, causing fire or explosion in the drier. The inside walls should be plastered with plaster of Paris, since gypsum, being the salt of a strong acid, yields calcium picrate only with difficulty. Lining the walls of the drier section with white glazed wall-paper is recommended. Heaters for heating the drying air should not be placed inside the drying premisses. Workman who have to enter the drying section should put on protective wooden-soled shoes with no nails in them. The floor should be swept frequently and washed with water.

To dry picric acid various drying systems are applied. The chamber drier is the simplest. The design of such a drier, used in the U.S.S.R. is shown in Fig. 121 (after Lebedev [5]). On shelves (I) wooden frames covered with linen are placed. Over each of them about 9 kg of picric acid (calculated on dry mass) is spread, so as to obtain a 3-4 cm thick layer. The heater (2) is located in the passage adjacent to the chamber. The natural flow of the heated drying air is shown in the diagram.

The drying of picric acid with a 7% moisture content at 50-60°C usually takes about 2 days. This period can be cut down to 16 hr by passing the drying air through the heater by means of a ventilator.

Tunnel driers may also be applied for drying picric acid.

For this, mechanical sieves made of aluminium or copper gauze, 50 meshes per 1 cm^2, are used. Figure 122 shows a system which may be used. A wooden funnel (1) serves for leading the product. Lumps of picric acid are retained by gauze (2) and may be removed from time to time through door (3). Crystals of the required size pass through the gauze into hopper (4).

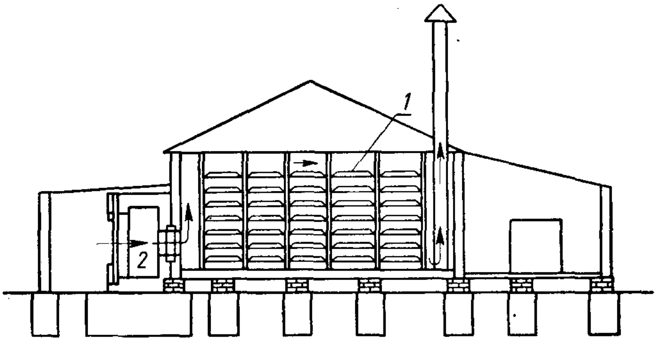


FIG. 121. Chamber drier for picric acid (Lebedev [5]).

The sieve is hung on straps from the ceiling and is kept in oscillating motion by means of an eccentric driven from a compartment adjacent to that in which the screening installation is located. The end product is transported in leakproof chests or in paper-lined barrels.

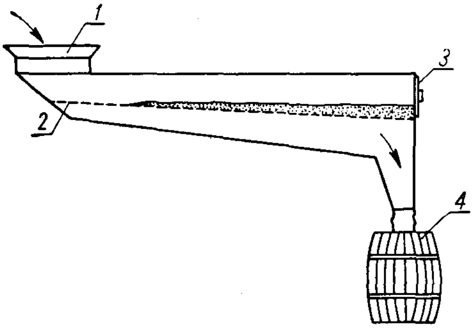


FIG. 122. Sieve for picric acid (Pascal [2]).

DINITROPHENOL NITRATION METHODS

The nitration of dinitrophenol is the most modern commercial method for the production of picric acid from chlorobenzene via chlorodinitrobenzene (for preparation of dinitrophenol from chlorodinitrobenzene, see p. 484).

Both dry and moist dinitrophenol may be nitrated, though the dry product is usually used.

Lebedev [5] describes the production process used in the U.S.S.R. Dinitrophenol from the centrifuge, containing 10-15% of moisture, is dried to obtain a product with only about 0.5% of moisture (drying is effected in picric acid driers).

Since the purity of picric acid depends to a high degree on the purity of the dinitrophenol, the quality standards for the latter should be strictly observed (see p. 486).

The reaction is carried out in a cast iron jacketed nitrator equipped with a stirrer and a stainless steel heating coil 2092 kg of spent acid are run into the nitrator and heated to 50°C. 750 kg of dinitrophenol are then added, the above temperature being maintained during this operation, which will take 30 min. The nitrating mixture prepared from 86% nitric acid (100 parts) and 20% oleum (200 parts) is then run into the nitrator during the course of 23 hr, the excess of the mixture being 25% of HNO_3. During this procedure the temperature should not be allowed to rise over 80°C. After 20 min of stirring, the nitrator contents are heated to 110 - 112°C (1 hr) and subsequently maintained at this temperature for one hour and a half. Altogether the process requires about 8 hr.

The reaction mixture is cooled to 25-30°C as quickly as possible, which takes about 2-3 hr. Picric acid precipitates in fine crystals. The nitrator contents are then drawn off into stainless steel centrifuges or onto iron vacuum filters. The charge of a centrifuge amounts to 250 kg. As a result, 750-780 kg of picric acid can be obtained, which constitutes about 85% of the theoretical yield.

Washing, drying, etc. of picric acid are effected as described above.

A flow sheet of the preparation of picric acid from chlorobenzene is presented in Fig. 123 (after Lebedev [5]).

According to the same author, the material consumption for preparing 1000 kg of picric acid is:

Benzene as feed stock:

Oleum (20%)	2600 kg
Nitric acid (86%)	1320 ,,
Benzene	610 ,,
Sodium carbonate	31 ,,
Chlorine	540 ,,
Sodium hydroxide 85%	680 ,,
Oleum for drying chlorine	95 ,,

Dinitrophenol as feed stock:

Dinitrophenol	1000 kg
Oleum (20%)	950 ,,
Nitric acid (86%)	475 ,,
Spent acid	2370 ,,

METHODS OF NITRATING BENZENE IN THE PRESENCE OF MERCURIC SALTS

During the 1914-1918 War attempts were made to apply industrially Wolffenstein and Böters's method [9] of nitration of benzene in the presence of mercuric salts (p. 110). Vignon [10] developed a method in which a mixture of di- and trinitrophenols in the ratio of about 40: 60 was obtained in nearly 85% yield. A mixture prepared in this way might have been applied directly for filling shells. Nevertheless, the method has not been used on an industrial scale due to the large quantities of mercury required for the production, amounting to about 10% of the benzene

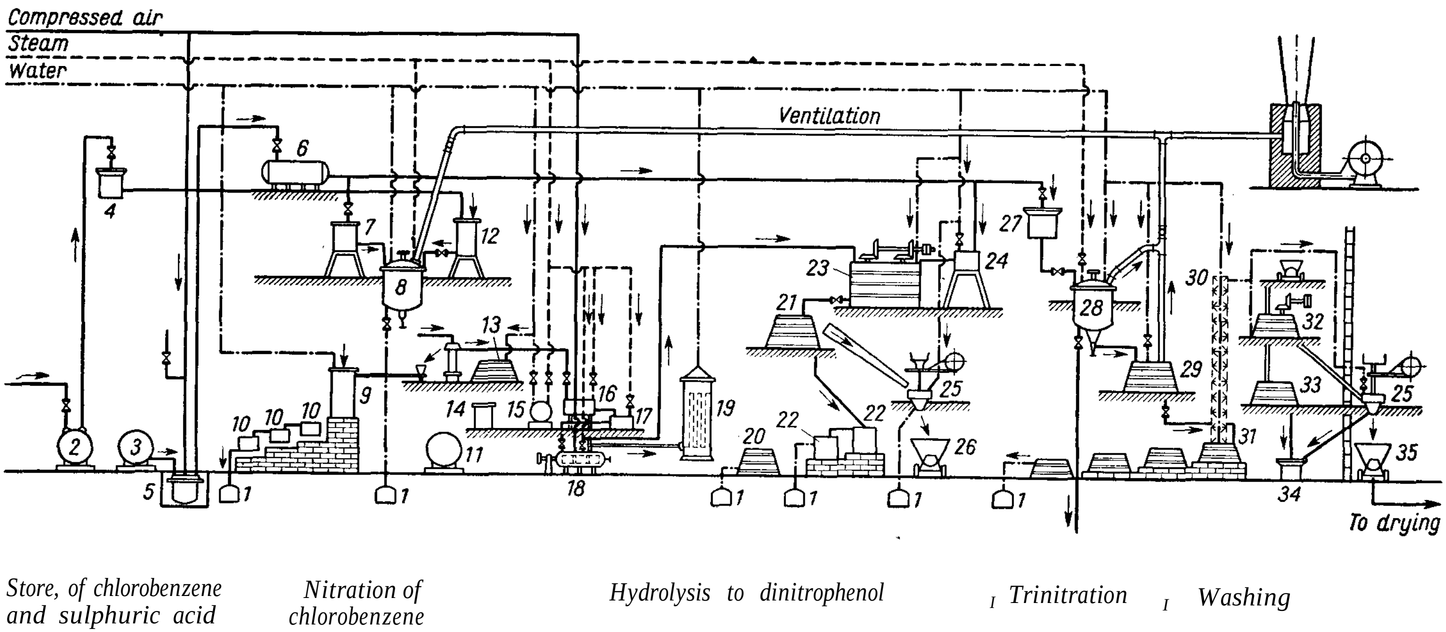


FIG. 123. Flow sheet of the production of picric acid from chlorobenzene (Lebedev [5]).

1 - drain; 2 - storage tank for chlorobenzene; 3 - storage tank for sulphuric acid; 4 - intermediate tank for chlorobenzene; 5 - pressure-egg; 6 - intermediate tank for sulphuric acid; 7 - metering tank for sulphuric acid; 8 - nitrator; 9 - diluting tank; 10 - labyrinth for sedimentation of chlorodinitrobenzene; 11 - tank for caustic soda; 12 - metering tank for chlorobenzene; 13 - vat for washing chlorodinitrobenzene; 14 - metering tank for caustic soda; 25 - tank for hot water; 16 - tank for chlorodinitrobenzene; 17 - metering tank for chlorodinitrobenzene; 18 - reactors for hydrolysis of chlorodinitrobenzene; 19 - condenser; 20 - filter for dinitrophenol from the labyrinth; 21 - filter for dinitrophenol; 22 - labyrinth for the sedimentation of dinitrophenol; 23 - neutralizer; 24 - diluting tank; 25 - centrifuge; 26 - truck with dinitrophenol; 27 - metering tank for sulphuric acid; 28 - nitrator; 29 - filter; 30 - lift; 31 - acid drains; 32 - decantation vat; 33 - titer; 34 - wash-water collector; 35 - truck with picric acid.

used. The recovery of mercury proved to be not worth-while, since its concentration in spent acid and in washing was much too low.

Vignon came to the conclusion that a certain temperature limit should not be exceeded, otherwise oxidation reactions would prevail. In addition, he found that although an excess of benzene resulted in an increased yield, at the same time it favoured the formation of dinitrophenol.

Nitration by Vignon's method on a semi-commercial scale, is carried out as follows: 2.5 parts of mercuric nitrate is dissolved in 100 parts of 52% nitric acid and the solution is mixed with 50 parts of benzene. The mixture is brought to 75-80°C and kept at this temperature for 5-7 hr, then cooled and the layer of benzene, containing nitrobenzene and nitrophenols, is separated by decantation. Benzene is distilled off and nitrobenzene is expelled by steam distillation. The remainder, constituting 125 parts, contains:

dinitrophenol	52%
picric acid	48%

Other authors report the yield obtained does not exceed 140 parts of benzene and the product is contaminated with mercuric picrate.

Broders [11] tried to develop another method of commercial production by passing benzene vapours through nitric acid containing mercuric nitrate. However, he did not succeed in obtaining a yield higher than 20% calculated on the benzene used.

During World War II Wright and his co-workers [12] continued the investigations on this method on large laboratory scale, and developed a process using 1250 ml of benzene for one run.

The reaction was effected at 65°C with 50% nitric acid, containing a dissolved catalyst consisting of

0.28	gramme-atom Al
0.015	gramme-atom Mn
0.0005	gramme-atom Al

calculated on 100 g of benzene. The yield obtained was 150 g of picric acid from 100 g of benzene, i.e. 50% of the theoretical. The consumption of nitric acid amounted to 140-160 g (calculated on HNO_3). Nitrobenzene and dinitrobenzene were formed as by-products.

Wright suggested the recovery of the nitrogen dioxide generated in the reaction and the recycling of spent acid to utilize the catalyst it contains. The results obtained by the author do not differ in principle from those of the earlier investigations. The method, however, like the earlier ones, has not found industrial application.

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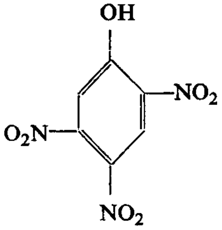
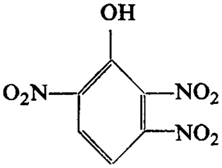
CHAPTER XV

OTHER NITRO DERIVATIVES OF PHENOLS

PICRIC ACID ISOMERS

APART from picric acid, unsymmetrical β– and γ– trinitrophenols are known:

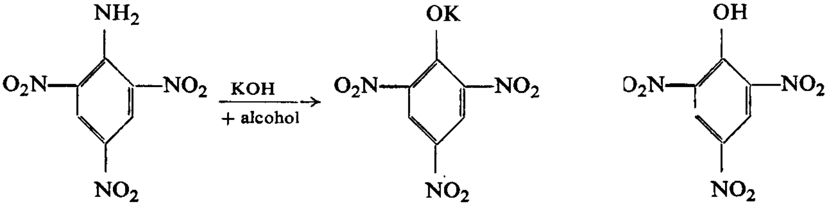

β


γ

The β– isomer or 2,4,5-trinitrophenol (m. p. 96°C) may be obtained by nitration of 3,4-dinitrophenol, the γ– isomer or 2,3,6-trinitrophenol (m. p. 118°C) by nitration of 2,3-dinitrophenol. Since they are not formed during the nitration of phenol, they are not present in picric acid and are not of any practical importance.

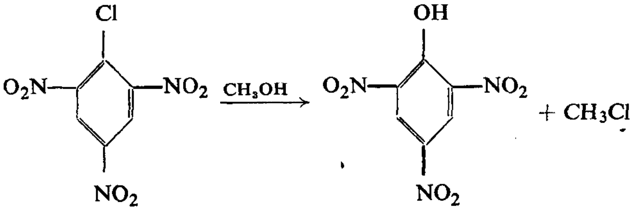
"ISOPICRIC ACID"

Nietzki and Dietschy [1] found the product they obtained by reacting an alcoholic solution of KOH with "trinitro-phenylhydroxylamine" (which later was proved to be trinitroaniline, as Borsche [2] showed in his investigation already mentioned) was a potassium salt of "isopicric acid" :


(1)

The melting point of the latter is close to that of picric acid (117-118°C) but the properties of its potassium salt (as for example the solubility) differ from those of potassium picrate.

The investigations of the above authors were checked by Desvergnes [3], who found the melting point of "isopicric acid" to be 119.7°C. Moreover, he was able to observe that picryl chloride, on boiling in water, alcohol or pyridine also gives a certain quantity of "isopicric acid", according to the equation:



(2)

The evidence for the existence of "isopicric acid" is not convincing.

PICRIC ACID SALTS

Metal salts of picric acid may be formed by the action of picric acid on metals, their oxides or carbonates and in certain cases also on their other salts. They are crystalline substances, mostly more sensitive to friction, impact and heat, than picric acid itself. Due to their high sensitivity to stimuli, the explosive properties of picrates were known long before those of picric acid.

Picrates formed by precipitation from aqueous solutions contain water of crystallization which may desensitize them. For example, the decahydrate of ferric picrate shows no sensitiveness to friction and impact and cannot be ignited when in direct contact with a flame, whereas the anhydrous compound is exceptionally sensitive to these stimuli.

The properties of picrates have been examined by several authors, e.g. Cheltsov [4], Will [5], Silberrad and Phillips [6], Kast [7], Krauz and Turek [8], Tucholski [9] and T. Urbanski and Slon [10].

Tucholski determined the dehydration temperatures of picric acid salts hydrates, their melting points, initiation temperatures and temperatures preceding explosion. T. Urbanski and Slon determined their sensitiveness to impact and flame.

The results obtained by the above authors are presented in Table 119.

All picrates, especially lead, barium, calcium, iron and nickel picrates, should be considered as highly undesirable in picric acid. They have caused a great number of accidents. Among them only potassium picrate has found some practical uses, viz. in some high explosive and propellant compositions no longer in use at the present time.

Nowadays the only picrates applied as explosives for military purposes are ammonium and lead picrates, the latter being an initiating explosive (Vol. III).

TABLE 119

PROPERTIES OF PICRIC ACID SALTS AND THEIR HYDRATES

According to Tucholski [9]					According to T. Urbanski and Slon [10]		
Picrate	Content of water of crystallization	Temperature of dehydration to the next lower hydrate °C	Meltin point °C	Initiatio temperaturc °C	Sensitiveness to impact (10% explosion)		Sensitiveness to flame (number of swings*)
					2 kg	10 kg	
Na	1 H_2O	154					
	anhydrous	-	210	313		19 cm	18
Mg	9 H_2O	59					
	6 H_2O	82					
	4 H_2O	125					
	2 H_2O	208					
	anhydrous	-	-	368		no explosion	9
Al	16 H_2O	58					
	13 H_2O						
	3 H_2O	156					
	anhydrous		-	390-395			71
K	anhydrous	-	250	331	21 cm	10 explosion	10.5
Ca	8 H_2O	14					
	6 H_2O	91					
	5 H_2O	122					
	1 H_2O	228.5			8 cm		10
	anhydrous	-	316	323			
Cr	2 H_2O	14					
	anhydrous	-	275.5	296.5	28 cm		53.5
Mn	8 H_2O	68.5					
	3 H_2O	130					
	anhydrous	-	-	289		60 cm	14.5
Fe II	8 H_2O	75					
	4 H_2O	97					
	anhydrous	-	275.5	296.5			
Fe III	10 H_2O	72.5					
	1 H_2O	100					
	anhydrous	-	155	247	10 cm		1
Co	8 H_2O	40					
	6 H_2O	78					
	2 H_2O	168					
	anhydrous	-	226	327.5,			
Ni	6 H_2O	35.5					
	5 H_2O	48					
	4 H_2O	94.5					
	1 H_2O	173.5					
	anhydrous	-	40-25~	348		40 cm	5.5

* Nitrocellulose ignites from 1 swing, gunpowder from 8 wings.

Table 119 (continued)

According to Tucholski [9]					According to T. Urbanski and Slon [10]		
Picrate	Content of water of crystallization	Temperature of dehydration to the next lower hydrate °C	Melting point °C	Initiation temperaturc °C	Sensitiveness to impact (10% explosion) 2 kg	Sensitiveness to impact (10% explosion) 10 kg	Sensitiveness to flame (number of swings*)
Cu	11 H_2O	30					
	8 H_2O	35					
	5 H_2O	12					
	3 H_2O	120.5					
	anhydrous	-	-	290	30 cm		16
Zn	10 H_2O	51					
	8 H_2O	54.5					
	6 H_2O	101					
	2 H_2O	151					
	anhydrous	-	-	303		no explosion	35
Sr	5 H_2O	87					
	1 H_2O	216			17 cm		
	anhydrous	-	290	341			
Ag	anhydrous	-	296	332			
Cd	7 H_2O	44					
	4 H_2O	69					
	1 H_2O	144					
	anhydrous	-	-	328			
Ba	6 H_2O	46.5					
	5 H2O	63					
	2 H_2O	86					
	1 H_2O	195			2.5 cm		4
	anhydrous		200	332			
Hg	4 H_2O	65					
	3 H_2O	ca. 103					
	1 H_2O	ca. 144	ca. 290	333			
Tl	anhydrous	-	-	301			
Pb	1 H_2O	130					
	anhydrous				2 cm		10

- Nitrocellulose ignites from 1 swing, gunpowder from 8 swings.

AMMONIUM PICRATE

There are two forms of ammonium picrate: yellow and red. Cahours [11] drew attention to this fact in 1849. Anselmino [12], Stepanov [13] and a number of other authors have studied the problem of the existence of two differently coloured forms of the compound. Dehn and Ball [14] expressed the opinion that the two forms of ammonium picrate are, as Hantzsch suggested, chromoisomers, and that the phenol form should be assigned to the yellow modification, while the red one should be regarded as the quinonoid form. Hale [15] found that the colour of ammonium picrate was darker (more red), the more concentrated the ammonia used for the neutralization of the picric acid. By heating to 150°C the red form changed into the yellow one.

T. Urbanski, Hackel and Galas [16] found that it was the pH of the solution in which picric acid was neutralized that was responsible for the colour of ammonium picrate crystals. The higher the pH the more readily the red crystals were formed. By neutralizing picric acid with an ammonium carbonate solution the authors always obtained a yellow product, whereas by using a 25% ammonia solution for neutralization, they obtained a red product. Both forms were found to have equal specific gravities, 1.6715, whereas they differed somewhat in their densities of loading when pressed. At low pressures, densities of loading of the red form were slightly higher. At high pressures the yellow form was observed to have the higher density (Table 120).

This difference in density values should be ascribed to the physical properties of crystals. At low pressures the crystals of the red form, due to their shape, can be packed more easily in a given space. At high pressures a lower mechanical strength of the yellow crystals plays a part, viz. being disintegrated they more readily fill up the space.

TABLE 120

DENSITY OF AMMONIUM PICRATE FORMS

Pressure, kg/cm^2	Density, g/cm^3	
	yellow form	red form
0 (loose)	0.891	1.045
110	1.244	1.299.
330	1.396	1.392
660	1.490	1.490
1100	1.553	1.529
1540	1.593	1.562
1910	1.596	1.569
2540	1.616	1.582

The above authors, in a detailed study of the explosive properties of the two forms of ammonium picrate, found no difference in their explosive power. However, the red form is slightly more difficult to bring to explode and it is to this property that differences in the figures obtained in determination of their explosive properties may be ascribed.

Here are the principal data obtained by T. Urbanski, Hackel and Galas [16]:

Sensitiveness to impact: 10% explosions from a 10 kg weight falling from a height of ca. 20 cm, which is in agreement with Kast's results [7]

sensitiveness to flame: yellow ammonium picrate ignites after 8 swings; the red form after 12.5 swings

initiation temperature (20°/min)	257-259°C
specific pressure, *f* (experimentally)	7200 m
expansion in the lead block test	330-335 cm^3

TABLE 121

DETONATION RATE OF AMMONIUM PICRATE (BOTH FORMS) AT VARIOUS DENSITIES (IN A STEEL PIPE 35/42 mm)

Density, g/cm^3	Detonation rate, m/sec	
	yellow form	red form
0.86	4380	-
1.11	-	5155
1.34	5835	-
1.35		5835
1.49	6950	-
1.50	-	6960
1.55	6995	-
1.56	-.	6995
1.58		6200
1.60	6030	-

As the highest rate of detonation under the above condition, 7000 m/sec for both forms has been taken. Thus, ammonium picrate should be considered as a somewhat more powerful explosive than TNT.

The thermochemical properties of ammonium picrate have been examined by several authors (no indication given as to the colour of the substance examined). Sarrau and Vieille [17] determined its heat of combustion as ranging from 693.2 to 708.9 kcal/mole.

T. Urbanski and Soroka [18] determined heats of combustion of the two forms and from these they calculated their heats of formation:

	Heat of combustion $(-\Delta H_R)$	Heat of formation $(-\Delta H_f)$
yellow form	687.3 kcal/mole	83.7 kcal/mole
red form	677.3 kcal/mole	93.7 kcal/mole

It can be seen that the calculated heat of explosion of the red form is somewhat lower than that of the yellow one.

These results do not agree with Hale’s data. He reported the fragmentation of 3 in. shells might indicate the higher explosive power of red ammonium picrate, and the equal abilities of the two forms to detonate under the influence of a detonator.

Ammonium picrate under the name of Explosive D was first used in the United States in 1901. It was Dunn [18a] who proposed using it as a high explosive material for filling shells. During both the World Wars armour piercing shells of the U. S. Navy were filled with this explosive. It is thought that ammonium picrate is less sensitive to impact and friction than TNT, and that is why it was used for the purpose. However, the above mentioned investigations by T. Urbanski and his co-workers did not confirm the view. Moreover, they revealed that ammonium picrate, and especially its yellow form, was easy to ignite when in contact with a flame, its flammability being of the same order as that of gunpowder.

GUANIDINE PICRATE

Guanidine picrate may be obtained by acting with a warm aqueous solution of ammonium picrate on an aqueous solution of guanidine nitrate. A yellow, crystalline precipitate of guanidine picrate (m. p. 319°C, with decomposition) is formed.

Guanidine picrate has been suggested in the United States as a high explosive, being of exceptionally low sensitivity to impact and friction.

DANGER PRODUCED BY PICRATES

If picric acid is free from picrates, its burning, even in large quantities, does not present any risk of explosion. A case is known (in the U.S.A.) when 100 tons of picric acid caught fire. It burned relatively smoothly although the flame attained a height of 10-15 m and a characteristic loud whistling noise was heard. Slight explosions were observed only when roof fragments fell into the burning mass, causing blast from a violent eruption of confined gases. However, had picrates been present, such a fire might have ended with a violent detonation but according to Sapozhnikov [19] it is sufficient for molten picric acid merely to come into contact with metal to create favourable conditions for the formation of picrates.

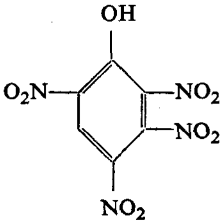
A violent explosion of picric acid in a Manchester factory in 1887 was ascribed to the formation of picrates. Burning, molten picric acid flowed down onto lithopone, forming lead picrate which in consequence caught fire. The latter, being an initiator, detonated and caused the picric acid to detonate.

A fire, followed by an explosion at Huddersfield in 1900 was also caused by detonation of iron picrate (presumably Fe^{2+}). The iron picrate had been formed on the surface of steam pipes located in the picric acid drier shop. It ignited when a plumber, unaware of the fact, struck one of the pipes with a hammer. The flame spread along the pipe and set the drying picric acid on fire.

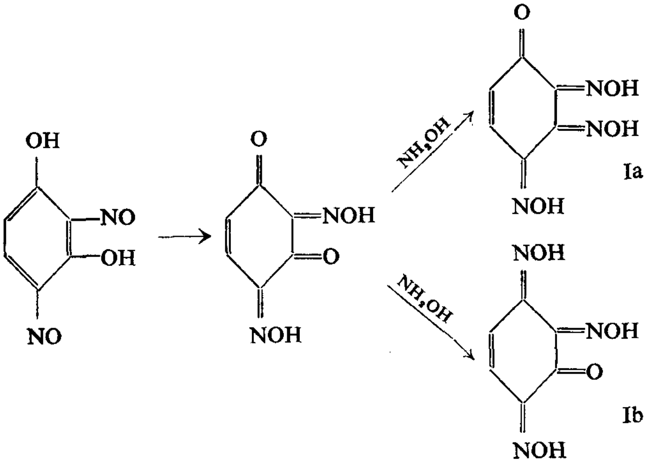
In a French factory streaks of picric acid had been formed alongside a narrow gauge railway. As the soil beneath was calcareous, calcium picrate formed which, having dried up in the summer, was ignited by friction or a blow, spreading flames all over those parts of the factory marked with calcium picrate streaks.

TETRA- AND PENTA-NITRO DERIVATIVES OF PHENOL

TETRANITROPHENOL



This compound (m. p. 140°C) was obtained by Nietzki and Burckhardt [20] from diquinoyltrioxime. The latter can exist in two isomeric forms, (Ia) and (Ib), which may be prepared by reacting hydroxylamine with dinitrosoresorcinol:



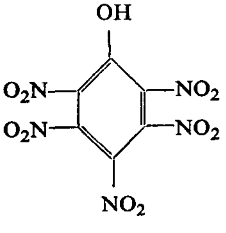
Tetranitrophenol forms by the action of 50% nitric acid followed by a 63% acid on diquinoyltrioxime at a temperature lower than the room temperature. By neutralizing the solution a sparingly soluble potassium salt is precipitated, which in turn may be converted by double decomposition into a still less soluble barium salt. From the latter, by the action of a calculated quantity of sulphuric acid, free tetranitrophenol may be obtained.

A product of higher purity than that obtained by Nietzki was prepared by Blanksma [21] by the nitration of *m*- nitrophenol with a mixture of nitric acid (sp. gr. 1.52) and concentrated sulphuric acid. As shown later (van Duin and van Lennep [22]) the product, if of high purity, exhibits fairly high stability against heating. It explodes at 245-251°C, whereas if it is contaminated it decomposes after it has been brought to its melting point, i.e. to 140°C.

The nitro group in position 3 in tetranitrophenol is very reactive. On boiling with water the compound yields trinitroresorcinol. With methyl alcohol it forms trinitroresorcinol monomethyl ether. With an alcoholic ammonia solution, tetranitrophenol gives aminotrinitrophenol.

Tetranitrophenol is more sensitive to impact than tetryl (van Duin and van Lennep [22]).

PENTANITROPHENOL



Pentanitrophenol (m. p. 190°C) was obtained by Blanksma [21], who nitrated 3,5-dinitrophenol with an anhydrous mixture of nitric and sulphuric acids. The product was precipitated, and could then be recrystallized from chloroform.

Both meta-nitro groups are reactive. With water, pentanitrophenol yields trinitrophloroglucinol, with alcoholic ammonia solutions it gives diaminodinitrophenol.

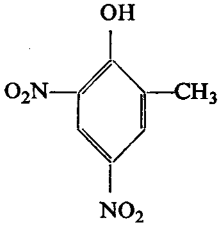
NITRO DERIVATIVES OF CRESOLS

Of the three isomeric cresols: *ortho*-, *meta*-, and *para*-, only *m*- cresol can be used as the starting material for introducing three nitro groups, viz. in the 2,4,6-positions. *Ortho* and *p*- cresols are able to form stable nitro group systems only when no more than two nitro groups are introduced. Under the conditions of the nitration of *m*- cresol to its trinitro derivative the o- and *p*- isomers are oxidized to oxalic acid.

Cresol for nitration should contain a high proportion of the *m*- isomer. Commercial "meta-cresol" usually contains about 60% of the *m*- isomer and 40% of *p*- cresol. The preparation of a much more costly raw material, containing 90% of *m*- cresol is also possible. It is clear that the yield of trinitro-m-cresol will correspond to the *m*- cresol content in the starting product.

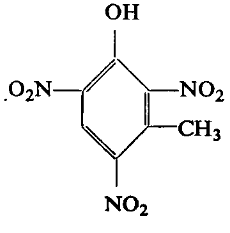
A methyl group present in the ring facilitates the introduction of nitro groups. This is why *m*- cresol is more readily nitrated than phenol. On the other hand a methyl group enhances oxidation processes. This accounts for the lower yield of trinitrocresol obtained, as compared with that of picric acid. Like picric acid, trinitrocresol has the disadvantage of readily forming metallic salts which are sensitive to impact.

All these factors have limited the practical application of trinitrocresol. France was the only country which used it, under the name of "Cresilite" mostly in mixtures with other nitro compounds to lower their melting points (Vol. III). Among nitro derivatives of cresols, dinitro-m-cresol (m. p. 86.5°C)



is of some practical importance, though not as an explosive but as a herbicide.

2,4,6-TRINITRO-m-CRESOL



Physical properties

2,4,6-Trinitro-m-cresol (m. p. 107-107.5°C) is less soluble in water than picric acid. With 100 g of water the following quantities go into solution:

at 6°C	0.15 g
15°C	0.2 g
100°C	1.83 g

Benzene dissolves 2,4,6-trinitro-m-cresol more readily than picric acid:

at 6°C	9.2 g
15°C	13 g

The compound is readily soluble in alcohol, ether and acetone.

Trinitro-m-cresol may be separated from picric acid in the form of its potassium salt, taking advantage of a difference in the solubility of the potassium salts of the two compounds, as shown below:

	Grammes of salt in 100 ml of water		
	at 6°C	at 15°C	at 100°C
potassium picrate	3.3	0.45	14.55
potassium trinitrocresate	1.4	3.4	over 50

On the other hand, trinitrocresolates of organic bases are more difficult to dissolve than the corresponding picrates. Solubilities in 100 ml of water of pyridine picrate and pyridine trinitrocresolate are given below for comparison:

	at 20°C	at 100°C
pyridine picrate	0.36 g	12.6 g
pyridine trinitrocresate	0.12 g	1.5 g

The specific gravity of trinitro-m-cresol is 1.64. Under a 1500 kg/cm^2 pressure this of 1.55 can be obtained, and under 2900 kg/cm^2 - 1.63.

Chemical properties

2,4,6-Trinitro-m-cresol forms addition compounds with aromatic hydrocarbons in the molecular proportion of 1:1:

	melting point, °C
with naphthalene	124.5 (Sapozhnikov, Rdultovskii [23])
„ acenaphthene	118 (Jefremov [24])
„ phenanthrene	113 „
„ fluorene	107 „
„ retene	118 „

On the whole the properties of trinitro-m-cresol are similar to those of picric acid. The properties of trinitrocresolates differ only slightly from those of picrates, as for example their lead salts. Ammonium trinitrocresolate has been used to some extent in Austria as a high explosive for filling shells.

Thermochemical and explosive properties

When heated, trinitro-m-cresol decomposes at about 200°C and at 275°C explodes. Its sensitiveness to impact is similar to that of picric acid, but its ability to detonate is lower. Thus, when compressed to a density of 1.63 it requires a powerful detonator (at least 2 g of mercury fulminate). Picric acid of the same density can be detonated by 0.6 g of the same detonator.

The following figures characterizing the explosive properties of trinitro-m-cresol were given by Kast [7]:

heat of explosion	925 kcal/kg
volume of gases, V_0	675 I./kg
temperature of explosion	2700°C
maximum rate of detonation	6850 m/sec
specific pressure, f	7595 m
expansion in the lead block	275 cm^3 (i.e. 90% of that given by picric acid)

The heat of the formation ($-\Delta H_f$) of trinitro-m-cresol is +54.1 kcal/mole, according to Koehler [25].

MANUFACTURE OF TRINITRO-m-CRESOL

In industrial practice, trinitro-m-cresol is prepared by the nitration of cresol. The manufacturing process is similar to that used for picric acid. It consists of two stages - sulphonation and nitration. However, due to the liability to oxidation, its yield does not exceed 150-160 parts from 100 parts of pure *m*- cresol, i.e. a maximum of 67-73% of the theoretical yield.

From 100 parts of commercial “meta-cresol” containing only 60% of the *m*- isomer (the rest being *p*- cresol) not more than 100 parts of trinitro-m-cresol can be obtained. *p*- Cresol is fully oxidized to oxalic acid, which then crystallizes from the spent acid.

The isolation of pure *m*- cresol has proved to be too expensive because the boiling points of the *m*- and *p* -isomers are too close to each other:

	boiling point, °C	melting point, °C
m- cresol	201	11-12
p- cresol	202	36
o- cresol	185	31

Experiments have been carried out to separate ***m*-** and *p*- cresols by sulphonation, as sulphonated *m*- cresol is a liquid substance, while sulphonated *p*- cresol is crystalline. The two isomers were then separated by centrifugation. However, the purity of the product obtained was not satisfactory enough, thus the process would not be economical.

In the absence of any other criteria, a sample of each “meta-cresol” batch to be nitrated should be subjected to a laboratory nitration test.

The process of cresol nitration is much the same as that for phenol. In France, where the output of Cresilite was highest, movable stoneware jar-nitrators (“tourills”), or the stationary type described above were used for the nitration (pp. 506, 509).

Nitration of *m*- cresol in stationary nitrators was carried out as follows:

1860 kg of 52% nitric acid is charged into the nitrator, followed at a fairly high rate by sulphocresol (obtained by sulphonation of 200 kg of commercial “meta-cresol” with 600 kg of sulphuric acid, sp. gr. 1.84, as described above in the picric acid manufacture). After the temperature in the nitrator has attained 45°C (which requires about 45 mm), the flow of sulphocresol is stopped.

The temperature rises spontaneously to 85°C and sulphocresol is then run in again at such a rate as to introduce the whole lot in no more than 2 hr. Towards the end of the process the temperature attains 100-103°C. The reaction mixture is allowed to remain at rest for half an hour, then compressed air is gently blown through for about 20 min, thus causing the temperature to fall to 90°C. A further temperature fall to 70°C is achieved by blowing air strongly for about one hour. At this stage of the process the granulation of the Cresilite begins, depending on the cooling rate and on the intensity of the air blowing.

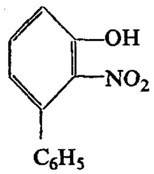
After granulation has been completed, the nitrator contents are allowed to remain at rest for 12-15 hr, then without any dilution the spent acid are drawn off by means of an aluminium siphon. The spent acid is passed through an asbestos filter to retain any Cresilite granules carried away.

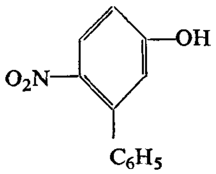
The product obtained is in the form of yellowish-brown granules, with a melting point of 101-103°C.

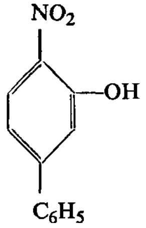
NITRO DERIVATIVES OF ARYLPHENOLS

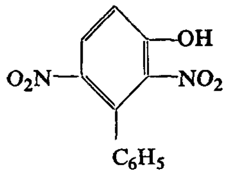
NITRO DERIVATIVES OF 3-HYDROXYDIPHENYL

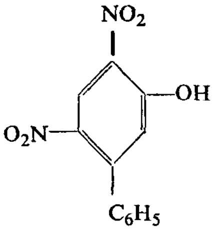
Colbert, Fox and Matuszak [26] nitrated 3-hydroxydiphenyl and obtained a number of its nitro derivatives:

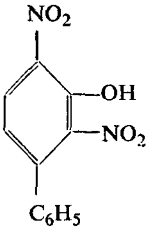


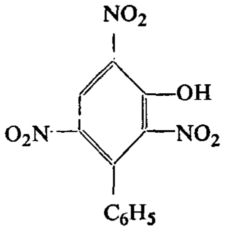












NITRO DERIVATIVES OF POLYHYDRIC PHENOLS

Among polyhydric phenols, only the nitro derivatives of resorcinol have gained considerable practical importance. The nitro derivatives of phloroglucinol may also be of some value. Both phenols have hydroxyl groups in the *meta* position to each other, thus enabling the introduction of three nitro groups. Among dinitro derivatives, those of pyrocatechol have found some uses.

The presence of a large number of hydroxyl groups in the ring increases the reactivity of phenol very considerably. That is why these compounds are very easy to nitrate, and in the nitration process by the conventional method for phenols, i.e. via sulphonation, followed by nitration, three nitro groups usually enter the compound. This is also the reason why the preparation of, for example, a nitro derivative of resorcinol with less than three nitro groups, requires the application of special methods. They may be divided into three groups.

1. Nitroso groups are introduced and subsequently they are oxidized to nitro groups. Since for each phenolic group one nitroso group can be introduced, the method may be applied for the preparation of nitro derivatives of polyhydric phenols in which the number of nitro groups is equal to the number of hydroxyl groups (e.g. dinitroresorcinol). The method is also applied when polyhydric phenols nitrate very easily (e.g. phloroglucinol), since their direct nitration proceeds too violently, and by breaking the process into two stages - nitrosation and oxidation of the nitroso groups - it can be made to run more smoothly.

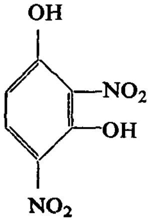
2. A compound is nitrated which in addition to phenolic groups contains some other which inhibits the introduction of nitro groups and after the nitration becomes so mobile that it can readily be removed. A carboxylic group may serve the purpose. For example, by the nitration of resorcylic acid, dinitroresorcinol may be obtained as an end product (for more details see p. 537).

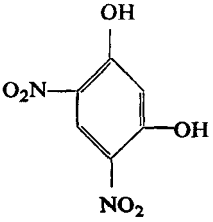
3. Halogenated phenols or polyhalogen derivatives of benzene are nitrated. After the compound has been nitrated, the halogen atom or atoms become reactive and may be removed by hydrolysis. This method, which is widely utilized in the preparation of dinitrophenol, has not found wider practical application because of difficulties in obtaining supplies of the corresponding starting materials (some halogen compound;).

Among all the possible nitro derivatives of resorcinol only di- and tri-nitroresorcinols are of practical value. Both are used as initiating explosives in the form of lead salts (Vol. III). The lead salt (Pb^{2+}) of dinitroresorcinol is also of some practical value and in this connection some data characteristic of the compound will be given.

DINITRORESORCINOL

Two isomers of dinitroresorcinol, 2,4- (or 2,6-) and 4,6-dinitroresorcinols are known (m. p. 148°C and 212.5°C respectively).



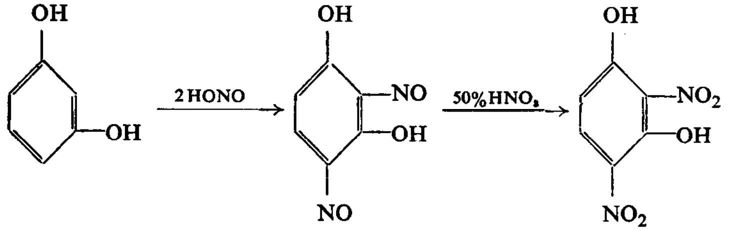


They are yellow substances, readily soluble in hot water, which dye animal fibres and leather.

Only the 2,4-isomer is of practical importance as the one most easily available. The 4,6-isomer cannot be obtained directly, though it may be prepared by the nitration of diacetylresorcinol.

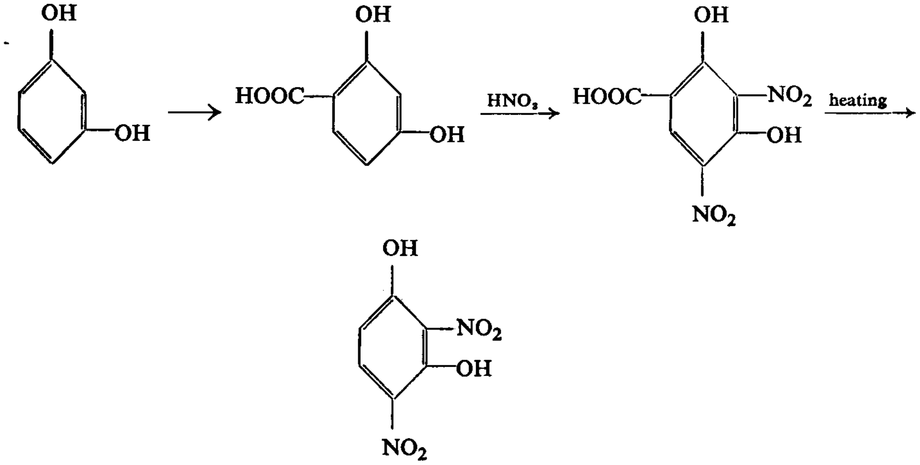
Since the nitration of resorcinol by the conventional method for phenols (i.e. sulphonation followed by the action of nitric acid) yields a trinitro derivative, two other methods for the preparation of dinitroresorcinol are possible, viz.: oxidation of dinitrosorcsorcinol or nitration of resorcylic acid followed by decarboxylation.

According to Kostanecki and Feinstein [27], the following reactions take place in the former process:



(4)

Hemmelmayer [28] presented the nitration of resorcylic acid and its subsequent decarboxylation by the following reactions :



(5)

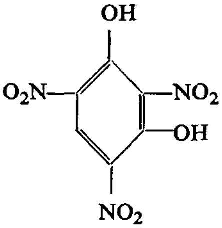
In practice the first process is applied, as it gives a higher yield of the product.

The nitrosation is effected in a well known way. A weak (2.75%) aqueous solution of one mole of resorcinol is acidified with 2 moles of sulphuric acid. The solution is cooled down to -2°C and a 10% aqueous solution of 2 moles of $NaNO_2$ is added, dropwise. Crystalline yellowish 2,4-dinitrosoresorcinol is precipitated in theoretical yield. The precipitate is washed and separated in a centrifuge or on a vacuum filter prior to oxidation. From dinitrosoresorcinol the divalent lead salt of dinitrosoresorcinol may be prepared, having initiating properties.

Dinitrosoresorcinol is oxidized with 50% nitric acid at a temperature below 0°C. Moist, freshly prepared dinitrosoresorcinol is charged into the reactor, containing nitric acid cooled down to -5°C. When calculating the concentration of nitric acid, the water content in dinitrosoresorcinol should be taken into account. Simultaneously with the dinitrosoresorcinol concentrated nitric acid is introduced into the reactor to keep the concentration of the acid in the reactor constant. After the reaction has been completed, the reactor contents are run out into icy water. The volume of the water containing ice should be several times as large as that of the product. Dinitroresorcinol is precipitated and is separated on a vacuum filter and washed with a small quantity of cold (ca. 0°C) water. The crude product contains some trinitroresorcinol. By crystallization from hot water a product is obtained which should not melt below 147°C. The yield of the reaction, calculated on the resorcinol used, is about 30% of the theoretical.

For the preparation of the divalent lead salt a moist product is used; its water content should be determined exactly.

TRINITRORESORCINOL (STYPHNIC ACID)



Physical properties

Trinitroresorcinol (m. p. 175.5°C), also known as styphnic acid, is a yellow crystalline product which dyes animal fibres intensely. 100 ml of water dissolves 0.641 g of it at 14°C, and 1.136 g at 62°C.

More recent solubility data by Aubertein and Emeury [29] are: in 100 g of water 0.45 g of styphnic acid are soluble at 15°C 0.55-0.58 g at 20°C 0.68-0.69 g at 25°C.

Knox and Richards [30] determined the solubility of styphnic acid in nitric acid of various concentrations at 25°C, expressed as the "normality" of the HNO_3 solutions. Aubertein and Emeury have recalculated their results expressing the solubility in a more convenient way:

HNO_3, wt. %	0	10.67	41.91	55.9	69.57
Solubility in 100 g of the acid, g	0.53	0.034	0.125	0.32	1.37

Aubertein and Emeury have also determined the solubility of styphnic acid in sulphuric acid of different concentrations at 25°C:

H_2SO_4, wt. %	0	6	20	50	80	92
Solubility in 100 g of the acid, g	0.65	0.07	0.01	0.10	0.13	0.13

The solubility of styphnic acid in nitric acid-sulphuric acid mixtures is very low.

Aubertein and Emeury examined the solubility in a spent acid mixture of the composition :

HNO_3	10%
H_2SO_4	72%
H_2O	18%

At room temperature it is below 0.005%. At 35-40°C the solubility is below 0.01%, and at 80°C it is below 0.1%.

Styphnic acid is slightly hygroscopic. It absorbs 2-3% of water after being exposed for 30-100 hr at an atmosphere of 60% humidity at 25°C [29].

Styphnic acid is readily soluble in glycol diacetate : 100 g of the solvent at 20-25°C can dissolve about 13 g of the substance.

Chemical properties

Trinitroresorcinol, like other compounds of this type, forms addition compounds with aromatic hydrocarbons. Some of them investigated by Jefremov [24], containing the two components in the molar ratio of 1:1, are listed below:

	melting point, °C
with naphthalene	165.5
„ acenaphthene	156.0
„ anthracene	176.3
„ phenanthrene	132.7
„ retene	135.7

With chloro- and bromo-naphthalenes it yields compounds melting within a wide temperature range.

With regard to explosive power and sensitiveness trinitroresorcinol is similar to picric acid. Since its price is considerably higher than that of picric acid it is not used in explosive technology. Only lead trinitroresorcinate is of great practical importance as an initiator (Vol. III). On the whole the properties of trinitroresorcinol salts are similar to those of picrates.

Purity

The purity of the product depends on the method of carrying out the reaction. The melting point of the product prepared by Aubertein and Emeury [29] was 176.2-176.5%.

However, high purity of styphnic acid is not required when the substance is used to produce the lead salt by the continuous method according to Meissner (Vol. III). Some manufactures claim to achieve better results with an impure brown product of low melting point - max. 170°C.

Styphnic acid of low purity can be obtained by sulphonating resorcinol with spent sulphuric acid or by sulphonation with sulphuric acid added with sodium nitrite according to the method of Wilkinson [31].

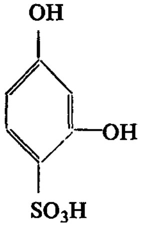
Wilkinson's method has been studied by Aubertein and Emeury [29]. They found that the yield of the product is reduced when the proportion of nitrite is increased, and the rate of reaction is diminished. A relatively high proportion of nitrite (2-4%) in the sulphonating acid considerably increases foaming during nitration. The quantity of sodium nitrite should, therefore, be kept within the limits of 1-2%. A temperature of 50-55°C should be maintained at the beginning of nitration. Increasing the temperature by 1.5°C reduced the yield by 1%.

The product thus obtained has a chestnut brown colour and m. p. 165-168.5°C depending on the proportion of nitrite used.

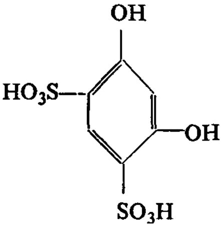
Method of preparation

Trinitroresorcinol is usually prepared by a method which consists in the sulphonation of resorcinol to disulphonic acid which is then nitrated. The process comprises two stages: sulphonation and nitration.

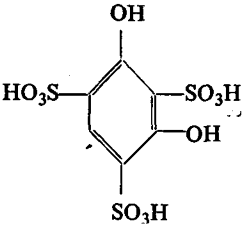
Sulphonation yields only three compounds: I, II, and III.



I



II



III

The sulphonic acids I and II can be obtained by sulphonation of resorcinol with sulphuric acid or oleum at temperatures which are not higher than 100°C (Mertz and Zetter [32]). The trisulphonic acid can only be prepared by the action of oleum at 200°C. According to Aubertein and Emeury [29], resorcinol can be sulphonated to the compound II by the action of a tenfold quantity (by weight) of sulphuric acid of concentration 92-97.5% H_2SO_4 or oleum (105% H_2SO_4) at 50°C. However, a small proportion (1%) of resorcinol remains unchanged and is subjected to oxidation during the subsequent nitration. It is responsible for foaming during the nitration. According to the above authors, prolonged sulphonation or application of more concentrated oleum does not prevent the presence of unsulphonated resorcinol.

Nitration can be achieved by acting with nitric acid (50-90% HNO_3) on sulphonated resorcinol partly dissolved and partly suspended in the excess of sulphuric acid (Mertz and Zetter [32]), keeping the temperature below 55°C on mixing the reagents and raising it to 80°C by the end of the reaction.

All who have carried out this reaction in practice know that during nitration foaming occurs and sometimes makes the process impossible on a larger scale. Strong foaming also means the formation of very fine crystals of styphnic acid difficult to filter.

Aubertein and Emeury [29] made a detailed examination of the causes of foaming. Oxidation of non-sulphonated resorcinol is the original cause of gas evolution during nitration. When the product is in the form of very fine crystals the gas bubbles attach themselves to the crystals and raise the product to the surface in the form of a foam. This does not occur when the crystals of the product are large. Therefore, the method of nitration should be such as to favour formation of large crystals of styphnic acid. To achieve this, Aubertein and Emeury advise:

(1) keeping the temperature of nitration constant and avoiding any fall in temperature;
(2) keeping the concentration of nitric acid during the nitration as constant as possible and the temperature near to 55°C;
(3) avoiding the application of too vigorous stirring particularly just before the styphnic acid begins to crystallize. Excessive stirring promotes foaming.

Aubertein and Emeury established the influence of various other factors upon the fineness of crystals and subsequently on the foaming. For example a lower concentration of sulphuric acid (92-97%) used for sulphonation favours the formation of fine crystals and hence of foam. This is the result of a low rate of nitration produced by the lower concentration of the nitrating acid.

The yield of styphnic acid depends on the excess of nitric acid. It falls from 86 to 82% of theoretical when the excess is reduced from 45 to 14%.

Styphnic acid of high purity

Sulphonation. 100 parts of resorcinol are introduced in small increments during a period of half an hour into 1000 parts of sulphuric acid (93-98%) under stirring. The temperature rises to 50°C and is maintained then for 15 min, when the mixture is ready to be nitrated.

Nitration. 200 parts of concentrated nitric acid (90% HNO_3) are added to the sulphonation mixture in such a way that the first 110 parts are introduced relatively quickly (within 30-50 min), and the temperature is kept between 50° and 55°C. After that, the rate of stirring and the rate of introducing nitric acid is reduced (3-5 times) to maintain the temperature at 55-60°C. Styphnic acid begins to crystallize. From this moment the rate of adding nitric acid is gradually increased and cooling is so arranged that the temperature finally reaches 60-65°C.

The whole is stirred for half an hour at this temperature, cooled, filtered, washed with cold water until the wash water is neutral to Congo paper and dried at 60°C.

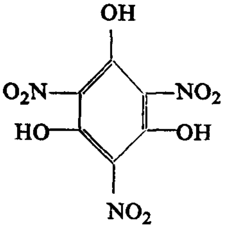
The yield of the product with m. p, 176°C is 180-185 parts.

Styphnic acid of low purity

Sulphonation. 10-20 parts of sodium nitrite are added to 1000 parts of sulphuric acid (92-98%) and 100 parts of resorcinol are introduced as above.

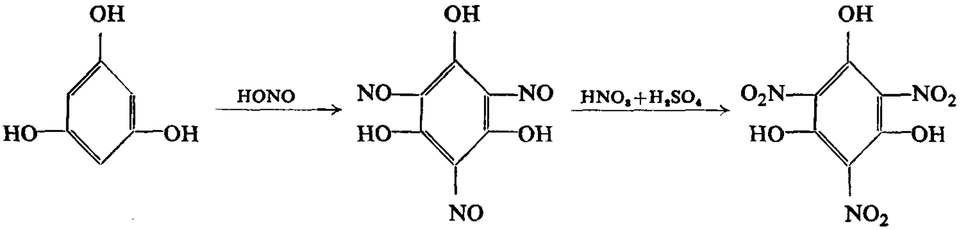
Nitration. Initially 125 parts of nitric acid (instead of 110 parts) are added. Otherwise the process is the same as described above.

TRINITROPHLOROGLUCINOL

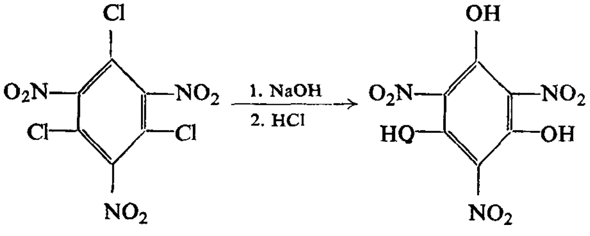


Trinitrophloroglucinol (m. p. 167°C) has not found any practical application, although several authors have proposed using trinitrophloroglucinol salts, primarily its lead salt, as an initiator (e.g. Friedrich [33]; Rathsburg [34]; Sorm and Drapalova [35]; T. Urbariski and Kruszyriska [36]).

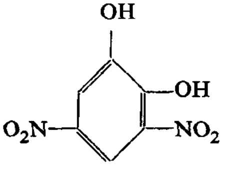
Trinitrophloroglucinol may be obtained in various ways, e.g. from phloroglucinol by nitrosation, followed by oxidation with nitric acid (Benedikt [37]):



or from trichlorotrinitrobenzene by boiling with a sodium hydroxide solution (Sorm and Drapalova [35]):



DINITROPYROCATECHOL



3,5-Dinitropyrocatechol (m. p. 164°C) was prepared by Nietzki and Moll [38] by nitrating pyrocatechol diacetate with cold cont. nitric acid, followed by hydrolysis of ester groups with sulphuric acid.

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CHAPTER XVI

PICRIC ACID ETHERS

As an explosive the acidic character of picric acid and its readiness to form picrates are serious drawbacks. In an attempt to eliminate these disadvantages the substitution of the acid hydrogen by an aliphatic or aromatic radical has been suggested. The compounds thus formed would be picric acid ethers. For the substitution of hydrogen by aromatic radicals the latter were connected with nitro groups.

Maxim [1] and du Pont de Nemours Inc. [2] were the first to suggest the application of the methyl ether, trinitroanisole, as an explosive.

During World War I materials of this type were used fairly extensively. However, it has been proved that some of them can undergo hydrolysis, yielding free picric acid, thus rendering any further use of such explosives unjustifiable. In addition, most of the products have strongly toxic properties. Hence during World War II compounds of this type were used only on a small scale.

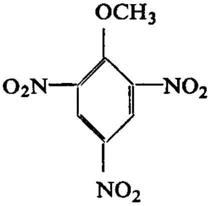
During the 1914-1918 War trinitroanisole was manufactured in Germany under the names of Nitrolit, Trinol and An. It was used alone or in admixture with ammonium nitrate, hexyl, or hexanitrodiphenyl sulphide, for filling high explosive shells and for submarine and land mines. Eventually it had to take the place of TNT.

In France trinitroanisole was made use of only on the semi-commercial scale, in mixtures with picric acid or with ammonium or sodium nitrate for filling bombs. During World War II trinitroanisole was manufactured in Japan for tiling armour piercing shells.

Trinitroanisole was first obtained by Cahours [2a] by the direct nitration of anisole. The reaction proceeds very vigorously, as the presence of a methoxy group greatly facilitates the introduction of nitro groups and some highly coloured by-products are formed [20]. For this reason it is preferable to prepare trinitroanisole via chlorodinitrobenzene (p. 547).

Similarly trinitrophenetole was first obtained by the direct nitration of phenetole, but at present this method is not used, chlorodinitrobenzene being a starting material. Trinitrophenetole is less important then trinitroanisole. Its manufacture never developed beyond the semi-commercial scale. Similarly other picric acid ethers, as for example nitro derivatives of phenyl ether, have not found any practical use.

TRINITROANISOLE

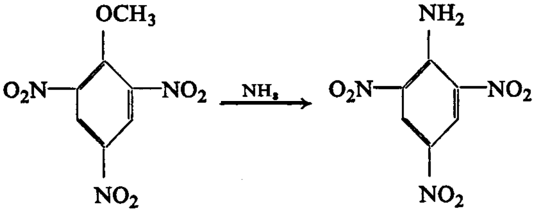


2,4,6-Trinitroanisole (m. p. 67°C) forms white needles (sp. gr. 1.408), very difficult to dissolve in water: at 15°C 100 ml of water dissolve only 0.02 g and at 50°C 0.137 g of trinitroanisole. The product is sparingly soluble in carbon disulphide and carbon tetrachloride, relatively easily soluble in alcohol and still more so in ether, benzene, chloroform and ethyl acetate.

CHEMICAL PROPERTIES

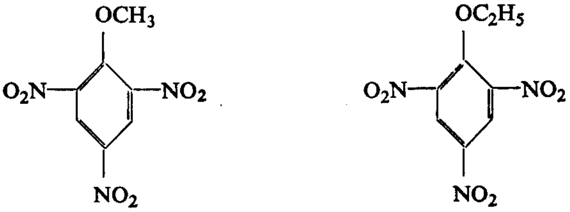
By the action of alkalis trinitroanisole is hydrolysed slowly in the cold and more rapidly in the hot, forming the corresponding picrates (Salkowski [3]). It also undergoes slow hydrolysis under the influence of water, picric acid being formed. Hydrolysis may take place even in the presence of moisture in the air, so that trinitroanisole may in the course of time form picrates.

The methoxy group is rather reactive and may be substituted. For example, boiling with ammonia leads to the formation of trinitroaniline:



(1)

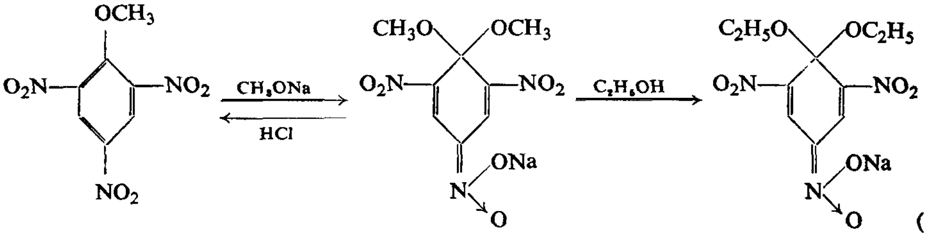
When boiled with ethyl alcohol trinitroanisole is converted to trinitrophenetole:



(2)

It is, therefore, necessary to use methyl alcohol as the solvent for the recrystallization of trinitroanisole.

With sodium- or potassium methoxide, trinitroanisole reacts like sym-trinitrobenzene or α– trinitrotoluene, viz. it adds on an alcoholate molecule, forming a red-coloured addition product (I) :



I II (3)

The quinonoid structure (see p. 202) is assigned to this product. It decomposes by the action of acids to yield trinitroanisole again. Boiling with ethyl alcohol converts the addition product into the analogous derivative of phenetole and sodium ethoxide (II).

TOXICITY

Trinitroanisole is highly toxic. According to Ilzhijfer [4], poisoning by this substance causes headache, weakness, loss of appetite, gastric disturbances and irritation of the mucous membrane of the upper respiratory tract. Its action on the skin is particularly harmful. It causes redness, peeling and in more severe cases blisters, which may join and burst, giving wounds that are difficult to heal. The sensitivity of individuals differs greatly. Inhaling the dust should be avoided. Protective clothing and a daily bath after work are highly recommended for those working with the material. Bare parts of the skin should be protected by a neutral, weakly absorbent ointment, as for example Vaseline (Lazarev [5]).

EXPLOSIVE PROPERTIES

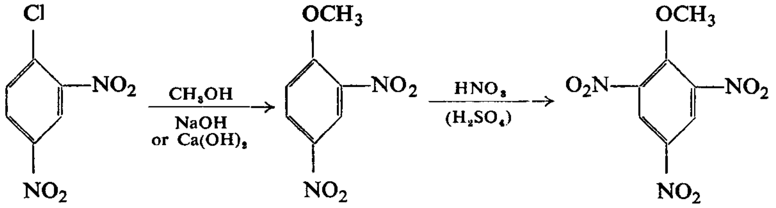
Dry trinitroanisole is very stable: heating at 95°C for 24 hr leaves it unaffected. It is distinctly less sensitive to impact than picric acid - the impact energy figure for explosion produced by a falling weight amounts to 124-129% of that for picric acid. Its explosive power is slightly less than that of picric acid. Desvergnes [6] gave the following comparative values determined in a manometric bomb for densities of loading d = 0.20 and 0.25 g/cm^3.

trinitroanisole	$A = 0.20$ g/cm^3	2145-2222	kg/cm^2
	$A = 0.25$ g/cm^3	2850	kg/cm^2
picric acid	$A = 0.20$ g/cm^3	2210-2310	kg/cm^2
	$A = 0.25$ g/cm^3	3230	kg/cm^2

The maximum rate of detonation is 7640 m/sec at a density of 1.60 g/cm^3.

MANUFACTURE OF TRINITROANISOLE

In industrial practice a process based on the following reaction:



(4)

is used.

In a Japanese factory at Maizuru a two stage process was used for the manufacture of trinitroanisole, namely: alcoholysis of 1-chloro-2,4-dinitroberuene to 2,4-dinitroanisole and subsequently nitration of di- to tri-nitroanisole.

Alcoholysis of 1-chloro-2,4-dinitrobenzene to 2,4-dinitroanisole. To 800 kg of methyl alcohol in the reactor 196 kg of sodium hydroxide and 600 kg of chlorodinitrobenzene are added in 10 equal portions. The reagents are added alternately. During this operation, which requires 7 hr, a temperature at 40-45°C is maintained. Then the temperature is raised to 50°C by heating the reactor jacket and kept there for 30 min, before cooling the whole mixture to 35°C (which takes 3 hr). The crystals of the product together with the mother liquor are then transferred to a vacuum filter for separation. The product obtained is washed four times with water, centrifuged and finally transferred to the nitration plant.

Some 550 kg of dinitroanisole can be obtained, i.e. the yield is 95% of the theoretical.

Nitration of di- to tri-nitroanisole. A conventional type of a nitrator, with a jacket for cooling or heating, but without a coil is used. 3200 kg of a mixture of acids :

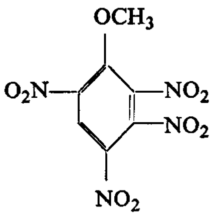
HNO_3	17%
H_2SO_4	77%
H_2O	6%

is charged into the nitrator. The mixture is prepared by fortifying the spent acid.

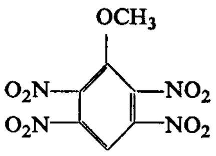
550 kg of dinitroanisole is hand-fed to the nitrator, which requires 6 hr. The temperature is allowed to rise to 50-55°C and is maintained there during the operation. The nitrator contents are then heated to 60-68°C and kept at this temperature for half an hour before being cooled to 35°C. This takes another 4 hr. The trinitroanisole formed is separated from the acid on a filter. The spent acid is fortified with nitric acid (sp. gr. 1.50) and is *m*- used for nitration. The product is washed five times with water which is subsequently removed by centrifuging. In this way 615-620 kg of trinitroanisole is obtained, which is 93% of the theoretical yield.

Purification of trinitroanisole. In the past trinitroanisole was purified by dissolving in methyl alcohol. The solution was filtered and the product precipitated by introducing the solution into water. Later the purification process was simplified, the crude trinitroanisole being agitated with hot water, the water decanted and cold water added to the molten product with constant stirring. In this way granules of trinitroanisole are obtained. They may be separated from water by filtration or centrifugation.

TETRANITROANISOLE



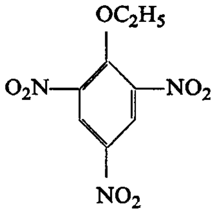
m. p. 94°C



m. p. 151°C

A mixture of the tetranitroanisole isomers may be obtained (according to Claessen [7]) by the nitration of *m*- nitroanisole. The compounds are not stable since their nitro groups in the *meta* position are readily hydrolysed or substituted (van Duin and van Lennep [8]). Their sensitiveness to impact is similar to that of TNT. The expansion they give in a lead block is about 135% of that given by TNT.

TRINITROPHENETOLE



The physical and chemical properties of trinitrophenetole (m. p. 78°C) are similar to those of trinitroanisole. Thus, for example, on the prolonged action of water it undergoes hydrolysis, and its OC_2H_5 group can easily be replaced by an amino group.

By crystallization from methyl alcohol trinitrophenetole is converted into trinitroanisole. It also adds on a molecule of sodium or potassium alcoholate to form a bright coloured salt.

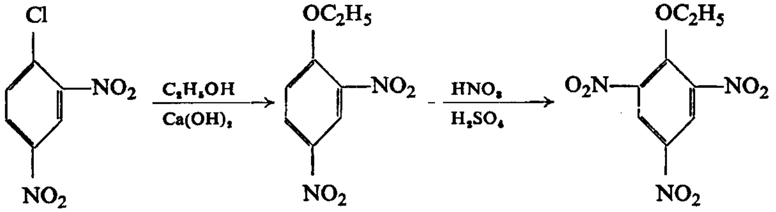
Trinitrophenetole may be exploded by an impact energy amounting to 120% of that required for picric acid. With regard to its explosive power, trinitrophenetole is somewhat weaker than trinitroanisole. Measurements in a manometric bomb by Desvergnes [5] gave the following results:

at a density of loading A = 0.20 g/cm^3 pressure produced was 1774 kg/cm^2
A = 0.25 g/cm^3 „ „ „ 2490 kg/cm^2
A = 0.3 g/cm^3 „ „ „ 3318 kg/cm^2

(see p. 546)

It gives a lead block expansion equivalent to 84% of that produced by picric acid. Its rate of detonation, however, is relatively high - its maximum value being 6880 m/sec.

Trinitrophenetole is prepared in a way similar in principle to that for trinitroanisole :



(5)

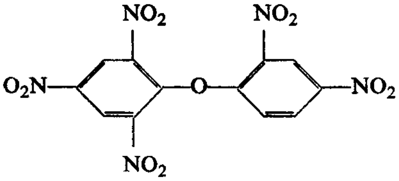
The greatest difficulty to overcome is the nitration of dinitrophenetole to trinitrophenetole, since it must be carried out within a narrow temperature range. Too high a temperature may result in a decomposition of the product, while too low a temperature causes a considerable part of the substance to remain unnitrated. Nitration at 60°C gives the best results.

POLYNITRO DERIVATIVES OF DIPHENYL ETHER

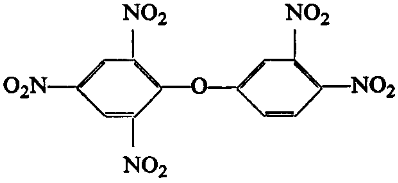
Polynitrodiphenyl ethers (for example hexanitro-) cannot be obtained by the direct nitration of diphenyl ether. Therefore attempts have been made to prepare the polynitro compounds (beginning with the pentanitro compounds) by indirect ways.

PENTANITRODIPHENYL ETHER

Two isomers of pentanitrodiphenyl ether are known:

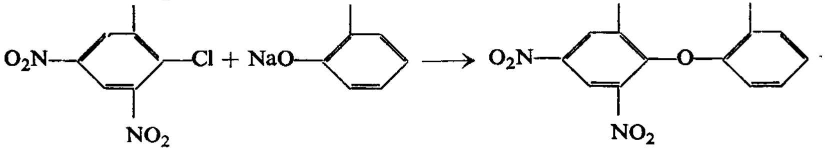


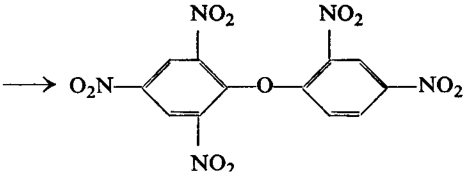
I



II

Isomer I (2,4,6,2’,4’-, m. p. 210°C was obtained by Desvergnes [6] by reacting picryl chloride with sodium *o*- nitrophenate, followed by the nitration:



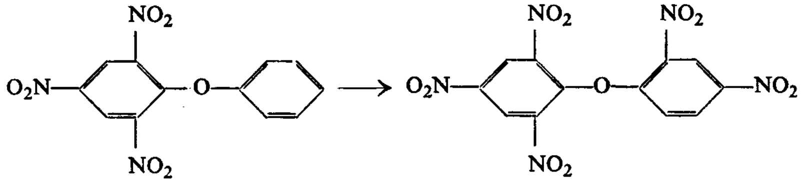


(6)

m. p. 208-210°C

An attempt to introduce one more nitro group so as to obtain symmetric picryl oxide failed, since under the necessary vigorous nitration conditions decomposition of the product took place.

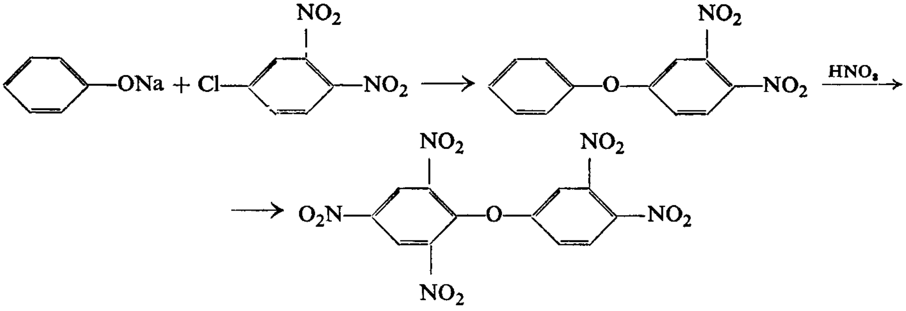
According to Okon [9], compound I may be obtained by the nitration of 2,4,6-trinitrodiphenyl ether (III), which in turn is formed by the action of phenol on picryl-pyridinium chloride (p. 464) :



(7)

III (m. p. 155-156°C) I

Isomer (II) 2,4,6,3',4'-pentanitrodiphenyl ether (m. p. 200°C) is usually prepared by a Westfalisch-Anhaltische Sprengstoffe A. G. method [10], based on the reactions:

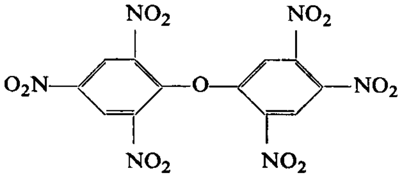


(8)

Neither substance is a strong enough explosive to make their rather expensive production economical.

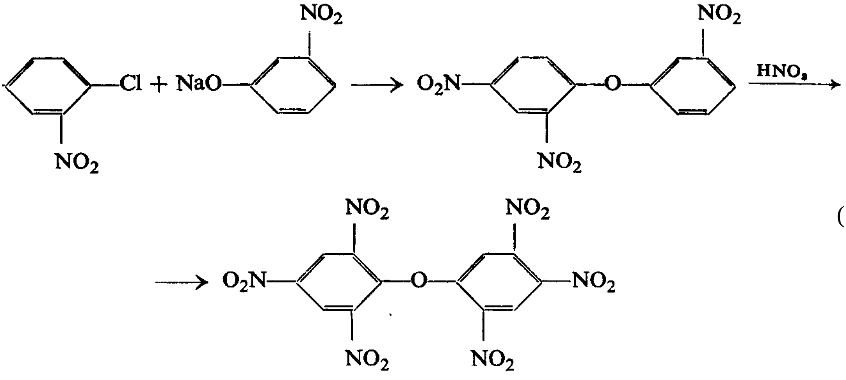
HEXANITRODIPHENYL ETHER

Only unsymmetrical 2,4,6,3',4',6'-hexanitrodiphenyl ether (VI) melting at 278°C (269°C) is known.



IV

It may be prepared by a method described in the patent filed by Westfälisch-Anhaltische Sprengstoffe [10], namely :



IV

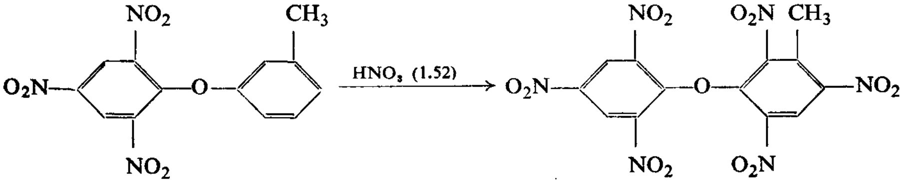
(9)

The authors state that the substance is less sensitive and more powerful than picric acid.

This was not confirmed by van Duin and van Lennep [8] who found the sensitivity of hexanitrodiphenyl ether to be higher than that of tetryl. The same authors determined the initiation temperature to be 318°C. Neither is the stability of the product satisfactory, since after 8 hr heating at 95°C the evolution of nitrogen oxides may be observed.

According to data reported in the literature, sym-hexanitrodiphenyl ether should be considered as an unstable compound and it is to this fact, that the failure to obtain it is usually ascribed.

Recently Okori and Grabowski [ll] have proved that the whole system can be stabilized by the presence of a methyl group on one of the benzene rings, in the *meta* position to the ether bond. The stable compound VI can be obtained by nitrating *m*- cresylpicric ether (V) with pure (100%) nitric acid:



V

VI

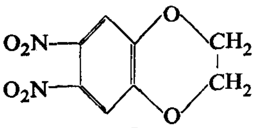
m. p. 220-222°C

(10)

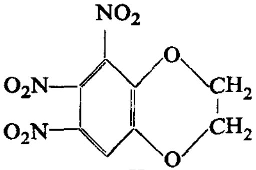
NITRO DERIVATIVES OF VARIOUS PHENOLIC ETHERS

Polynitro derivatives of the simplest cyclic ether of pyrocatechol-1,2-ethylenedioxybenzene are interesting because of the position of the nitro groups (Vor-Kinder [12]).

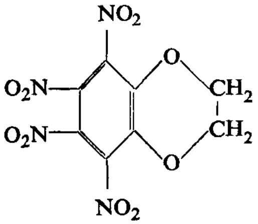
They are di-, tri- and tetra-nitro compounds (I), (II) and (III) respectively:


I

m. p. 132-134°C


II

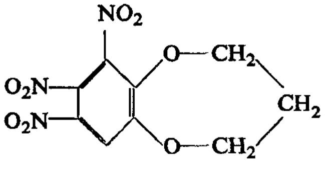
m. p. 156°C


III

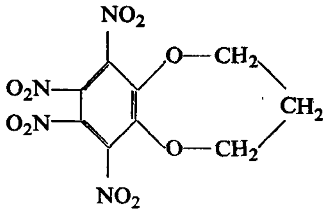
m. p. 286°C

(G. M. Robinson and R. Robinson [13], Gosh [14], Heertjes, Dahmen and Wierda [11).

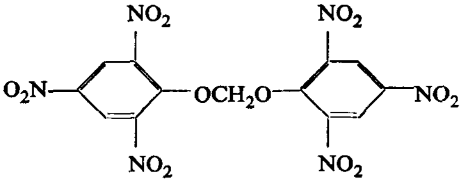
Hackel and Kuboszek [16] prepared tri- and tetra-nitro derivatives of l,2-propylenedioxybenzene, (IV) and (V) respectively:


IV

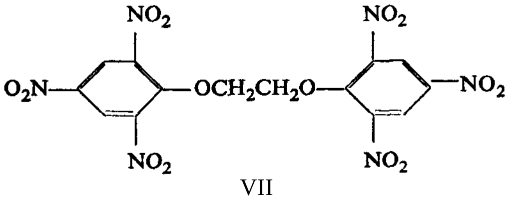
m. p. 170°C


V

m. p. 185°C


VI

m. p. 105-107°C

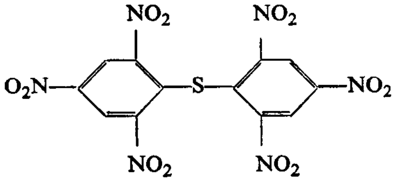

VII

m. p. 196-197°C

The two compounds VI and VII were prepared by nitrating methylene- and ethylene-diphenyl ethers respectively (Stefanovic and Ciric [16a]).

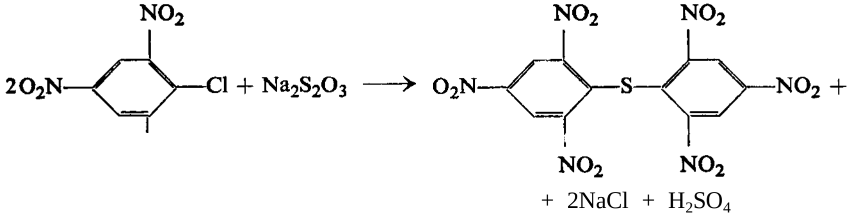
HEXANITRODIPHENYL SULPHIDE

Only one representative of this group is known in industrial practice, namely hexanitrodiphenyl sulphide (picryl sulphide, hexasulphide, Hexide) of melting point 234°C.



2,2',4,4',6,6'-Hexanitrodiphenyl sulphide forms golden crystals, difficult to dissolve in most organic solvents.

The compound was first obtained by Sprengstoff A. G. Carbonit [17], in 1912, from picryl chloride and sodium thiosulphate in alcoholic solution in the presence of magnesium carbonate for binding the sulphuric acid which forms in the reaction:



(11)

The yield obtained is about 90% of the theoretical. According to Giua [18], thiourea may be used in place of sodium thiosulphate.

The compound may also be prepared from picryl-pyridinium chloride (see p. 464).

The product does not colour the skin and, according to the German literature, is not toxic. However, Roche and V. Thomas [19] reported its vapour to be strongly irritant. During World War I the Germans used picryl sulphide in mixtures with TNT, with or without ammonium nitrate, for filling bombs.

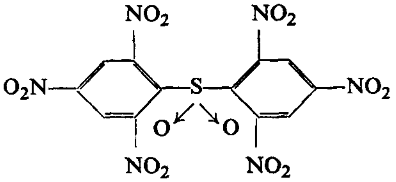
Since the explosive decomposition of picryl sulphide and of its mixtures yields SO_2 among other decomposition products, the compound has been proposed for filling shells to be used against confined objectives, such as ships' interiors, bunkers, etc. As a result of explosion a noxious atmosphere containing SO_2 would result.

Picryl sulphide is a stable explosive. Van Duin and van Lennep [8] found its initiation temperature to be 302-319°C depending on the rate of heating. When kept at 95°C for 30 days the substance remained unchanged.

Its sensitiveness to impact is somewhat lower than that of tetryl, but higher than that of hexyl or picric acid.

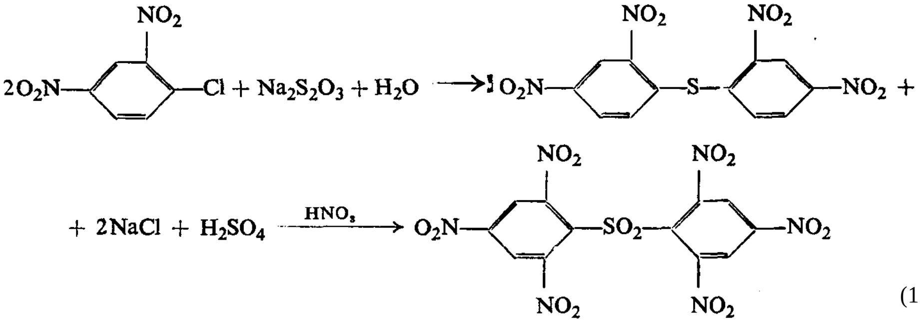
The lead block expansion given by picryl sulphide is equal or, according to some authors, slightly larger than that given by picric acid (325-350 cm^3).

HEXANITRODIPHENYL SULPHONE



2,2’,4,4’,6,6’-Hexanitrodiphenyl sulphone (m. p. 307°C, decomposition) forms yellowish crystals difficult to dissolve in most organic solvents.

In 1912 Sprengstoff A. G. Carbonit [17] was granted a patent for a method of preparation of this explosive, consisting in reacting hexanitrodiphenyl sulphide with nitric acid. Since picryl chloride, as the starting material for picryl sulphide was rather expensive, another method of preparation of hexanitrodiphenyl sulphone, via tetranitrodiphenyl sulphide, was also used. The latter was obtained by treating chlorodinitrobenzene with sodium thiosulphate. Then it was nitrated and oxidized simultaneously with nitric acid to hexanitrodiphenyl sulphone:



(12)

During World War I the compound was used by the Germans in mixtures with TNT and sometimes also with ammonium nitrate for filling bombs.

Hexanitrodiphenyl sulphone proved to be a stable compound. According to van Duin and van Lennep [8], it withstands heating at 95°C for 30 days. Its initiation temperature is 297-308°C depending on the rate of heating.

It is a more powerful explosive than hexyl or picryl sulphide, mainly due to a more favourable oxygen balance, and also surpasses picric acid. Its sensitivity to impact is of the order of tetryl.

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CHAPTER XVII

NITRO DERIVATIVES OF ANILINE

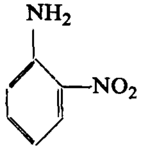
Apart from tetryl, which is discussed in the chapter on nitramines (Vol. III), the only aniline nitro derivative that has gained any considerable importance as an explosive is hexanitrodiphenylamine, or hexyl. None of the other nitro derivatives has proved of greater interest: though some achieved temporary importance (as for example tetranitroaniline) or aroused a theoretical interest.

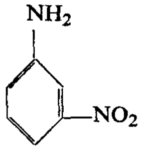
The introduction of nitro groups to a compound containing a NH_2 group presents some difficulties, because of the high reactivity of this group and because of the readiness of such compounds to undergo oxidation. Therefore, a nitro group should be introduced into aniline or its homologues (other than N-substituted) only after the amino groups had been protected by acylation, for example to acetanilide.

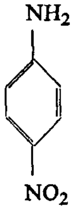
A more modern method of preparation of nitroaniline derivatives consists in using chlorodinitrobenzene as starting material. Advantage is taken of the reactivity of its chlorine atom which can be substituted by an amino group.

MONONITRO DERIVATIVES OF ANILINE

Three isomeric nitroanilines: ortho- (m. p. 71.5°C), *meta*- (m. p. 114°C) and *para*- (m. p. 148°C) are known.







Para-nitroaniline was obtained by A. W. Hofmann [1] who nitrated acetanilide to *p*- nitroacetanilide which was then hydrolysed with a sodium hydroxide solution.

Khmer [2] found that acetanilide when nitrated also yields *o*- nitroacetanilide, from which *o*- nitroaniline may be obtained by hydrolysis. The nitration of acetanilide had been applied for a long time as a commercial method of preparation of *o*- and *p*- nitroanilines and was investigated by a number of authors including Beilstein and Kurbatov [3] and Holleman [4]. The mononitation of acetanilide can be effected even with 80% nitric acid.

Walker and Zincke [5] found that *o*- and *p*- nitroanilines could be obtained by heating corresponding bromonitro derivatives of benzene with ammonia under elevated pressure. The high yield of the reaction was due to the enhanced reactivity of Br in the presence of the nitro group. The reaction has been utilized for the commercial preparation of *o*- and *p*- nitroanilines. *Ortho*- or *p*- chloronitrobenzenes are used as starting material.

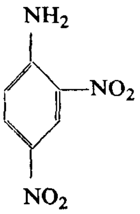
Meta- nitroaniline was first prepared by Muspratt and A. W. Hofmann [6] in 1846, by the reduction of *m*- dinitrobenzene with ammonium sulphide. Nowadays with sodium sulphide used as reducing agent, this method is applied for the commercial production of *m*- nitroaniline.

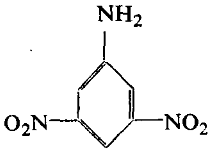
Nitroanilines may also be obtained by direct nitration of aniline (Bruns [7]), provided that a solution of aniline sulphate in sulphuric acid is prepared first, and then carefully introduced into a mixture of nitric acid with concentrated sulphuric acid. A condition necessary for success is that the reaction temperature must not exceed 0°C.

Among the three isomeric nitroanilines only *m*- nitroaniline was of any importance in explosives technology, being a starting material for the preparation of tetranitroaniline.

DINITRO DERIVATIVES OF ANILINE

From among a number of dinitroaniline isomers known, only the 2,4- and 3,5-isomers (m. p. 187°C and 161°C respectively) are of importance from the point of view of explosives chemistry:





2,4-Dinitroaniline forms yellow needles, difficult to dissolve in cold alcohol. The compound was obtained by Rudnev [8] by vigorous nitration of acetanilide to 2,4-dinitroacetanilide with an almost anhydrous nitrating agent, followed by hydrolysis of the product.

Nowadays 2,4-dinitroaniline is prepared on a large scale by treating chlorodinitrobenzene with ammonia. The method was first reported by Engelhardt and Lachinov [9] in 1870. Heating 2,4-dinitrophenol with an excess of urea at 208°C

(Kym [10]) is another convenient method of preparation of 2,4-dinitroaniline. Further nitration of 2,4-dinitroaniline leads to 2,4,6-trinitroaniline (picramide).

3,5-Dinitroaniline is usually obtained from 1,3,5-trinitrobenzene by reduction of a nitro group with sodium hydrosulphide. It may be used as starting material for the preparation of pentanitroaniline.

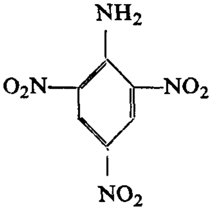
2,4-Dinitroaniline has weak explosive properties of the order of *m*- dinitrobenzene. However, its sensitivity to impact, according to Wöhler and Wenzelberg [10] is considerably higher than that of dinitrobenzene and similar to that of TNT.

The manufacturing process applied for the production of 2,4-dinitroaniline at I. G. Höchst was as follows:

To 1700 1. of water 600 kg of chlorodinitrobenzene (m. p. not below 50°C) are added while stirring, followed by 530 1. (480 kg) of 26.5% aqueous ammonia. The whole is kept at 70°C for 2 hr. When the reaction has started the steam flow must be stopped for a while since the temperature rises spontaneously to 115-120°C (within 152 hr) due to the heat of the reaction. The pressure in the reactor rises to 2 atm. After the temperature has become constant, steam is passed again to keep the reactor contents at this temperature for another 4 hr. The temperature should not exceed 130°C.

Then the reaction mixture is cooled while stirring, the precipitated product is filtered off on a stoneware filter, washed with water until neutral and dried in a shelf drier at 50°C for 12-16 hr. The product is obtained in almost theoretical yield.

TRINITROANILINE (PICRAMIDE)



Picramide or 2,4,6-trinitroaniline (m. p. 190°C) forms deep yellow crystals, difficult to dissolve in alcohol and ether but easily soluble in hot acetone, benzene and ethyl acetate.

The compound was first obtained by treating picryl chloride (Pisani [12]) or trinitroanisole with ammonia (Salkowski [13]). Later Witt and Witte [14] obtained it by the nitration of *o*- or *p*- nitroacetanilide in oleum solution. For the nitration a solution of KNO_3 in concentrated sulphuric acid was used. Spencer and Wright [15] applied Kym's method [lo] for the preparation of picramide, heating picric acid with urea at 173°C for 36 hr. The yield obtained was about 90% of the theoretical.

CHEMICAL PROPERTIES

Like most polynitro-aromatics, picramide forms addition compounds with condensed ring aromatic hydrocarbons. Compounds containing their constituents in 1:1 molecular proportion include those with:

	melting point, °C
naphthalene, orange crystals	168-169
anthracene, red crystals	165-170
aniline, dark red crystals	123-125
dimethylaniline, dark blue crystals	139-141

By thermoanalysis Jefremov [16] found that similar compounds, also in the molecular proportions of 1:1, were formed by picramide with:

	melting point, °C
acenaphthene	195.4
phenanthrene	160.2
retene	125.1
fluorene	(non-uniformly melting)

According to Jefremov, picramide forms eutectics with:

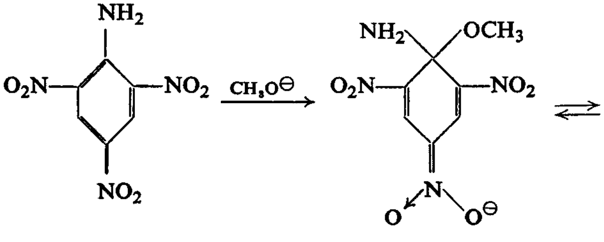
	melting point, °C
11.5% of picric acid	113.5
15.9% of tetryl	110.8
76.5% of trinitroxylene	110.8

Picramide may be used for the preparation of tetranitrobenzene (p. 257). Boiling picramide with a sodium hydroxide solution results in its hydrolysis, picric acid and ammonia being formed. This is due to an action of nitro groups on the amino group.

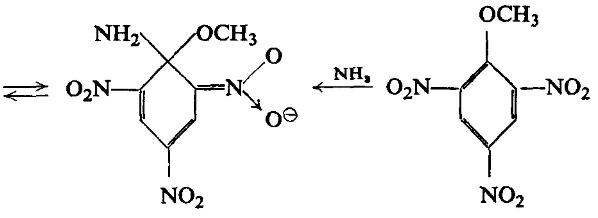
Picramide reacts with sodium methoxide in the same manner as trinitrobenzene, forming coloured solutions. Some solid salts have been prepared by Busch and Kögel [17]. Recently Farmer [18] found that the coloured compound I can be obtained by two methods:

(a) by the action of methoxides on trinitroaniline;

(b) by the action of ammonia on trinitroanisole:



Ia

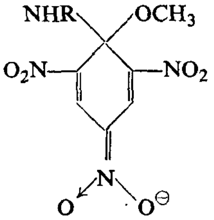


Ib

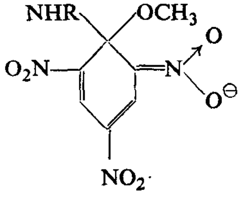
(1)

Acidification of I regenerates picramide.

If instead of ammonia a primary amine NH_2R is used N-substituted picramides are formed through an intermediate IIa or IIb:

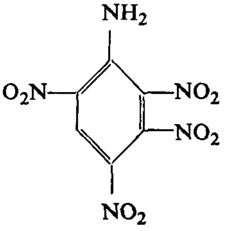


IIa



IIb

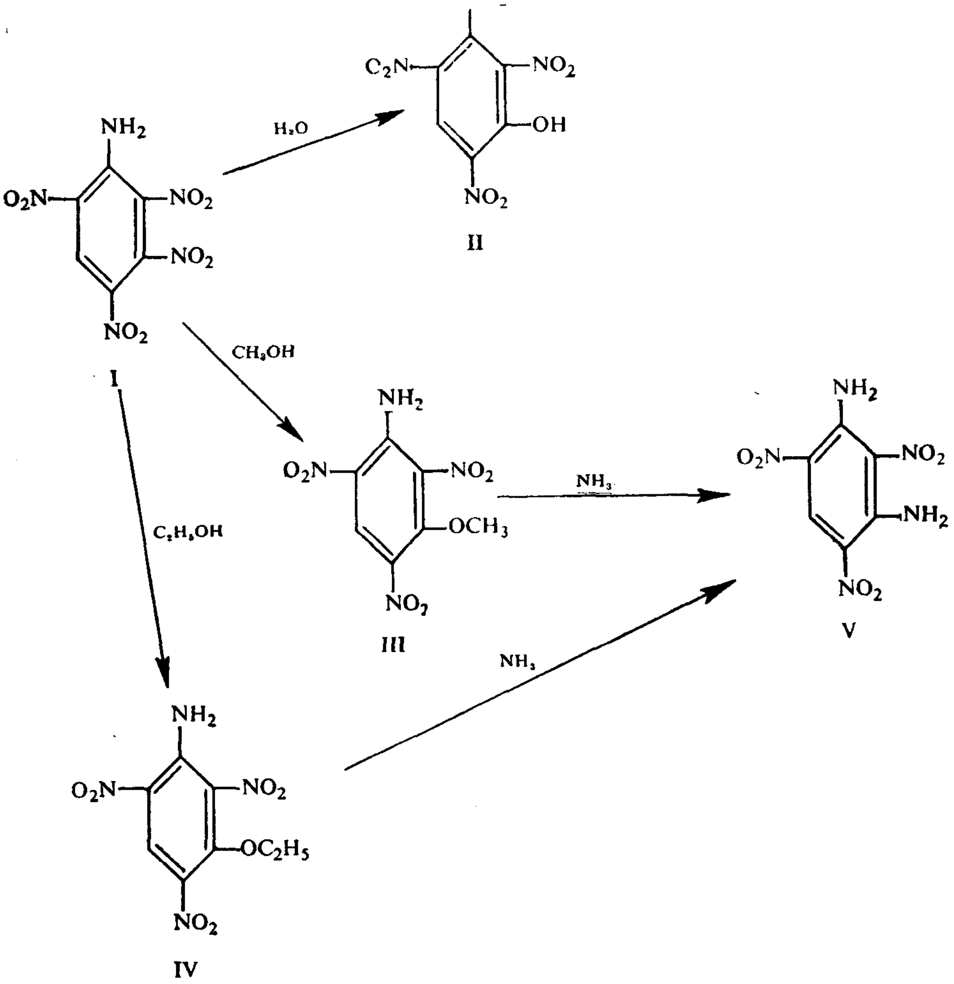
TETRANITROANILINE



2,3,4,6-Tetranitroaniline (m. p. 215°C, decomposition) is a yellowish crystalline substance, difficult to dissolve in most of organic solvents but soluble in acetone (17 parts in the boiling solvent) and *o*- nitrotoluene (some 33 parts at 140°C).

Tetranitroaniline was first obtained by Flürscheim [19, 19a], who proposed its use as an explosive because its properties were similar to those of tetryl. For the preparation of tetranitroaniline Flürscheim nitrated *m*- nitroaniline with a mixture of concentrated acids at 70-80°C. The yield was 64-69% of the theoretical (from 100 kg of *m*- nitroaniline only 130-140 kg instead of 204 kg could be obtained).

Tetranitroaniline is a rather unstable compound. Thus, when boiled with water its *meta*- nitro group undergoes hydrolysis to a phenolic group (II), while on boiling with methyl- or ethyl alcohol it yields an anisole- (III) or phenetole derivative (IV), which with ammonia may form trinitro-m-phenylenediamine (V):



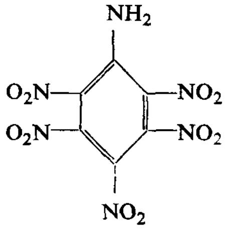
Although, according to Flürscheim, tetranitroaniline has sufficient thermal stability, even a product of the highest purity does not give a satisfactory heat test.

According to Ingraham [19b], tetranitroaniline has shown evidence of decomposition by the heat test at 65.5°C when only a small amount of moisture was piesent. The main product of decompositions was II. Prolonged heating at 75°C results in loss of a nitro group. At 120°C decomposition takes place which proceeds in a way similar to that of tetryl. The initiation temperature is 231-233°C. The specific gravity of the product is 1.867 [19].

With regard to explosive power and sensitiveness to impact tetranitroaniline does not differ from tetryl. However, because of its poor stability it has not found any practical use.

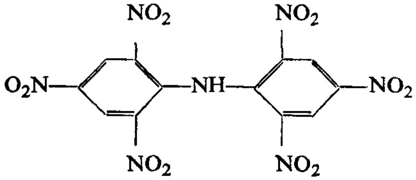
Tetranitroaniline may be utilized as starting material for the preparation of stable compounds II, III and V. However, none of them exhibits any properties which would justify the high costs of their application as explosives.

PENTANITROANILINE



Flürscheim and Holmes [20] obtained pentanitroaniline (m. p. 238°C, decomposition) by the nitration of 3,5-dinitroaniline (p. 557). The product has proved to be a powerful explosive, of the order of penthrite or hexogen. However, its nitro groups located in the 3- and 5-positions can readily be split off or substituted, making the compound insufficiently stable for use as an explosive.

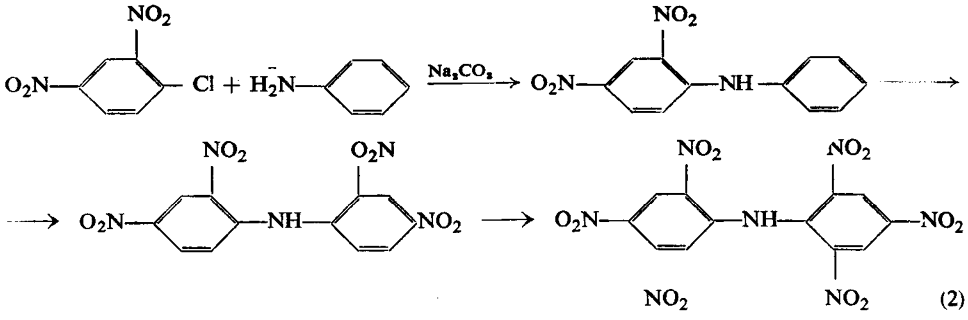
HEXANITRODIPHENYLAMINE (HEXYL)



2,2',4,4',6,6'-Hexanitrodiphenylamine (m. p. 243-245°C) was first mentioned in the chemical literature in 1876 and as long ago as 1891 Haussermann [21] drew attention to its explosive properties. The product is known under the names of Dipicrylamine, Hexyl, Heksyl, Hexamite, Hexamin, etc.

The application of hexyl as an explosive goes back as far as 1910. It was widely used in Germany during the two World Wars, mostly in fusible compositions, with TNT and with or without ammonium nitrate as a third constituent for filling torpedoes, marine mines, bombs and whenever a particularly high explosive power was required. During World War II aluminium was also added to hexyl compositions (Vol. III).

Gnehm [22] prepared hexanitrodiphenylamine by the nitration of diphenylamine with nitric acid, while Mertens [23] used a mixture of anhydrous nitric acid with concentrated sulphuric acid for the purpose. This method was applied in 1910 for the commercial preparation of hexyl. Since the yields obtained were too low (some 60% of the theoretical), during World War I a method patented in 1895 by the Griesheim Works was introduced, the starting materials being chlorodinitrobenzene and aniline. The method consists in the preparation of dinitrodiphenylamine (m. p. 156-167°C) which is then nitrated in two stages, to obtain first tetranitrodiphenylamine (m. p. 199°C) and then hexyl:



(2)

PHYSICAL PROPERTIES

2,2',4,4',6,6'-Hexanitrodiphenylamine forms yellow needles, which decompose while melting. It is difficult to dissolve in concentrated sulphuric acid and in most organic solvents. It dissolves more easily in hot acetic acid, nitrobenzene and acetone. The pyridine salt of hexyl is still more readily soluble in acetone.

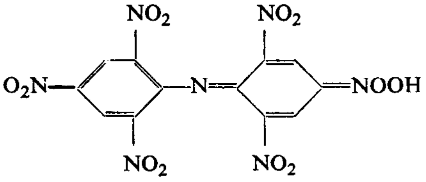
At room temperature hexyl is only slightly hygroscopic: when exposed to the air saturated with water vapour it absorbs only 0.09% moisture. The specific gravity of hexyl crystals is 1.653. Hexyl is rather difficult to press, but when mixed with 1% stearic acid more satisfactory pressing can be achieved and a uniform material obtained.

Densities obtainable under various pressures are :

below	330	kg/cm^2	density	1.43	g/cm^3
,,	660	,,	,,	1.56	,,
,,	1000	,,	,,	1.59	,,
,,	1330	,,	,,	1.60	,,

CHEMICAL PROPERTIES

The acidic character of hexyl is one of its most important features. It was first observed by Aleksandrov [24] when preparing ammonium salt of hexyl. Later this property was investigated by Hantzsch and Opolski [25], who obtained the O-methyl ether of the aci-form of hexyl, according to Hantzsch's nomenclature (Ia). The aci-form of the compound can yield salts and O-ethers (esters). It is intensely coloured due to the presence of the quinonoid ring.



Ia

The ammonium salt of hexyl known as "Aurantia" had been used for a long time as a yellow dye for silk and wool.

Hexyl seriously attacks the skin. First it dyes it yellow, then a serious eczema appears, with blisters often reminiscent of those caused by burns. Air-borne dust of the product may cause severe irritation of the mucous membranes and of the respiratory tract. Workers exposed to the action of large quantities of hexyl should be protected from inhaling its dust and from contact of the latter with the skin, by good ventilation and protective masks and clothing. The toxicity of hexyl is much higher than that of TNT (p. 161).

EXPLOSIVE PROPERTIES

Hexyl is a chemically stable compound. As van Duin and van Lennep [26] found it can withstand 30 days' heating at 95°C. They also determined its initiation temperature as being 250°C when heated at a rate of 5°/min.

Its sensitivity to impact is lower then that of tetryl but somewhat higher than that of picric acid. Kast [27] found that picric acid is exploded by a 2 kg weight falling from 60 cm, while tetryl and hexyl are exploded by fall from 40 cm.

With a 10 kg falling weight picric acid exploded at the 20 cm height, hexyl at 10 cm and tetryl at 8 cm.

Salts of hexyl, in particular those formed with heavy metals, are more sensitive to impact and friction than hexyl itself. They are inflammable and can be ignited by a flame. The ammonium salt is an exception here, being the least sensitive and not ignited by the flame, behaving like hexyl itself.

Haussermann [22] pointed out that hexyl is a more powerful explosive than TNT. Further investigations yielded the following data on the explosive properties of the substance (Kast [27]):

heat of explosion	1035 kcal/kg
volume of gases, V_0	675 I./kg
temperature, t	3450°C
specific pressure, f	9545 m

According to Kast, the heat of formation is negative and amounts to -4.6 kcal/kg (dH_f = +4.6 kcal/kg).

For rate of detonation the following figures have been reported:

at a density of 1.58 g/cm^3	6900 m/sec	(J. Marshall [28])
,, ,, ,, ,, 1.64 ,,	7100 ,,	(Kast [27])
,, ,, ,, ,, 1.67 ,,	7150 ,,	(J. Marshall [28])

The lead block expansion given by hexyl is 325-350 cm^3 - larger than that caused by picric acid.

Hexyl can be brought to detonation as easily as tetryl, or even more easily. For example, J. Marshall [28] has determined the minimum quantities of fulminate of mercury and potassium chlorate mixtures (90:10), required for detonation of:

hexyl	0.18 g
tetry1	0.20 ,,
TNT	0.25 ,,

HEXYL MANUFACTURE

Preparation of dinitrodiphenylamine (Ludwigshafen Process)

An emulsion of 380 kg of aniline in about 1600 1. of an aqueous solution containing 230kg of sodium carbonate and 1 kg of Nekal (emulsifier) is prepared. After the emulsion has been heated to 60°C, 800 kg of molten 2,4-chlorodinitrobenzene is run in. Then the whole is heated to 90°C. The formation of solid dinitrodiphenylamine may serve as a control indicating the progress of the reaction.

The solution is cooled to about 50°C, dinitrodiphenylamine is separated by tentrifuging, washed with diluted acid (from the nitration process) to remove aniline, then thoroughly with water, dried at 100°C and pulverized. The product can be obtained in almost theoretical yield 95-98%.

Nitration of di- to tetra-nitrodiphenylamine (after J. Marshall [28])

100 parts of dry dinitrodiphenylamine are charged into the nitrator, containing 350-400 parts of a nitrating mixture of the composition:

HNO_3	30-45%
H_2SO_4	40-50%
H_2O	15-20%

a temperature of 70°C being maintained during this procedure. When all the substance has been run in, the whole is heated to 80-90°C and kept at this temperature until nitrogen dioxide stops evolving, which takes about 2 hr. Then the nitrator contents are cooled and the yellowish brown crude product is separated from the spent acid by filtration.

The approximate composition of the spent acid obtained in a series of runs averaged :

HNO_3	14%
H_2SO_4	51%
nitrosylsulphuric acid	7.5%
H_2O	26%
organic matter	1%

Nitration of tetranitrodiphenylatiine to hexyl (after J. Marshall [28]).

Immediately after being filtered off, tetranitrodiphenylamine (containing some acid) is taken in a quantity corresponding to 100 parts of the dry substance and added to 375 parts of a nitrating mixture:

HNO_3	60%
H_2SO_4	40%

When using a mixture poorer in nitric acid, consisting e.g. of 25% of HNO_3 and 75% of H_2SO_4, a very fine crystalline product difficult to filter is obtained.

During the reaction a temperature of 70°C is maintained. After all the tetranitrodiphenylamine has been added, the reaction mixture is heated to 90°C, kept at this temperature for one hour, cooled down to room temperature and filtered on a vacuum filter. A yellow crystalline, easily filterable product is obtained. The spent acid is approximately of the following composition:

HNO_3	34%
H_2SO_4	40%
nitrosylsulphuric acid	11%
organic matter	1%

The product is well washed with water, then transferred to a washing tank, where it is washed 2-3 times by agitating with boiling water. The washings are separated by decantation. The water remaining in the washed product is separated on a vacuum filter (J. Marshall recommends a centrifuge for this purpose but this procedure should be considered as too hazardous). The wet product, after being dried at 80°C, is of high purity, as reflected by its melting point which ranges from 238.5° to 239.5°C.

The yield obtained for the conversion of dinitrodiphenylamine into hexyl is 86% of the theoretical.

Japanese method

Japanese process for preparing hexanitrodiphenylamine from dinitrodiphenylamine was applied at the Maizuru Works. A stainless steel nitrator is charged with 80% nitric acid, followed by dinitrodiphenylamine. A temperature of 45-55°C is maintained during this procedure, which takes 4 hr. Then the temperature is raised to 90-95°C during one hour and a half and kept there for another hour and a half. Then the whole is cooled to 45°C, the precipitated hexanitrodiphenylamine is filtered off on a vacuum filter and transferred to a tank, where it is washed with cold water, then three times with hot water, and finally again with cold water. The remaining water is separated from hexyl by centrifugation, followed by drying.

The spent nitric acid may be fortsed by mixing with 98% nitric acid.

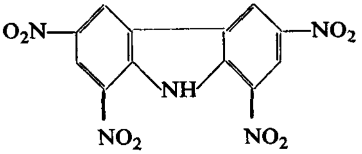
NITRO DERIVATIVES OF CARBAZOLE

The nitration of carbazole has been studied by Graebe [29], Ciamician and Silber [30], VotoEek [31], Escales [32] and Raudmtz [33].

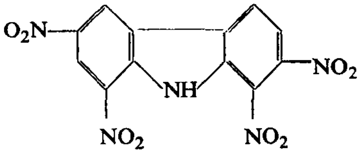
Mono-, di- and tetra-nitro derivatives of carbazole have been obtained. Among them only tetranitrocarbazole is of practical importance. It was used in Germany under the name of “Nitrosan” as an insecticide. During World War II it was used under the name of “Gelbmehl” in combustible compositions for delayed action time fuses.

TETRANITROCARBAZOLE

There are two isomeric tetranitrocarbazoles: 1,3,6,8- (I) (m.p. 296°C) and 1,2,6,8- (II) (m.p. 153-154°C).



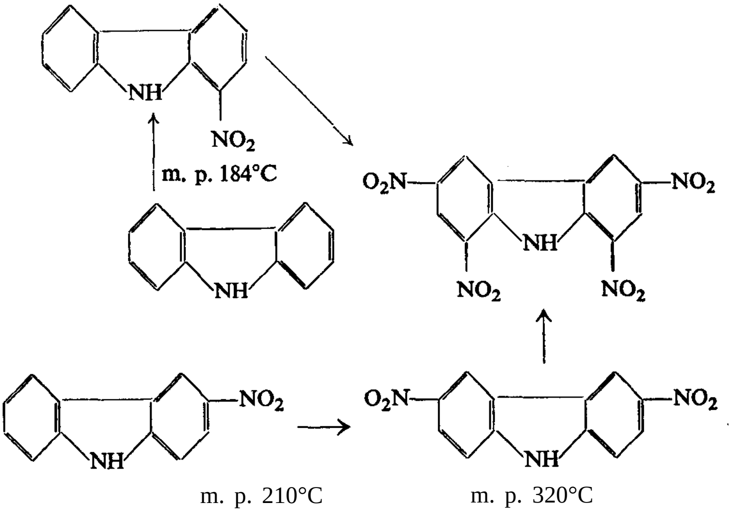
I



II

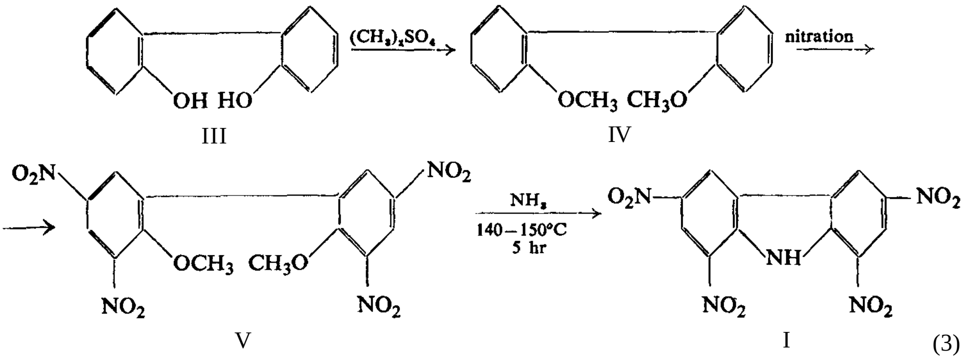
They are usually prepared by the direct nitration of carbazole with a mixture of nitric and sulphuric (or acetic) acid. The most convenient way of nitrating carbazole is sulphonation followed by the action of concentrated nitric acid. 1,3,6,8-Tetranitrocarbazole (I) is obtained as the principal product.

The following intermediate products have been isolated in the course of the nitration of carbazole :



In addition to the 1,3,6,8-isomer a product, named by Ciamician and Silber the γ– isomer, has been obtained, which, according to recent investigations, has proved to be the 1,2,6,8-isomer (II). From the reaction product pure compound I may be isolated by extraction with toluene, followed by crystallization from acetic acid. The pure product I may also be obtained by treating the crude product with sodium sulphite. According to Murphy, Schwartz, Picard and Kaufman [34], the melting point of the product may be raised in this way from 278° to 296°C at the cost of a 10% loss of yield. The same authors found that during the nitration process the 1,2,6,8-isomer (II) is formed along with the principal product. This isomer may be obtained in a larger quantity if carbzole is subjected to sulphonation with oleum prior to nitration.

The constitution of tetranitrocarbazole (I) was determined by Borsche and Scholten [35] from the following reactions, of which the final stage was the formation of tetranitrocarbazole with a certain quantity of 3,3',5,5'-tetranitro-2,2'-dimethoxydiphenyl (V). The sequence of the reactions was as follows:



(3)

MANUFACTURE OF 1,3,6,8-TETRANITROCARBAZOLE

In a method applied at Höchst, 1896 kg of 96% sulphuric acid are charged into the sulphonator, followed by 950 kg of commercial grade carbazole (88-95° purity). The whole is stirred at room temperature for 50 min. Then the temperature is raised to 95°C and stirring is continued until a sample taken from the sulphonator dissolves completely in water. At this stage of the process disulphonic acid is formed. Then the sulphonator contents are cooled to 70°C and the remainder of the sulphuric acid, i.e. 1561 kg (the total quantity being 3430 kg) is added. Further sulphonation takes place, resulting in the formation of 1,3,6-trisulphonic acid.

It has been proved that carrying out the reaction in two stages, as described above, makes the sulphonation process proceed more quietly and prevents the SO_3H group from entering position 7 (otherwise, the sulpho group in position 7 would not be substituted by a nitro group, causing the nitration product to remain soluble in water).

A two stage process is applied for the nitration of the sulphonic acid obtained. The product is transferred to nitrator I and here half the total nitrating acid is added. Then half the contents of nitrator I are transferred to nitrator II followed by the second half of the nitrating acid. The sulphonated product is transferred from the sulphonator to nitrator I, containing half of the previous batch, for repeating the first nitration stage, then half of this reaction mixture is transferred to nitrator II, and so on.

Nitrator I contains half of the previous batch to which the sulphonator contents and a portion of nitrating acid, consisting of 870 kg of concentrated nitric acid and 4350 kg of 20% oleum, have been added. The nitrating acid should be run into the nitrator at a temperature of 40°C (vigorous cooling is necessary). This nitration stage, including the transfer of the sulphonated product, takes about 8 hr.

The other half of the contents of nitrator I is conveyed to nitrator II and the second half of the nitrating mixture, consisting of 870 kg of concentrated nitric acid and 4350 kg of 20% oleum, is run in, a temperature of 50°C being maintained.

Then the whole is heated to 60°C which initiates a further spontaneous temperature rise. Care should be taken by cooling to prevent the temperature rising above 95°C, otherwise the yield might decrease. The process in nitrator 11, including the transfer of contents from nitrator I, takes approximately 8 hours.

Half the contents of nitrator II is then transferred to a tank with 6000 1. of water, a temperature of it below 50°C being maintained. This operation requires from 4 to 6 hr, and when the tank has been discharged, the second half of the contents of nitrator I1 is treated in the same way.

The precipitated product is filtered off and washed with water warmed to a temperature not exceeding 50°C. Since moist tetranitrocarbazole is thixotropic the filtration and washing is rather difficult to effect. The moist product is mixed in a tank with a concentrated solution of 20 kg of sodium carbonate to deacidify it, then filtered off and dried.

The product meets the following specifications:

melting point	281-290°C
sulphur content	0.8-1.3%
moisture	1-2%
nitrogen content	18.5-19.5% (theoretical 20.2%)

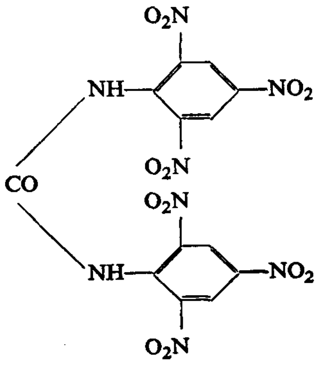
PREPARATION OF 1,2,6,8-TETRANITROCARBAZOLE

According to Murphy, Schwartz, Picard and Kaufman [34], 50 parts of carbazole is dissolved in 300 parts of 30% oleum at a temperature of 40-50°C. The mixture is kept at 90-100°C for 2 hr. A sample of the mixture taken after this time should dissolve completely in water. Then the mixture is cooled and 160 parts of 93% nitric acid are added, the temperature being maintained at 40-60°C. 1,2,6,8-Tetranitrocarbazole precipitates, and may be recrystallized from nitrobenzene solution. The 1,3,6,8-isomer remains in the solution.

AMIDE DERIVATIVES OF TRINITROANILINES

Several rather simple acid amides have been tested as explosives. However, they have not found practical used since they readily undergo hydrolysis.

HEXANITRODIPHENYLUREA



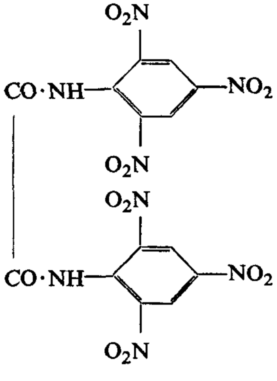
Hexanitrodiphenylurea (hexanitrocarbanilide, sym-dipicrylurea) forms pale yellow crystals melting at 208-209°C (with decomposition). It was obtained by Perkin [36] and Reudler [37]. Davis [38] was the first to suggest its use as an explosive. The compound is prepared by the nitration of sym-diphenylurea, which may be obtained by reacting phosgene with aniline, or more simply, by heating aniline with urea at 160-165°C. Davis proposed the nitration of diphenylurea in two stages: first tetranitrodiphenylurea is obtained, and this in turn is nitrated to hexanitrodiphenylurea.

When heated with dilute sulphuric acid, hexanitrodiphenylurea is hydrolysed, forming picric acid. With ammonia it produces a deep red colour, which is ascribed to the formation of an ammonium salt of the aci-form. Boiling with aqueous ammonia solution causes hydrolysis with the formation of picramide.

The compound has a high initiation temperature (345°C). However, because of its susceptibility to hydrolysis its chemical stability is too low for it to be used as an explosive, although its explosive power is somewhat higher than that of TNT. Its sensitivity to impact is similar to that of tetryl.

HEXANITRO-OXANILIDE

The use of hexanitro-oxanilide (m. p. 295-300°C) as an explosive material was suggested by the Societe Anonyme d’Explosifs [39].

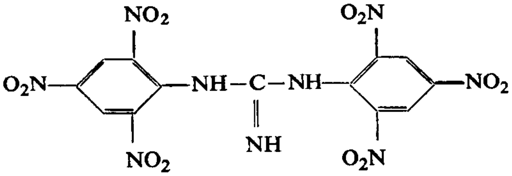


The compound is prepared by the direct nitration of oxanilide (Mixter and Walther [40]). Domanski and Mieszkis [41] investigated the explosive properties of hexanitro-oxanilide and found the following values for the rate of detonation of the pressed product mixed with 2% of dinitrotoluene:

at a density of 0.90 g/cm^3	5100 m/sec
,, ,, ,, ,, 1.20 ,,	5500 ,,
,, ,, ,, ,, 1.47 ,,	6800 ,,

It follows from the above that the explosive power of the compound is similar to that of TNT. The fact that it readily undergoes hydrolysis, forming picric acid and oxamide is a serious drawback and prevents its use as an explosive.

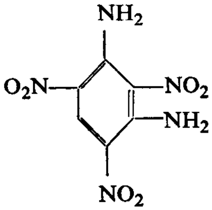
HEXANITRODIPHENYLGUANIDINE



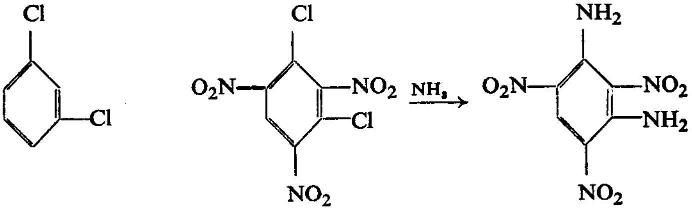
This compound was suggested by Jackman and Olsen [42] as an explosive. The authors prepared it by the nitration of diphenylguanidine.

NITRO DERIVATIVES OF AMINOPHENOLS

TRINITRO-m-PHENYLENEDIAMINE



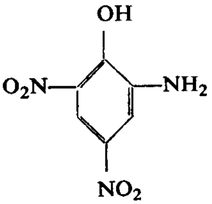
This explosive (m. p. 285°C) was first obtained by Korner and Contardi [43] in 1909, using the reaction:



The compound may also be prepared by other methods; for example, van Duin and van Lennep [26] obtained it by reacting ammonia with trinitroanisidine. They also investigated its explosive properties.

The compound is known to be stable : when heated at 95°C for 30 days it remains unchanged. However, on boiling with a dilute sodium hydroxide solution it decomposes to trinitroresorcinol and ammonia. It is less sensitive to impact than tetryl, but more sensitive than picric acid. The initiation temperature is 335°C.

PICRAMIC ACID

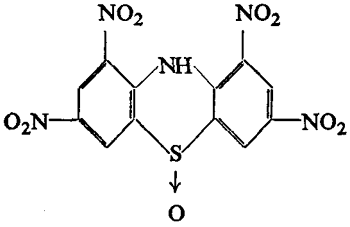


Picramic acid or 4,6-dinitro-2-aminophenol (m. p. 169-179°C) forms dark red crystals, readily soluble in benzene and acetic acid, but difficult to dissolve in other organic solvents.

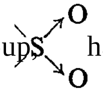
The compound is prepared by reacting sodium sulphide with picric acid (Girard [44]). It is of some importance as an intermediate in the manufacture of azo dyes. It has not found any use as an explosive. being none the less a source for the initiating explosive dinitrodiazophenol (Vol. III).

NITRO DERIVATIVES OF PHENOTHIAZINE

Phenothiazine nitrated to its tetranitro derivative was used by the Germans during World War II as a component of a non-fusible explosive composition known under the name of “Pressling”. Monard, Ficheroulle and Fournier [45] found the compound to be phenothiazine tetranitrosulphoxide (I) (m. p. 368°C):



The compound may be prepared in 70% yield by the nitration of phenothiazine with a mixture of 98% nitric acid and anhydrous sulphuric acid at 60°C. In addition to nitration, oxidation of the sulphur atom also takes place, resulting in the formation of the sulphoxide.

Bernthsen [46], Kehrmann and co-workers [47] and Gilman and Shirley [48] also observed similar oxidation of the sulphur atom when nitrating phenothiazine derivatives. The oxidation of sulphur to the sulphonyl group  has been observed in the nitration of diphenyl sulphide (p. 554). As T. Urbanski, Szyc-Lewatiska and Kalinowski [49] found, methylene blue, when nitrated, yields derivatives having a sulphonyl group (see Vol. III for more details).

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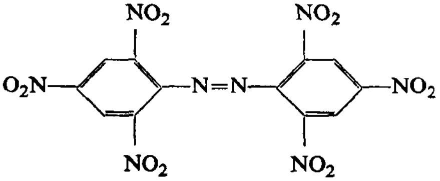
CHAPTER XVIII

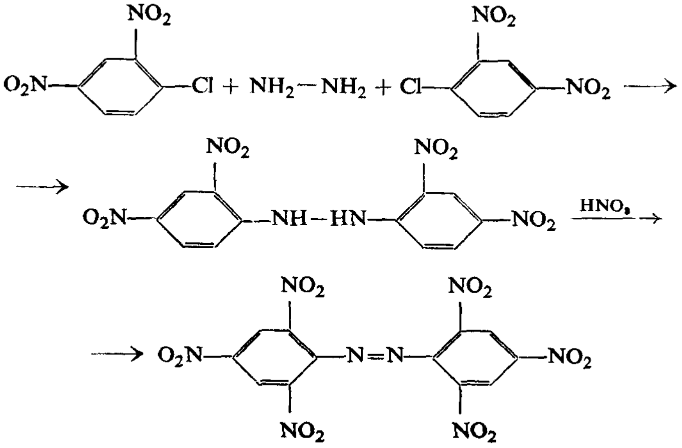
NITRO DERIVATIVES OF AZO- AND HYDRAZO-BENZENES

Nitration of azo compounds leads to mixtures of nitro derivatives of azo and azoxy compounds (Werner and Stiasny [l]). Thus, by nitrating azobenzene with 98% nitric acid at a temperature not exceeding +6°C, these authors obtained a mixture of *p*- nitroazobenzene, *p,p'*- dinitroazobenzene and *p*- nitroazoxybenzene. With 98% nitric acid without cooling, mainly a mixture of the trinitroazoxybenzene isomers was obtained.

HEXANITROAZOBENZENE



2,2’,4,4’,6,6’-Hexanitroazobenzene (m. p. 215-216°C) forms orange coloured needles. It was prepared by Grandmougin and Leeman [2] by acting with hydrazine on picryl chloride. In a more recent method chlorodinitrobenzene is reacted with hydrazine to yield tetranitrohydrazobenzene which is then further nitrated. Simultaneously the oxidation of the hydrazo to an azo group takes place:

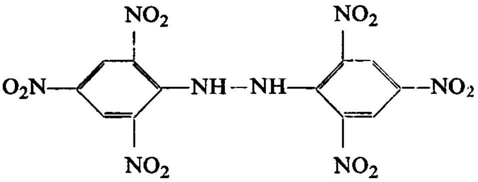


(1)

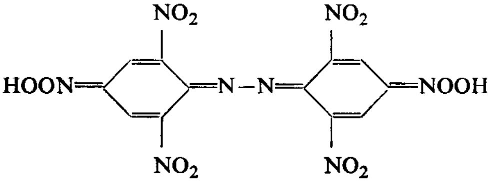
The process is carried out in water suspension in the presence of agents to bind the hydrogen chloride evolved.

Hexanitroazobenzene is a more powerful explosive than hexyl, being of the same order as tetryl. Sensitivity to impact is also similar to that of tetryl.

HEXANITROHYDRAZOBENZENE



The compound (m. p. 210-202°C) was first obtained by Grandmougin and Leeman [2] in 1908. They reacted picryl chloride with hydrazine. The product is rather reactive: for example, its aci-form



readily forms salts with metals. It can also be oxidized to hexanitroazobenzene and in the presence of aniline internal oxidation to a phenazine compound takes place. That is why it has not been regarded as an explosive of any practical value.

The same holds for pentanitrohydrazobenzene $C_6H_3(NO_2)_2NH\text{-}NHC_6H_2(NO_2)_3$, which may be obtained by reacting picryl chloride with dinitrophenylhydrazine.

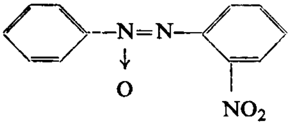
NITRO DERIVATIVES OF AZOXYBENZENE

Nitration of azoxybenzene may lead to the formation of various nitro derivatives, differing in the number of nitro groups.

MONONITRO DERIVATIVES

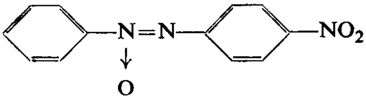
Thus, when nitrated with nitric acid alone (sp. gr. 1.45) azoxybenzene yields a mixture of 2- and 4-nitroazoxybenzenes (I) and (II) (Zinin [3] ; Werner and Stiasny [1]).

The 4-isomer has two crystalline forms IIa and IIb (Angeli and Alessandri [4]; Angeli and Valori [5]).



1

m. p. 49°C

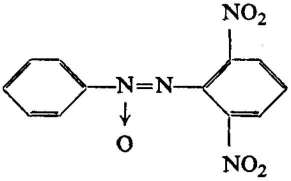


II

m. p. 153°C (IIa)
149°C (IIb)

DINITRO DERIVATIVES

More vigorous nitration with nitric acid of specific gravity 1.48 and at temperatures up to 100°C results in the formation of 2,6-dinitroazoxybenzene (III) (Valori [6]).

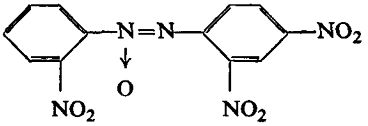


III

m. p. 172°C

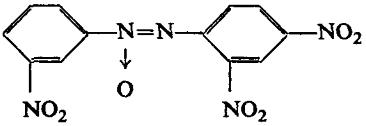
TRINITRO DERIVATIVES

Even more vigorous nitration, with boiling nitric acid of specific gravity 1.51, leads to the formation of a mixture of trinitroazoxybenzenes: 2,4,2'- (IV); 2,4,3'- (V) and 2,4,4'- (VI):



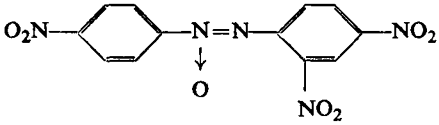
IV

m. p. 192°C



V

m. p. 178°C



VI

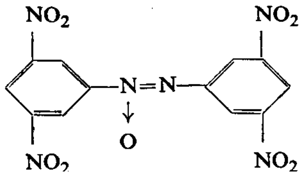
m. p. 135-136°C

All the compounds are formed in the nitration of azobenzene (Werner and Stiasny [1]).

The 2,4,4'-isomer may also be obtained either by the nitration of azobenzene or of 4,4'-dinitroazoxybenzene with nitric acid sp. gr. 1.51 Klinger and Zuurdeeg [7]). 4,4'-Dinitroazoxybenzene may be obtained by the action of alkalis on *p*- dinitrobenzene (Lobry de Bruyn [8]; Lobry de Bruyn and Blanksma [9]; Lobry de Bruyn and Greuns [10]) or by the oxidation of *p*- nitroaniline with persulphuric acid (Bamberger and Hübner [11]).

TETRANITRO DERIVATIVES

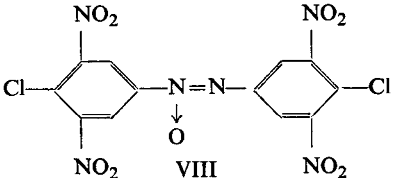
To obtain higher nitrated azoxybenzenes, indirect nitration methods must be applied. 3,5,3',5'-Tetranitroazoxybenzene (VII), for example, may be prepared from sym-trinitrobenzene either by boiling with a dilute sodium carbonate solution (Lobry de Bruyn and Leent [12]) or by partial reduction (Blanksma [13]).



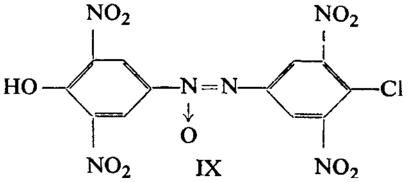
VII
m. p. 185°C

It is interesting to note that the two azoxybenzene rings differ in their readiness to be nitrated. Angeli [14] was the first to draw attention to this fact. From it he inferred that the azoxy group has an unsymmetrical structure: $-\underset{\overset{\downarrow}{O}}{N}=N-$. This opinion was confirmed later by several authors (e.g. G. M. Robinson [15] ; Behr [16]; T. Urbanski and J. Urbanski [17]).

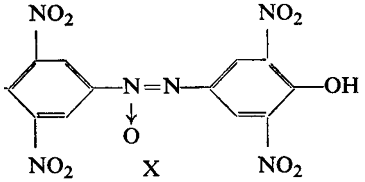
Among other higher nitrated azoxybenzene derivatives the following chloro-, phenol-, methoxy- and methylamine derivatives were recently obtained by T. Urbanski and J. Urbanski [17] :



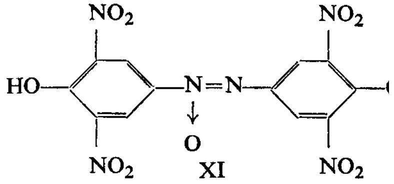
VIII
m. p. 226-228°C



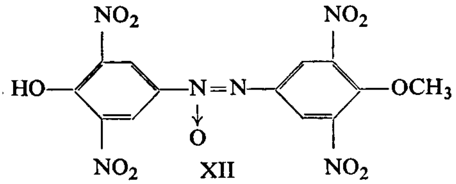
IX
m. p. 198-201°C



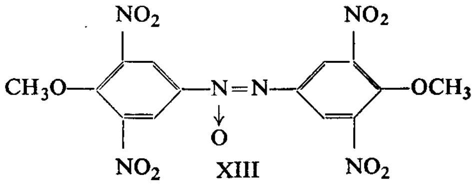
X
m. p. 214-217°C



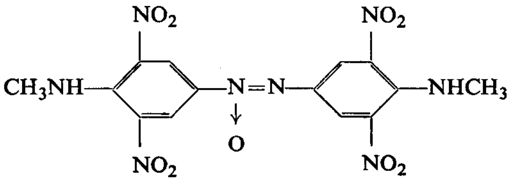
XI
m. p. 186487°C



XII
m. p. 191-192°C



XIII
m. p. 239-240°C



XIV
m. p. 260-261°C (decomposition)

The successful preparation of isomers IX and X as well as the different reactivities of the chlorine atoms in the two rings of compound VIII and different tendency to hydrolysis shown by the methoxy groups in compound XIII provide further evidence in favour of an unsymmetrical structure of the azoxy group, in accordance with Angeli's view.

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CHAPTER XIX

ALIPHATIC NITRO COMPOUNDS

UNTIL recently only the higher nitrated paraffins were considered to have explosive properties or to be of use in explosive compositions. It was only quite recently that nitromethane was discovered to possess powerful explosive properties, although it requires a strong initiator. Among other nitro compounds tetranitromethane deserves special attention. Due to its high oxygen content it may be considered as an oxygen carrier.

NITROMETHANE

Nitromethane, CH_3NO_2, is a volatile liquid. It may be obtained by direct vapour phase nitration of paraffinic hydrocarbons either with nitric acid vapours (Hass et *al.* [1-8]) or with nitrogen dioxide (T. Urbanski and Slebodzinski [9]). It may also be prepared by the action of sodium- or potassium nitrite on chloroacetic acid (Kolbe [10]):

$$NaNO_2 + ClCH_2COOH \rightarrow NaCl + CH_3NO_2 + CO_2 \tag{1}$$

or by reacting dimethyl- or methylsodium sulphate with sodium nitrite (Krause Elm:

$$2NaNO_2 + (CH_3)_2SO_4 \rightarrow 2CH_3NO_2 + Na_2SO_4 \tag{2}$$

$$NaNO_2 + CH_3NaSO_4 \rightarrow CH_3NO_2 + Na_2SO_4 \tag{2a}$$

A method consisting in reacting silver nitrite with methyl iodide or bromide is of value as a laboratory method only.

In 1951 Médard [12] found that nitromethane could be detonated by means of a strong initiator.

As a combustible with a rather high oxygen content nitromethane, alone or in various mixtures, has been gaining even increasing use as a rocket fuel. This great interest in nitromethane provided an incentive for the investigation of its physical and chemical properties.

PHYSICAL PROPERTIES

According to Toops [13], the boiling point of nitromethane at 760 mm is 101.2°C and the temperature coefficient of pressure dp/dt is 0.0427°/mm, its freezing point is -28.55°C and its density at 20° and 30° is 1.13816 g/cm^3 and 1.12439 g/cm^3 respectively.

The temperature coefficient of density dd/dt = 0.001377.

A number of authors have determined vapour pressures of nitromethane (Hodge [14]; W. M. Jones and Giauque [15]). More recent data are given by McCullogh, Scott *et al.* [16]:

Temperature, °C	55.71	61.30	72.56	83.92	95.41	101.19	112.83	124.56	136.40
Vapour pressure, mm Hg	149.4	187.6	289.1	433.6	634.0	760.0	1074.6	1486.1	2026.0

Vapour pressure can be expressed by the Antoine equation:

$$\log p = 7.274170 - 1441.610 / (t + 226.939) \tag{3}$$

Cox [17] suggested another equation:

$$\log P = A\ (1 - 374.347 / T) \tag{4}$$

Here log A = 0.845118 - 6.1497 x $10^{-4}T$ + 6.0541 x $10^{-7}T^2$, p is in mm Hg, P in atm, t in °C, T in °K.

McCullogh, Scott et al. [16] pointed out that Cox's equation also holds true beyond the usual experimental temperature range: 55 - 136°C.

Pitzer and Gwinn [18] and later McCullogh, Scott et al. [16] determined the heat of vaporization of nitromethane:

at 45.3°C $\Delta H_v = 8883 \pm 1$ cal/mole
at 101.4°C $\Delta H_v = 8120 \pm 1$ cal/mole

The following empirical equation has been given by McCullogh and his colleagues :

$$H_v = 11730 - 4.9977\ T - 1.24 \times 10^{-2}T^2 \text{ cal/mole} \tag{5}$$

The heat capacity of the vapour is given approximately by eqn. (6):

$$C_p = C_p^0 - PT\left(\frac{d^2B}{dT^2}\right) + 2[P^2/R]\left[B\left(\frac{d^2B}{dT^2}\right)\right]\left[1 - 3\,\frac{BP}{RT}\right] \tag{6}$$

C_p^0 is the heat capacity in the ideal gaseous state and B is the second virial coefficient. The last term in eqn. (6) is usually neglected, but for a highly polar molecule, such as that of nitromethane, it should be retained.

C_p^0 and B are given by the following equations:

$$C_p^0 = 2.352 + 4.288822 \times 10^{-2}T - 1.694 \times 10^{-5}T^2 \text{ cal deg}^{-1} \text{ mole}^{-1} \tag{7}$$

$$B = -300 - 12.97 \exp (1700/T) \text{ cm}^3 \text{ mole}^{-1} \tag{8}$$

McCullogh, Scott et al. also give the values of thermodynamic functions such as entropy, standard heat, standard free energy etc., at temperatures from 0° to 1500°K.

The heat of combustion of nitromethane at atmospheric pressure and 20°C is 169.4 kcal/mole, according to Kharasch [19].

The standard heat of formation of liquid nitromethane H_f^0 (liq.) is -27.03± 0.15 kcal/mole at 298.16°K.

The standard heat of formation in the gaseous state ΔH_f^0 (gas.) is -17.86 kcal/mole at 298.16°K (McCullogh, Scott et al. [16]).

The other physical constants are:

Viscosity at 15°C 0.694 cP
at 30°C 0.595
(according to Tikmermans and Hennalt-Roland [20])
Surface tension at 15°C 37.74 dynes/cm
at 30°C 35.48
(according to Hennaut-Roland and Lek [21]).

STABILITY

When stored in glass apparatus at a temperature slightly higher than room temperature (30°C) nitromethane was found to develop a partial vacuum (0.2 atm) (Bellinger, Friedmann, Bauer, Eastes, Bull [22]). This indicates an absorption of oxygen insufficient, however, to change the appearance or other physical properties of the substance. On long storage at 48.9°C or more, nitromethane undergoes slight decomposition with the evolution of traces of nitrogen dioxide.

The thermal stability of nitromethane can be improved by adding a small amount of boric acid. It reduces the tendency of nitromethane to decompose on distillation (Lippincott [23]). The addition of a small amount (0.2-1.0%) of phenolic antioxidants, such as hydroquinone, has also been suggested, i.e. substances having a critical oxidation potential as low as the air oxidation potential of α– naphthol (Senkus [24]).

IGNITION AND BURNING

Nitromethane can be ignited by an open flame. Corelli [25] reported, that the “flash point” in the Abel-Pensky apparatus is 35-37°C and the temperature of auto-ignition is 440°C (Constam and Schlaepfer’s method).

The flash point (by Marcusson’s method) is 42-43°C. Makovky and Lenji [26] report that nitromethane has a threshold explosion temperature of 312°C.

The problem of ignition is very important when nitromethane is to be used as rocket monofuel. Ignition of nitromethane with oxygen is not reliable (Bellinger, Friedmann, Bauer, Eastes, Goss [22]) and very often leads to ignition failure and explosion. The presence of oxygen makes nitromethane more sensitive to detonation.

There is very little danger that burning nitromethane will explode. The following test, described by Commercial Solvents Corporation [27], is rather significant from this point of view. A 55-gallon sealed drum filled with nitromethane, was enclosed in a concrete chamber in a mass of pine wood which was ignited quickly throughout by charges of smokeless powder. Although the temperature inside the chamber was higher than 700°C the heat merely caused the drum to burst, after which the contents burned quietly for about 30 min.

Since nitromethane should be considered as an oxidizing agent and since at elevated temperatures the oxidation processes can assume a rapid rate, it is recommended that nitromethane should not be heated in the presence of hydrocarbons or other combustible substances in a confined space. Thus explosion may occur during the heating of nitromethane-lubricating oil mixtures to high temperature under pressure.

The possible use of nitromethane as a liquid monofuel for rocket propulsion has aroused interest in the problem of its thermal decomposition.

Although this has come about only recently, the first experiments on the subject were carried out as long ago as 1935 by H. A. Taylor and Vesselovsky [28]. The experiments were related to the temperature range of 380-420°C and 200 mm pressure. The reaction was found to be of the first order, with an activation energy of 61.0 kcal/mole.

Subsequently, Frejacques [29] and Cottreh, Graham and Reid [30] continued the experiments within the ranges of 310-440°C and 380-430°C, under 4-40 mm and 200-400 mm pressures respectively. They confirmed the previous statement that the reaction is of the first order, with activation energies of 42.8 and 53.6 kcal/mole respectively. The reaction constant, ***k,*** may be calculated, according to Cottrell et ***al.,*** from the equation

$$\boldsymbol{k} = 10^{14.6} \exp \frac{-53,600}{TR} \sec^{-1} \tag{9}$$

Hillenbrand and Kilpatrick [31] investigated the same problem at 420-480°C. They confirmed the previous results and obtained a value of 50,000 for the activation energy.

Gray, Yoffe and Roselaar [32] examined the decomposition of nitromethane at 447°C.

Experiments by Müller [33] and Makovky and Günwald [34] on the decomposition of nitromethane under pressures of 12.2-20.2 and 40 atm and at temperatures of 355°C and 312-340°C respectively are particularly interesting. The reaction constant, according to these investigators, was

$$k = 5.4 \times 10^{13} \exp \frac{-49,200}{R_T} \sec^{-1} \tag{10}$$

T. Urbanski and Pawelec [351 found the activation energy to be 45.0 kcal/mole for the range 460-570°C.

The products of decomposition at low pressures were: NO, N_2O. H_2O, CO, CO_2, CH_4, small amounts of ethylene and ethane, and trace of NO_2 (Cottrell ef al. [30]). Nitrogen oxide was the principal nitrogen-containing compound.

Decomposition under pressure led to the formation of N_2, NO, H_2O, CO, CO_2, CH_4, HCN and small quantities of CH_3CN, C_2H_5CN, CH_2O, N_2O (Müller [33]).

The main difference between decomposition at high pressure and at low pressure is the presence of hydrogen cyanide as the principal carbon compound in the former case.

In addition to gaseous products, solid (ill-defined) compounds formed, particularly when decomposition took place at high pressure.

The presence of oxygen accelerated decomposition, whereas hydrogen slowed it down. Addition of small amounts of nitrogen oxide or nitrogen dioxide had no influence on the rate of decomposition under high pressure, although high concentrations of these-gases had an inhibiting effect.

With regard to the mechanism of decomposition, some authors (Taylor and Vesselovsky [28]) suggest N-O bond fission

$$CH_3NO_2 \rightarrow CH_3NO + O \qquad (11)$$

while others (Frkjacques [29], Cottrell et al. [25], Gray et al. [32]) assume the rupture of C-N bond:

$$CH_3NO_2 \rightarrow CH_3 + NO_2 \qquad (12)$$

More recently Müller, and also Makovky have reported both mechanisms taking place at elevated pressure.

Hillenbrand and Kilpatrick [31] suggested that the decomposition was partly due to intramolecular rearrangement. Makovky assumes that it proceeds by a radical chain mechanism with very short chains.

The following scheme has been suggested by Taylor and Vesselovsky [28] for the initial steps of the reaction at low pressure:

$$CH_3NO_2 \rightarrow CH_3 + NO_2 \qquad (13a)$$

$$CH_3 + CH_3NO_2 \rightarrow CH_4 + CH_2NO_2 \qquad (13b)$$

$$CH_2NO_2 + NO_2 \rightarrow CH_2O + NO + NO_2 \qquad (13c)$$

$$CH_2O + NO_2 \rightarrow CO + NO + H_2O \qquad (13d)$$

$$CH_3 + CH_3 \rightarrow C_2H_6 \qquad (13e)$$

At high pressure the following radical reactions also take place:

$$CH_3NO_2 \rightarrow CH_3NO + O \qquad (14a)$$

$$O + CH_3NO_2 \rightarrow CH_2O + HNO_2 \qquad (14b)$$

$$CH_3 + CH_3NO_2 \rightarrow CH_4 + CH_2NO_2 \qquad (14c)$$

It is possible that the presence of hydrocyanic acid in the product of decomposition at high pressure may be ascribed to the formation of CH_3NO:

$$CH_3NO + CH_2{=}NOH \rightarrow HCN + H_2O \tag{15}$$

(reaction described by Mitchell and Hinshelwood [36]).

Nitrosomethane is likely to be formed as a result of N-O fission or from the CH_3 radical :

$$CH_3 + NO \rightarrow CH_3NO \tag{16}$$

EXPLOSIVE PROPERTIES

Reliable evidence that nitromethane possesses properties characteristic of an explosive has been provided relatively recently. In particular two disastrous railway accidents which occurred in 1958 in the U.S.A. (one at Niagara Junction and the other at Mount Pulaski, Ill.) gave decisive proof that nitromethane should be considered as an explosive and classified as such when subjected to transportation. Both accidents occurred with nitromethane in tank cars. Since then nitromethane has been the only nitroparaffin which is not allowed to be shipped in tank cars but only in smaller containers, such as drums.

Bellinger, Friedmann, Bauer, Eastes and Bull [22] brought about the detonation of nitromethane confined in a heavy-walled container by the severe impact produced by firing 0.50 caliber ammunition at it. When a thin-walled container was substituted for the heavy-walled one, no detonation occurred. According to Cass [37], nitromethane subjected to an impact test exploded under the impact of a 2 kg weight falling from a height greater than 1.95 m. Nitroglycerine explodes under similar conditions when the dropping height is only 35 cm. According to Commercial Solvents Corporation [27], liquid nitromethane can detonate under a sudden impact of compressed air ca. 2000 lb/in^2. Apparently air compressed to 1200 lb/in^2 may be applied safely.

Nitromethane will detonate only when a very strong initiator is used. According to Makovky and Lenji [26], 10 g of hermetically sealed nitromethane can be detonated by 2.5 g of tetryl initiated in turn by 0.5 g of lead azide.

According to T. Urbanski and Pawelec [35], nitromethane could not be detonated completely by means of a No. 8 detonating cap alone or with addition of 1-8 g of tetryl, when nitromethane was confined in copper tubes of 13.6/14.8 mm and 23/25 mm diameter and 15 cm length.

The sensitivity of nitromethane to detonation increases with increase in temperature. The following figures (Table 122) were obtained by Kaplan, Johnston, Sill, and Peebles [38]. Nitromethane was confined in 3 in. stainless-steel tubing and explosion was initiated by No. 8 detonator.

The addition of certain compounds can render nitromethane more sensitive to detonation by a No. 8 cap, for instance strong bases and acids, such as aniline, ethylenediamine, methylamine, aqueous NH_3, KOH, Na_2CO_3, formic, nitric, sulphuric and phosphoric acids.

TABLE 122

°F	°C	Number of tests	Number of explosions
60-90	15.6-32.2	numerous	0
100-110	31.8-43.3	25	1
120-125	38.9-51.7	13	4
130-140	54.4-60	10	5
160-180	71.1-82.2	18	13

The data on the rate of detonation of nitromethane have been obtained only recently.

Médard [12] found the rate to be 6600±132 m/sec when in a glass tube 30 mm in diameter and 1.8 mm thick, or in an aluminium tube of the same diameter and 2.5 mm thick. A particularly strong initiator was used. Nachmani and Manheimer [39] reported lower figures (Table 123 and 124).

TABLE 123

NITROMETHANE CONFINED IN PAPER

Diameter mm	Detonation rate m/sec
44	6280
34	6260
29	6150
26.5	partial detonation
25	no detonation

TABLE 124

NITROMETHANE CONFINED

Tubes made of:	Internal diameter mm	Wall thickness mm	Detonation rate m/sec
iron	40	4	6320
	27	3	6300
	25	17	6280
brass	7	0.8	6060
polyvinyl chloride	7.5	1.0	no detonation
rubber	8	2	,,
	10	3	,,
polyester	8	7	,,

According to T. Urbanski and Pawelec [35], the rate of detonation of nitromethane can be expressed by the following figures (Table 125).

TABLE 125

Tubes made of:	Diameter mm	Initiation	Rate of detonation average values m/sec	Method
copper	18/20	No. 8 detonator and 1-5 g tetryl	6190	Dautriche
copper	23/25			
steel	22/27			
copper	18/20	No. 8 detonator and 6.2g tetryl	6405	Electric Chronograph

Van Dolah, Herickes, Ribovich and Damon [40] found values of 6275 and 6285 m/sec in steel and aluminium tubes respectively of 27 mm internal diameter. The same authors confirmed that addition of small quantities of various substances significantly affects the susceptibility to detonation of the resulting solution.

Bases (ethylenediamine, triethylamine, pyridine) were found to be strong sensitizers. Acids (sulphuric acid, acetic acid) were found to be much weaker sensitizers. Dibutyl phthalate, benzene, cyclohexane were found to be weak desensitizers.

According to Médard [12], in the lead block test nitromethane gives figures similar to picric acid. T. Urbanski and Pawelec [35] found 325-360 cm^3, averaging 345 cm^3, i.e. 110% of that of picric acid. The same authors determined the lead block expansion when nitromethane was detonated by means of a No. 8 detonator and 1 or 5 g of tetryl. The expansion given by tetryl was deducted from the bulk expansion (Table 126).

TABLE 126

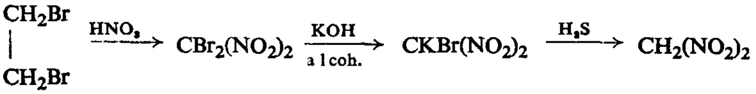
Charge			Expansion	
nitromethane 8 -	detonator No.	tetryl g	total cm^3	after deduction of tetryl expansion cm^3
10	8	1	445	420
-	8	1	25	
10	8	5	640	
-	8	5	145	495

Salts of nitromethane are extremely sensitive to flame and bum readily. They are also sensitive to friction, impact and electric discharge. Mercuric salt can be transformed into mercuric fulminate (Vol. III).

DINITROMETHANE

$CH_2(NO_2)_2$

Dinitromethane is a volatile liquid with a sharp, acid smell. It was first obtained by Villiers [41] and Losanitsch [42]:



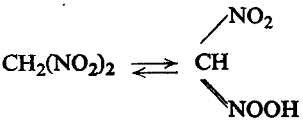
$$\begin{matrix} CH_2Br \\ | \\ CH_2Br \end{matrix} \xrightarrow{HNO_3} CBr_2(NO_2)_2 \xrightarrow[\text{alcoh.}]{KOH} CKBr(NO_2)_2 \xrightarrow{H_2S} CH_2(NO_2)_2 \qquad (17)$$

Duden [43] improved the last stages of the method:

$$CBr_2(NO_2)_2 \xrightarrow{KOH+As_2O_3} CK_2(NO_2)_2 \xrightarrow{H_2SO_4} CH_2(NO_2)_2 \qquad (18)$$

It is unstable at room temperature and is readily decomposed with evolution of nitrogen dioxide. It can be kept for longer periods only at temperature below 0°C or in solution in benzene or some other solvents.

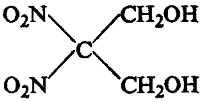
Dinitromethane can exist in two tautomeric forms:



I II

This was based on examination of the ultra-violet and visible spectra (Hedley [44], Hantzsch and Voigt [45]) and electroconductivity measurements (Hantzsch and Veit [46]). The nitro form (I) is colourless, the aci-form (II) is yellow. The aci-form is a relatively strong mono-acid ($K_a = 1.43 \times 10^{-4}$ at 0°C and 2.68×10^{-4} at 25°C).

Dinitromethane reacts with two mol. of formaldehyde to form the diol (III) [47]



III

Dinitromethane forms salts which are (generally speaking) unstable and decompose at temperatures not very much above 100°C.

TRINITROMETHANE (NITROFORM)

Trinitromethane $CH(NO_2)_3$ forms white crystals (m. p. 25°C). It was first obtained as its ammonium salt by Shishkov [48], by hydrolysis of trinitroacetonitrile with water. It was also Shishkov who obtained trinitroacetonitrile (m. p. 41.5°C) by treating the sodium salt of fulminuric acid with a mixture of nitric and sulphuric acid. Trinitroacetonitrile also exhibits explosive properties.

Baschieri [49] found that nitroform was produced in the reaction of acetylene with anhydrous nitric acid (sp. gr. 1.52). Tetranitromethane, when hydrolysed, also yields nitroform. Hantzsch and Rinckenberger [50] obtained its ammonium salt by treating tetranitromethane with aqueous ammonia. This method is mostly applied for the laboratory preparation of nitroform.

Nitroform can exist in two forms [50]: a nitro form (I) and an aci-form (II)

$$\underset{\text{I}}{(O_2N)_3CH} \rightleftarrows \underset{\text{II}}{(O_2N)_2C{=}NOOH}$$

The colourless form (I) exists in solution acidified with hydrochloric or sulphuric acid and also in anhydrous benzene, carbon disulphide and ether. Aqueous and basic solutions are intensely yellow due to the presence of the form II. Solutions in acetic acid are slightly yellow, which would indicate that the two forms exist in equilibrium in this medium.

Most salts derive from the aci-form (II). However, the silver and mercuric salts exist in two forms: colourless and yellow. This would indicate that two forms of these salts - nitro and aci - can exist.

The explosive properties of nitroform have been proved by Shishkov [48]. Nitroform salts also exhibit explosive character.

Trinitromethane reacts with formaldehyde forming trinitroethyl alcohol (Hurd and Starke [51]) :

$$CH(NO_2)_3 + CH_2O \rightarrow C(NO_2)_3.CH_2OH \qquad (19)$$

The reaction is highly exothermic. It should be controlled, so as to prevent its temperature exceeding 70-80°C. Trinitroethyl alcohol is an unstable, crystalline compound, melting at 36-37°C (Ficheroulle and Gay-Lussac [52]). Its initiation temperature is about 120°C.

Trinitroethyl alcohol may be esterified with acetic anhydride to the acetate, which is much more stable than the alcohol itself and at temperatures of 120-140°C shows no distinct signs of decomposition. Both alcohol and acetate are very good solvents for nitrocellulose.

TETRANITROMETHANE

Tetranitromethane was first obtained by Shishkov [48] in 1857, but it was only during the World War II that the Germans experimented with it on a large scale, using mixtures of tetranitromethane with various combustible materials as rocket propellants.

PHYSICAL PROPERTIES

Tetranitromethane, $C(NO_2)_4$, is a heavy oily liquid (sp. gr. 1.65), which solidifies at +3°C and boils at 126°C without decomposition. It is insoluble in water, but it dissolves easily in alcohol and benzene. It is a volatile substance with a characteristic smell, reminiscent of nitrogen oxides.

Menzies [53], later Nicholson [54] and Edwards [551 measured the vapour pressures of tetranitromethane and obtained similar values.

Nicholson found the following vapour pressures for temperatures ranging from 0°C to 40°C:

Temperature, °C	0	13.8	20	30	40
Vapour pressure, mm Hg	1.9	5.7	8.4	14.9	25.8

Changes in the vapour pressure of tetranitromethane depending on temperature may be expressed by a first degree equation:

$$\log p = 8.63-2260/T$$

From the above data Nicholson has calculated the latent heat of evaporation 10.3 kcal/mole. Edwards has given the following figures for temperatures ranging from 40°C to 100°C

Temperature, °C	40	50	60	70	80	90	100
Vapour pressure, mm Hg	26.5	43.3	68.0	108.0	164.0	239.0	339.6

He has presented changes in vapour pressures as a variable dependent on temperature, according to the equation:

$$\log p = 7.23-2130/T$$

and has calculated the latent heat of evaporation to be 9.7 kcal/mole.

CHEMICAL PROPERTIES

Although tetranitromethane does not contain active hydrogen it readily enters certain reactions. With water it reacts slowly to form trinitromethane, i.e. nitroform:

$$C(NO_2)_4 + HOH \rightarrow CH(NO_2)_3 + HNO_3 \qquad (20)$$

With potassium hydroxide, tetranitromethane readily yields its potassium salt of nitroform :

$$C(NO_2)_4 + 2KOH + CK(NO_2)_3 + KNO_3 + H_2O \qquad (21)$$

It react with sodium sulphite to yield sodium trinitromethanesulphonate

$$C(NO_2)_4 + NO_2SO_3 \rightarrow (O_2N)_3CSO_3Na + NaNO_2 \qquad (22)$$

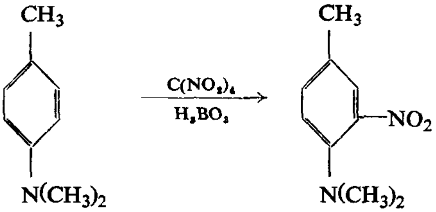
With copper or nickel in the presence of ammonia it forms complex salts having initiating properties (Vol. III).

Tetranitromethane is added to compounds having double bonds to form brown or yellow products. The reaction is very sensitive and may be utilized, for example, for detecting traces of olefins in paraffin fractions (Werner [56]).

Tetranitromethane reacts with tertiary amines, causing their degradation with the formation of N-nitroso derivatives of secondary amines. In this way tertiary amines may be converted to secondary ones (E. Schmidt and co-workers [57, 58]):

$$\begin{tikzcd}
(R.CH_2)_3N + C(NO_2)_4 \rightarrow (R.CH_2)_2N.NO \arrow[d, "HCl"] & + R.CHO + CH(NO_2)_3 \\
(RCH_2)_2NH_2Cl: \arrow[r, "OH^-"] & (R.CH_2)_2NH
\end{tikzcd} \qquad (23)$$

Tetranitromethane may be used for nitrations in the presence of boric acid. Dialkylanilines may be nitrated by this method, as for example N,N-dimethyl-p-toluidine (E. Schmidt and H. Fischer [57]):



Tetranitromethane like polynitro-aromatic hydrocarbons is able to form addition compounds (p. 222, Fig. 47). Nevertheless, the existence of an addition compound of tetranitromethane with benzene has not been proved by thermal analysis, when this was carried out recently by T. Urbanski, Piskorz, Centner and Maciejewski [59]. They also examined a number of other systems by means of thermal analysis. The compositions of various eutectics determined by the above authors are shown in Table 127.

TABLE 127

EUTECTICS OF TETRANITROMETHANE

Compound added	Tetranitromethane content, wt. %	Freezing point, °C
Benzene	70.0	-16.1
Nitrobenzene	57.0	-19.1
o- Nitrotoluene	41.5	-28.5
m- Nitrotoluene	47.5	-24.0
p- Nitrotoluene	81.5	+ 1.5
m- Dinitrobenzene	97.0	+11.3
α– Trinitrotoluene	97.0	+12.3
α– Nitronaphthalene	90.0	+ 9.3
Tetryl	(restricted solubility)	-

Macbeth and his co-workers [60, 61] found that tetranitromethane produced yellow or brown colour with a number of other compounds as well, for example, with mercaptans, dioxane, and aliphatic amines. The absorption spectra of such solutions showed maxima at about 350 mµ.

EXPLOSIVE PROPERTIES

According to Roth [62], pure tetranitromethane cannot be detonated even when using 10 g of tetryl as detonator. However, the ability of tetranitromethane to detonate increases considerably when it contains organic impurities, even in small quantities.

Tetranitromethane forms very powerful explosive mixtures with combustible substances, for example with nitrobenzene, and toluene. The explosive properties of such mixtures were investigated in detail after an accidental explosion had occurred in Münster University in 1920.

Naoum [63] gave the following data on the explosive properties of tetranitromethane and of its mixtures. Alone, tetranitromethane gives a lead block expansion of only 40 cm^3 including 8 cm^3 contributed by the detonator.

A mixture of 83.8% of tetranitromethane, 4.9% of toluene and 11.3% of cotton wool gives a lead block expansion of 435 cm^3, i.e. of the order of the most powerful explosive. The above mixture contains a 13% excess of oxygen.

A stoichiometric mixture, with its ingredients taken in such quantities as to have all the oxygen consumed, containing 86% of tetranitromethane and 13.5% of toluene gives an expansion of 465 cm^3.

The density of the mixture is 1.45. According to the Chemisch Technische Reichsanstalt [64] measurements, its rate of detonation is exceptionally high:

in a glass tube of 12 mm diameter 7100 m/sec
in a steel tube of 25 mm diameter 8300-9300 m/sec

Behrens [65] measured the lead block expansions given by tetranitromethane alone or in mixtures with nitrogen dioxide and benzene. Detonators of various strengths from No. 1 to No. 8 were used as initiators. Tests with TNT and nitroglycerine were made for comparison. The results obtained are shown in Table 128.

In another set of experiments Behrens investigated mixtures of tetranitromethane with benzene for their ability to detonate and for explosive power. He found stoichiometric mixtures to be the most powerful.

TABLE 128

No. of detonator	Expansion, cm^3				
	Tetra-nitromethane	Mixture $C(NO_2)_4$ 70% N_2O_4 30%	Mixture $C(NO_2)_4$ 87% Benzene 13%	TNT	Nitroglycerine
1	12	0	413	0	171
2	44	0	404	0	172
3	65	13	404	218	379
5	86	48	404	268	407
8	71	37	445	332	445

The explosive properties of nitrobenzene-tetranitromethane solutions were examined in detail by Roth [62] who measured rates of detonation power (on a 10.5 by 7 mm crusher gauge), and sensitiveness to impact, using nitroglycerine and TNT as standards (Table 129). Lead block expansions are not included here as they were not determined by standard methods.

TABLE 129

Concentration of nitrobenzene %	Rate of detonation m/sec	Crusher gauge figures mm	Sensitiveness to impact kgm/cm^2
5.0	6870	4.32	4.80
10.0	7030	4.50	4.30
15.0	7480	5.25	4.30
20.0	7550	5.43	3.65
22.5	7700	5.45	5.15
25.0	7575	5.66	8.06
30.0	7500	5.25	8.06
35.0	7220	5.20	15.00
40.0	7000	4.92	15.00
50.0	6700	4.40	no explosion
70.0	5800	3.20	,,
80.0	no detonation	no detonation	,,
Nitroglycerine	7450		4.75
TNT	7200	4.2	11.1

The highest rate of detonation was obtained with a solution containing 22.5% of nitrobenzene, which also proved to be more powerful than nitroglycerine. With regard to sensitiveness to impact, a solution containing 5-10% of nitrobenzene has shown some similarity to nitroglycerine, while that containing 30-40% of nitrobenzene resembled TNT.

T. Urbanski, Piskorz, Maciejewski and Cetner [59] investigated the properties of stoichiometric mixtures of tetranitromethane with benzene and with aromatic nitro compounds. The results obtained are tabulated below (Table 130).

TABLE 130

Composition of the mixture			Density g/cm^3	Rate of detonation† in 20 mm glass tube m/sec	Lead block expansion cm^3
Other component	Concentration wt. %	Tetra-nitromethane concentration wt. %			
Benzene	13.75	86.25	1.47	7180	520
Nitrobenzene	23.15	76.85	1.53	7430	470
o- Nitrotoluene	21.30	78.70	1.52	7770	480
p- Nitrotoluene	21.30	78.70	1.52	8170	495
m- Dinitrobenzene	34.05	65.95	1.53	6670	650
TNT	39.85	60.15	1.58	6670	565
α– Nitronaphthalene	19.70	80.30	1.57	8160	490
Tetryl	51.00	49.00	1.63	7100	570

† For the initiation a No. 8 detonator and 10 g of TNT were applied.

The high, values for the lead block expansion test given by mixtures of tetranitromethane with higher nitrated aromatic compounds are striking. On the other hand, the rates of detonation of these mixture are lower than those of mixtures containing lower nitrated compounds or benzene.

As illustrated by Table 13 1, the sensitiveness to impact of the same mixtures with dinitrobenzene, TNT or tetryl is distinctly higher than that of pure dinitrobenzene, TNT and tetryl.

TABLE 131

Other component	Sensitiveness of the pure component (impact energy) kgm	Sensitiveness to impact of the mixture (impact energy) kgm
m- Dinitrobenzene	19.5	12
α– Trinitrotoluene	12	7
Tetryl	7	3

These mixtures are also more sensitive to flame than nitro compounds alone and can be ignited more readily. A mixture with benzene ignites most readily, hence it can be inferred that ignition is initiated in the gaseous phase.

TOXICITY

Tetranitromethane is highly toxic. Kiese [48] found that 25 mg/per kg of body weight of tetranitromethane slowly injected intravenously caused transitory methaemoglobinaemia, as well as lung oedema and damage to the liver, kidney and central nervous system. Tetranitromethane injected quickly caused necrosis around the puncture which could be fatal.

PREPARATION

Shishkov obtained tetranitromethane by treating nitroform with a mixture of fuming nitric acid with sulphuric acid. Pictet [67] found that tetranitromethane was formed when nitric acid was reacted with acetic acid, or acetyl nitrate with acetic anhydride.

For the preparation of tetranitromethane on the laboratory scale Chattaway's method [68] is commonly used. It consists in treating acetic anhydride with fuming nitric acid at room temperature or below. After a few days the homogeneous solution is poured into water, causing the oily tetranitromethane to separate.

This method was applied in the U.S.A. on a larger scale by Nitroform Products Co., Inc., Newark, N. Y. However, the plant was completely destroyed by an explosion that occurred in the manufacture of tetranitromethane.

Investigation indicated [69] that the probable cause was a rise of temperature in the mixing tank, where nitric acid and acetic anhydride reacted at a temperature of 15-20°C, maintained by cooling and stirring. The rise of temperature may have been due to breakdown of the stirring equipment. It was also suggested that the presence of iron oxide or some other catalyst may have sensitized the mixture or promoted it to a “wild” side-reaction.

Tetranitromethane may also be obtained by reacting nitric acid with ketene (which may be regarded as a kind of acetic anhydride), according to d’Arsens and G. Levy [70].

Tetranitromethane is also formed during the nitration of aromatic hydrocarbons under very vigorous conditions, for example, when benzene or toluene is nitrated to the trinitro derivative.

MacKie and Orton [71] found that tetranitromethane could be obtained by reacting anhydrous nitric acid with acetylene in the presence of mercuric nitrate. During World War II the Germans manufactured tetranitromethane by this method on a semi-commercial scale, after they had developed the industrial process (Schimmelschmidt [72]).

The reaction takes place in the presence of mercuric nitrate as a catalyst at temperatures ranging from 45°C to 50°C (max. 60°C).

$$CH{=}CH + 2HNO_3 + (NO_2)_2CH\text{-}CHO + H_2O \qquad (24a)$$

$$(NO_2)_2CH\text{-}CHO + HNO_3 \rightarrow (NO_2)_3C\text{-}CHO + H_2O \qquad (24b)$$

$$(NO_2)_3C\text{-}CHO + 2HNO_3 \rightarrow (NO_2)_3C\text{-}COOH + H_2O + 2NO_2 \qquad (24c)$$

$$\downarrow$$

$$(NO_2)_3CH + CO_2$$

$$(NO_2)_3CH + HNO_3 \rightarrow (NO_2)_4C + H_2O \qquad (24d)$$

The overall reaction may be presented as:

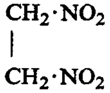
$$C_2H_2 + 6HNO_3 \rightarrow (NO_2)_4C + CO_2 + 4H_2O + 2NO_2 \qquad (25)$$

in addition a side-reaction

$$C_2H_2 + 10HNO_3 \rightarrow 2CO_2 + 6H_2O + 10NO_2 \qquad (26)$$

also takes place.

1,2-DINITROETHANE



$$\begin{array}{l} CH_2{\cdot}NO_2 \\ | \\ CH_2{\cdot}NO_2 \end{array}$$

m. p. 39°C, b. p. 135°C

1,2-Dinitroethane may be obtained by the action of nitrogen dioxide on ethylene at low temperature (about 0°C) (Semenoff [73]; Demyanov [74], [75]). According to N. Levy, Scaife, Smith [76], the use of a mixture of ethylene with oxygen in the volume ratio of about 4:1 gives good results.

Besides 1,2-dinitroethane a nitrous ester (nitroethyl nitrite) is also formed which is unstable and may decompose. According to N. Levy et ***al.,*** nitroethyl nitrite may be hydrolysed by dissolving the reaction mixture in methyl alcohol. Dinitroethane then precipitates as a crystalline mass.

Nitration is always accompanied by the oxidation of the olefin (Baldock, N. Levy and Scaife [77]).

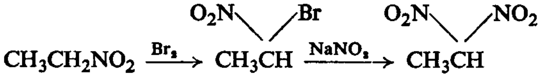
Dinitroethane is a very powerful explosive, giving a lead block expansion of 140-150 (picric acid = 100). Its density is 1.46. It is less sensitive to impact than picric acid. Since it is highly reactive, and hence unstable, it has not found any use as explosive. It reacts most readily with bases. For example, when stored in a glass vessel it decomposes after a few weeks as the result of its contact with glass, which has basic properties. Levy suggests adding to the product an organic acid, as for example *p-* toluenesulphonic acid, as a stabilizer. Under the influence of bases dinitroethane may form nitroethylene, as well as other less defined products, which can readily polymerize to form resinous substances.

1,1-DINITROETHANE

$CH_3CH(NO_2)_2$

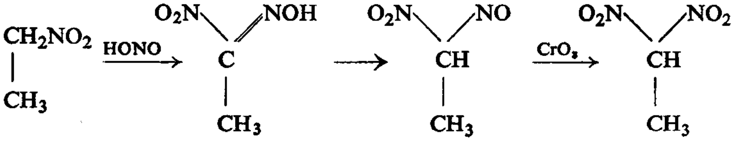
m. p. 37.5°C, b. p. 185°C

This substance was obtained by ter Meer [78] by acting with sodium nitrite on 1-bromo-1-nitroethane:



(27)

It can also be obtained by oxidation of nitrolic acid derived from nitroethane (Topchiyev [79]) :



(28)

Chancel [80a] described another general method of preparing 1,1-dinitroparaffins and in particular 1,1-dinitroethane, starting from ethyl acetoacetate and its derivatives :

$$CH_3COCH(R)COOC_2H_5 \xrightarrow{HNO_3} R\text{-}CH(NO_2)_2 + CH_3COOH + CO_2 + C_2H_5ONO_2$$

The yield of the reaction is relatively low (5-6%).

Recently Novikov [81] prepared 1,1-dinitroethane using this method.

A new excellent method of preparing gem-dinitroparaffins was recently reported by Kaplan and Shechter [97]. It consist in acting with $AgNO_3 + NaNO_2$ on sodium salts of nitroparaffins.

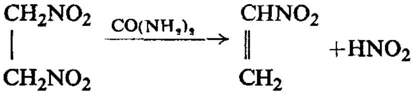
This substance has been suggested as monofuel for rocket propulsion (Wood [82]).

POLYNITROETHYLENE

$(CH_2{=}CHNO_2)_n$

Nitroethylene monomer, $CH_2{=}CHNO_2$, is a yellowish-green, strongly lachrymatory liquid, boiling at 35°C (at 70 mm Hg). It may be prepared by acting with bases on 1-nitro-2-chloroethane or by the action of potassium hydrogensulphate on 2-nitroethyl alcohol (Wieland and Sakellarios [83]). Very satisfactory results may be obtained with phthalic anhydride as dehydrating agent (Buckley and Scaife [84]; Boileau and Runavot [85]; Sokolov, Perekalin et al. [98]).

It can also be obtained by acting with urea on 1,2-dinitroethane:



$$\begin{matrix} CH_2NO_2 \\ | \\ CH_2NO_2 \end{matrix} \xrightarrow{CO(NH_2)_2} \begin{matrix} CHNO_2 \\ \| \\ CH_2 \end{matrix} + HNO_2 \qquad (29)$$

Nitrous acid then reacts with an excess of urea in the usual way.

Nitroethylene readily polymerizes to yield a white powder, insoluble in water and in most organic solvents. It may be obtained by direct action of bases on nitroethyl nitrate or -acetate or on dinitroethane.

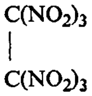
Polynitroethylene burns without melting. It is a very weak explosive, which gives a lead block test amounting to about 30% of that given by TNT. It has not found any practical uses because of its low thermal stability.

A number of other nitro-olefins can be prepared in a similar way as nitroethylene [86].

SYM-TETRANITROETHANE

This compound is known in the form of the potassium salt $C(NO_2)_2KC(NO_2)_2K$. Its preparation and use in the production of hexanitroethane is discussed below.

HEXANITROETHANE



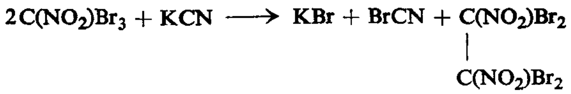
$$\begin{matrix} C(NO_2)_3 \\ | \\ C(NO_2)_3 \end{matrix}$$

m. p. 142°C

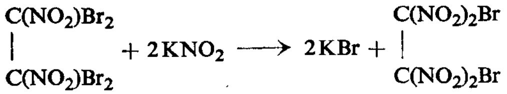
The product is known as a colourless crystalline, rather non-volatile substance, having explosive properties, It was first obtained by Will [87] when acting with nitric acid on potassium salt of tetranitroethane:

$$C_2(NO_2)_4K_2 + 4HNO_3 \rightarrow C_2(NO_2)_6 + 2KNO_3 + 2H_2O \qquad (30)$$

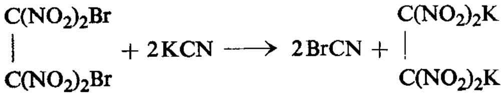
For the preparation of the latter, Will applied Scholl's method [88], consisting in reacting potassium cyanide and nitrite with bromopicrin, according to the reactions :



$$\mathrm{2C(NO_2)Br_3 + KCN \longrightarrow KBr + BrCN + \begin{array}{c}C(NO_2)Br_2\\|\\C(NO_2)Br_2\end{array}} \qquad (31a)$$



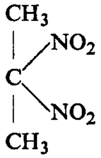
$$\mathrm{\begin{array}{c}C(NO_2)Br_2\\|\\C(NO_2)Br_2\end{array} + 2KNO_2 \longrightarrow 2KBr + \begin{array}{c}C(NO_2)_2Br\\|\\C(NO_2)_2Br\end{array}} \qquad (31b)$$



$$\mathrm{\begin{array}{c}C(NO_2)_2Br\\|\\C(NO_2)_2Br\end{array} + 2KCN \longrightarrow 2BrCN + \begin{array}{c}C(NO_2)_2K\\|\\C(NO_2)_2K\end{array}} \qquad (31c)$$

Hexanitroethane gives a lead block expansion of 180 cm^3. It is more difficult to explode by impact than picric acid. With TNT or tetryl (in stoichiometric ratio) it forms exceptionally powerful explosives. Since it has the ability of gelatinizing nitrocellulose the Köln-Rottweil powder factory [89] tried to use it as a smokeless powder component to increase the explosive power of the latter. However, because of the high production costs of hexanitroethane, it has not found a practical use. In addition, its chemical stability is rather low: when heated it begins to decompose at 75°C.

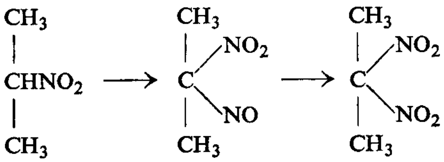
2,2-DINITROPROPANE



m. p. 51-52°C

2,2-Dinitropropane forms white crystals, insoluble in water.

It is usually obtained by oxidizing pseudonitrole formed from secondary nitropropane (Born [go]), Denton ***et al.*** [99].



(32)

2,2-Dinitropropane exhibits strong explosive properties. The initiation temperature, with an induction period of 5 sec is 360°C. Its sensitiveness to impact is of the order of TNT. The explosive power of dinitropropane is higher than that of TNT: it amounts to about 120, compared with 100 for TNT.

2,2-Dinitropropane has the disadvantage of being highly volatile: when stored in a vessel that is not quite tight at 75°C for 48 hr it loses about two thirds of its volume.

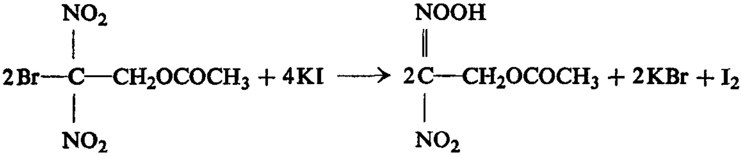
2,2-Dinitropropane has been suggested (Albright, Nelson and Raymond [91]) as an additive for Diesel engine oil to increase its octane number. With a 0.1%

content of dinitropropane the octane number of the fuel increases from 44 to 51, while with 0.5% it increases to 53.5.

OTHER POLYNITRO ALIPHATIC COMPOUNDS

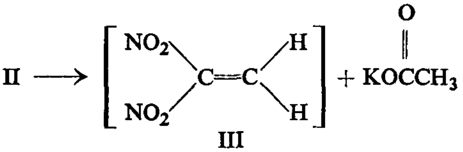
A new general method of preparing polynitro aliphatic compounds was recently described by Frankel [92]. The reaction consists in acting with 2-bromo-2,2-dinitroethyl acetate (I) on metallic salts of organic and inorganic compounds having active hydrogen atoms.

The following mechanism is given by the author, for the formation of 2,2,4,4-tetranitrobutyl acetate (V) :



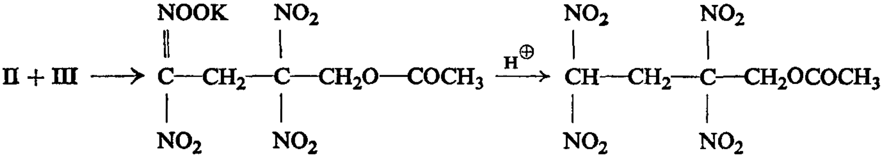
$$2Br-\underset{NO_2}{\overset{NO_2}{C}}-CH_2OCOCH_3 + 4KI \longrightarrow 2\underset{NO_2}{\overset{NOOH}{\overset{\|}{C}}}-CH_2OCOCH_3 + 2KBr + I_2 \qquad (33a)$$

I II



$$II \longrightarrow \left[\begin{matrix} NO_2 & & H \\ & C{=}C & \\ NO_2 & & H \end{matrix}\right] + K\overset{O}{\overset{\|}{OC}}CH_3 \qquad (33b)$$

III



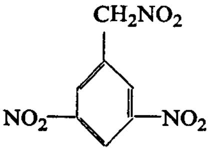
$$II + III \longrightarrow \underset{NO_2}{\overset{NOOK}{\overset{\|}{C}}}-CH_2-\underset{NO_2}{\overset{NO_2}{C}}-CH_2O-COCH_3 \xrightarrow{H^{\oplus}} \underset{NO_2}{\overset{NO_2}{CH}}-CH_2-\underset{NO_2}{\overset{NO_2}{C}}-CH_2OCOCH_3 \qquad (34)$$

IV V

It is suggested that the reaction occurs through the intermediate formation of 1,1-dinitroethylene (III). The reaction was described as "dinitroethylation".

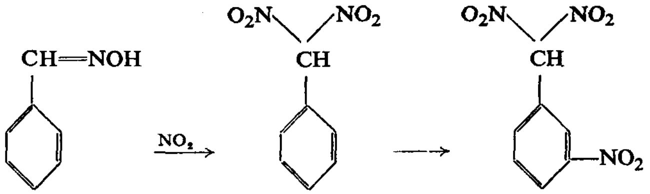
NITROAROMATIC DERIVATIVES OF MONO-, DI-, AND TRI-NITROMETHANE

T. Urbanski and Gedroyc [93] prepared dinitrophenylnitromethane (I) - a trinitrotoluene isomer - by nitration of phenylnitromethane. The compound has proved to have explosive properties similar to those of TNT.

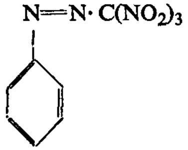


I

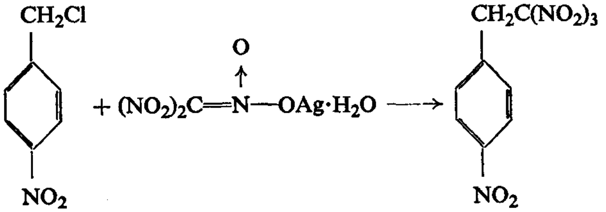
Milone and Massa [94] prepared another isomer of trinitrotoluene, namely nitrophenyl dinitromethane (II) by the action of nitrogen dioxide on benzaldoxime followed by the nitration of the resultant product:


(35)

Ponzio [95] obtained unstable aromatic azo derivatives of trinitromethane (of the type III) by reacting the ammonium salt of trinitromethane with diazonium salts:

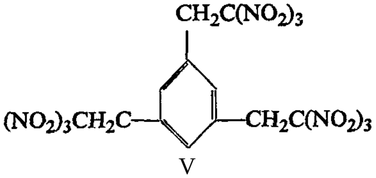

III

W. S. Reich [96] prepared aromatic derivatives of trinitromethane (of the type IV) by acting with the silver salt of nitroform on ar-alkyl chlorides, as for example *p*- nitrobenzyl chloride :


IV

(36)

In a similar way he obtained compound V from w,w',w"-triiodomesitylene:


V

Compounds of this type are powerful explosives.

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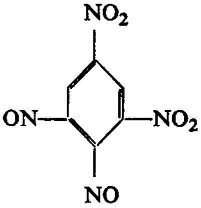
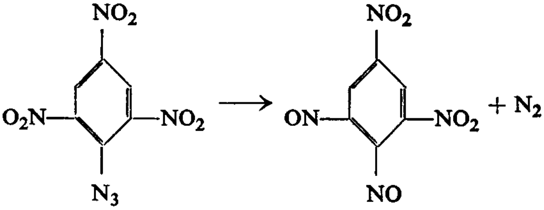
CHAPTER XX

NITRONITROSO AND NITROSO COMPOUNDS

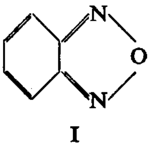
DINITRODINITROSOBENZENE



THE METHOD of the preparation of dinitrodinitrosobenzene has already been discussed (see p. 263). This product also forms in the thermal decomposition of picryl azide at temperatures of 90-100°C. In addition, nitrogen is generated in the reaction (Rathsburg [I]):

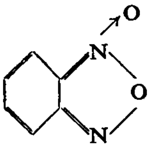


More recent studies on the structure of *o*- dinitroso derivatives of benzene indicate they may have the benzofurazan ring (I) which was described for the first time by Forster and Fierz [2].

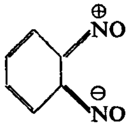


I

Green and Rowe [3] suggested a benzofuroxane structure (II) for *o*- dinitrosobenzene and its derivatives. This view was further developed by Hammick, Edwards and Steiner [4] and also by Gaughran, Picard and Kaufman [5]. However, Boyer expressed the view that the *o*- dinitroso structure (III) is more probable:

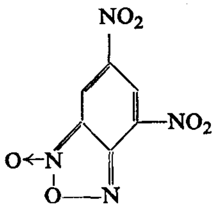


II

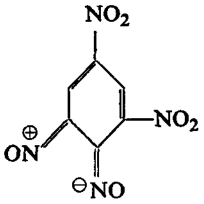


III

In the light of the above, the structure of dinitrodinitrosobenzene should be presented by the formulae IIa and IIIa respectively:



IIa

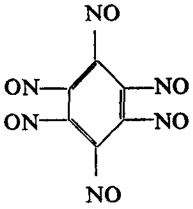


IIIa

In the end the benzofuroxane structure (II) was accepted for *o*- dinitrosobenzene (mainly on the basis of the NMR spectrum (Engler [7]).

Dinitrodinitrosobenzene is a powerful explosive: it gives a lead block expansion of 360 cm^3.

HEXANITROSOBENZENE

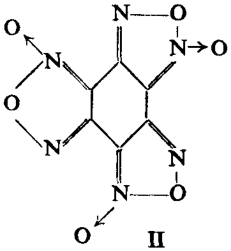


I

By heating trinitrotriazidebenzene (see Vol. III) at 100°C or higher Turek [8] obtained a compound to which he assigned the structure of hexanitrosobenzene (I, m. p. 159°C).

Hexanitrosobenzene is a stable, non-hygroscopic substance. It is more sensitive to impact than tetryl. The lead block expansion it gives is larger than that given by tetryl.

In the light of the above considerations the benzotrifuroxane structure (II) might be assigned to the Turek’s hexanitrosobenzene,



II

Nitrosophenols have already been dealt with in the chapter on nitrophenols.

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AUTHOR INDEX

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CHAPTER XX. SALTS OF OXY-ACIDS OF CHLORINE

CHAPTER I

NITRIC ESTERS—GENERAL OUTLINE

STRUCTURE

ESTERS of nitric acid are characterized by the following atomic grouping:

$$—C—O—NO_2$$

that is by the presence of the nitroxy group. The nitro group in nitric esters is attached to a carbon atom by means of an oxygen atom, i.e. they are O-nitro compounds. This is confirmed by the fact that nitric esters undergo hydrolysis, and that as the result of reduction of the nitro group, an alcohol is obtained:

$$R—ONO_2 \xrightarrow{[H]} R—OH + NH_3$$

This reaction shows the essential difference between nitric esters and nitro compounds: the latter form amines under these conditions.

The structure of the nitro group present in nitric esters is the same as that in nitro compounds.

The reactivity of nitric acid esters and in particular the complicated chemical composition of the products formed by their hydrolysis led some investigators [1, 37] to express the view that nitric esters may have the structure of peroxy-compounds (I):

$$R—O—O—NO$$

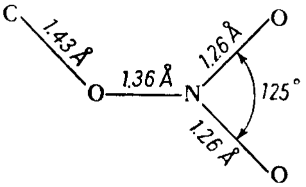
I

However there exists no evidence for this. Moreover, investigation of the absorption spectra of nitric acid, nitrous acid and aliphatic nitro compounds indicates that the peroxide structure hypothesis is incorrect, because nitric acid esters behave as compounds having the normal ester structure (II) (Crigee and Schnorrenberg [1a], Matsushima [1b]):

$$R—O—NO_2$$

II

X-Ray investigations, electron diffraction, Raman and infra-red spectra, and dipole moment measurements of nitric esters also support the idea of a symmetrical structure for the nitrate group (in spite of certain discrepancies obtained by different authors):



The bond distances and angles approximate to these found in nitro compounds. The most accurate figures were determined with methyl nitrate [109].

PHYSICAL PROPERTIES

Esters formed by combination of nitric acid with lower alcohols are liquids, the boiling points of which are slightly higher than the boiling temperatures of the respective alcohols, but significantly higher than the boiling points of esters of nitrous acid. C-nitro compounds are characterized by higher boiling temperatures than the corresponding nitric acid esters (Table 1).

TABLE 1

BOILING POINTS OF ALCOHOLS, ESTERS AND NITRO COMPOUNDS, °C

Alkyl	Alcohol	Nitric ester	Nitrous ester	Nitro compound
Methyl	65	65	−12	101
Ethyl	78	88	17	114
n-Propyl	96	111	47	131
Isopropyl	82	102	45	120
n-Butyl	117	136	75	151

The small differences between the boiling points of the alcohols and their nitric acid esters can be explained by the fact that the alcohols are highly associated liquids (mainly through hydrogen bonds). Due to this molecular association the viscosity of the alcohols is also higher than the viscosity of their nitric esters. On the other hand the presence of a semi-polar bond in the nitro group of nitric esters is responsible for their relatively high vapour pressure, as in nitro compounds, causing them to be more volatile than the corresponding alcohols.

De Kreuk [2] made the first systematic study of the various physical constants of nitric esters, i.e.: dielectric constant (ε_{20}), refractive index (n_{∞}^{20}), density (d_4^{20}) and viscosity (η_{20}), (Table 2). Figures for tribromohydrin and triacetin are given for comparison.

According to de Kreuk the difference between the viscosity values of similar compounds (e.g. 1,3- and 1,2-propanediol dinitrates, 1,3- and 2,3-butanediol dinitrates) may be attributed to rotational isomerism. Free rotation makes possible the formation of *trans* isomers which according to this author should possess a higher viscosity. This would explain the relatively high viscosities of 1,3-propanediol and 1,3-butanediol dinitrates.

Boileau and Thomas [3] have determined certain physical constants for nitroglycerine and a few glycol dinitrates of practical importance (Table 3).

TABLE 2

Substance	ε_{20}	n_{∞}^{20}	d_4^{20}	η_{20} (cP)
n-Butyl nitrate	13.10	1.39526	1.0156	0.87
Ethylene glycol dinitrate	28.26	1.43235	1.4918	4.61
1,3-Propanediol dinitrate	18.97	1.43476	1.3952	5.8
1,2-Propanediol dinitrate	26.80	1.42720	1.3774	4.65
1,3-Butanediol dinitrate	18.85	1.43259	1.3167	6.00
2,3-Butanediol dinitrate	28.84	1.42754	1.3061	4.7
Nitroglycerine	19.25	1.45731	1.5931	37.8
3-Chloro-1,2-propanediol dinitrate	17.50	1.45850	1.5323	12.4
1,3-Dichloro-2-propanediol nitrate	13.28	1.46032	1.4630	4.8
Tribromohydrin	6.45	1.56190	2.4360	
Triacetin	7.19	1.41929	1.1596	

TABLE 3

Ester	Viscosity, η		Density d_{16}^{16}	Refractive index $n_D^{21.2°}$
	temp., °C	P		
Nitroglycerine	5.1	1.033	1.5985	1.4725
	20.0	0.352		
	55.0	0.0875		
Dinitroglycol	7.1	0.0633	1.4918	1.4463
	20.0	0.0423		
	54.4	0.0198		
1,3-Propanediol dinitrate	6.3	0.0940	1.4053	1.4483
	20.2	0.0550		
	54.2	0.0275		
Diethylene glycol dinitrate	5.3	0.133	1.3890	1.4505
	20.4	0.0727		
	54.4	0.0337		
Triethylene glycol dinitrate	6.0	0.257	1.3291	1.4542
	20.3	0.119		
	54.2	0.015		

Dipole moments

Dipole moments of alkyl nitrates were determined by Cowley and Partington [4]. They found the value $\mu = 2.73$ D for methyl nitrate. The values of μ in the instance of longer chain alkyls do not differ essentially from this figure.

De Kreuk [2] also calculated dipole moments using his observed values of ε and n_{∞}^{20}. His figures are given in Table 4.

TABLE 4

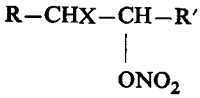
Substance	Dipole moment, μ (D)	
	Pure substance	In benzene solution
n-Butyl nitrate	2.90	2.98
Ethylene glycol dinitrate	4.00	3.28
1,3-Propanediol dinitrate	3.50	3.14
1,2-Propanediol dinitrate	4.24	3.72
1,3-Butanediol dinitrate	3.74	3.45
2,3-Butanediol dinitrate	4.72	4.12
Nitroglycerine	3.82	3.16
3-Chloro-1,2-propanediol dinitrate	3.46	3.05
1,3-Dichloro-2-propanediol nitrate	2.86	2.59
Tribromohydrin	1.63	1.58
Triacetin	2.50	2.58

The difference between the dipole moments of the pure substance and their value in benzene solution is (according to de Kreuk) due to the possible formation of a certain amount of *trans* rotation isomer in benzene. High values for pure 1,2-propanediol dinitrate and 2,3-butanediol dinitrate are due to the presence of a high proportion of the *cis* form in the pure liquids.

Although the conclusion of de Kreuk on the influence of rotational isomerism on dipole moments is correct, his quantitative estimation of the proportion of isomers is not convincing as it was based on some assumptions.

Mortimer, Spedding and Springall [5] examined the dipole moments of pentaerythritol tetranitrate and also concluded that the existence of rotational isomers was possible.

Recently T. Urbański and Witanowski [6] have suggested, on the basis of infra-red absorption spectra, that rotational isomers are present in nitrates of the general formula



$$\mathrm{R{-}CHX{-}\underset{\displaystyle ONO_2}{\underset{|}{CH}}{-}R'}$$

when X is relatively large, e.g. X = ONO_2, NO_2, CN, I, Br, Cl (see pp. 6 and 45).

Spectroscopy

The O-nitro group (the nitroxy group) gives an absorption band of about 270 mμ, in the ultra-violet region, i.e. a band similar to that of the C-nitro group. A relatively small amount of work has been done on the ultra-violet absorption spectra of nitric acid esters but it has been established that in esters containing no other chromophoric groups absorption is extremely low ($\varepsilon = 10$–20) even lower than in case of aliphatic nitro compounds.

Data published by Masaki [7] and by R.N. Jones and Thorn [8] are collected below in Table 5.

TABLE 5

Compound	Solvent	Maximum absorption		Author
		wavelength mμ	extinction ε	
$C_2H_5ONO_2$		270	10	Masaki
$C_2H_5ONO_2$	Ethanol	265	14.8	Jones and Thorn
α-Methyl-glucose 6-nitrate	Water	265	19.0	Jones and Thorn
2,3,4-Trimethyl-methyl-α-glucose 6-nitrate	Ethanol	265	21.4	Jones and Thorn

A few ultra-violet spectra of nitric esters were also given by Dalmon and Bellin [9].

As early as 1929 Plyler and Steele [10] began an investigation of the infra-red spectra of nitric esters in the range methyl to n-butyl nitrates. Dadieu, Jele and Kohlrausch [11] studied the Raman spectra of nitric esters as well as inorganic nitrates, and aliphatic and aromatic nitro compounds.

The Raman spectra of nitric esters have received relatively less attention for two reasons:

(a) their tendency to decompose under irradiation with ultra-violet light,

(b) the greater danger involved in using the relatively large samples needed.

Nevertheless a number of important researches were carried out prior to 1945, i.e. at the time when the infra-red technique was not fully perfected, among which the experiments of Médard [12], Chédin [13], Lecomte and Mathieu [14], Wittek [15], Nielsen and Smith [16] are worthy of note.

Further experiments on the infra-red spectra of alkyl nitrates were carried out by: Kettering and Sleater [17], Lenormant and Clement [18], Brand and Cawthon [19], Kornblum, Ungnade and Smiley [20], Carrington [21], Guthrie and Spedding [22].

Kumler [23], McCallum and Emmons [24] examined the infra-red spectra of nitric esters of hydroxyacids.

Namba, Yamashita and Tanaka [25] investigated the infra-red spectra of penta-, dipenta- and tripentaerythritol nitrates.

An extensive study was carried out by Brown [26] who examined over twenty esters of nitric acid and found the characteristic stretching frequencies of the NO_2 ester group:

asymmetric	1639 ± 13 cm^{-1}
symmetric	1279 ± 7 cm^{-1}

Bellamy [27] examined a number of nitric esters, among them ethylene glycol dinitrate and pentaerythritol tetranitrate and found the stretching frequencies to be 1650–1610 and 1300–1250 cm^{-1} respectively.

This is well in line with the Raman spectrum which, according to various authors, gives two frequencies near 1640 and 1290 cm^{-1} characterizing vibrations of the NO_2 group. Similar figures were given for Raman spectra by Nielsen and Smith [16].

Among more common nitric esters, nitrocellulose was examined by Ellis and Bath [28] and Nikitin [29] (p. 287). Nitroglycerine and diethylene glycol dinitrate were examined for the first time by Pinchas [30]. Pristera [31] investigated a number of nitrates used as propellant ingredients, such as nitroglycerine, metriol trinitrate, diethylene glycol dinitrate (DEGN) and triethylene glycol dinitrate (TEGN). According to Pristera all of them give two bands with frequencies near 1667 cm^{-1} (6 μ) and 1282 cm^{-1} (7.8 μ). The particular compounds vary in details with regard to the shape of the absorption curves. Thus, the tip of the symmetric stretching band of diethylene glycol dinitrate (*ca.* 1639 cm^{-1}) has a shoulder, whereas that of triethylene glycol dinitrate has not. The 1282 cm^{-1} band of nitroglycerine has a strong shoulder which does not exist in the spectra of other nitrates. The shoulders are most likely due to rotational isomerism [6].

On the basis of the results obtained with more than 40 nitric esters, T. Urbański and Witanowski [6] have found the following frequencies of vibrations characteristic to nitric esters:

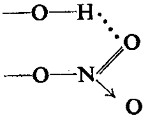
asymmetric stretching	ν_{as}	(NO_2)	1675–1621 cm^{-1}
symmetric stretching	ν_s	(NO_2)	1301–1268 cm^{-1}
stretching	ν	$(C-O)$	1100–950 cm^{-1}
stretching	ν	$(O-N)$	880–815 cm^{-1}
wagging	γ_w	(NO_2)	760–737 cm^{-1}
bending	δ	(NO_2)	710–640 cm^{-1}
rocking	γ_r	(NO_2)	*ca.* 580 cm^{-1}

It was found that asymmetric NO_2 vibrations are readily subject to a change in frequency when R in the molecule $R-ONO_2$ is changed. A positive and negative induction effect of R respectively lowers and raises the frequency of ν_{as} (NO_2). This fact makes it possible to distinguish between primary, secondary and tertiary alkyl nitrates.

Both the asymmetric and symmetric NO_2 vibration bands are shifted towards higher frequencies when the ONO_2 group is approaching another bulky group. This helps in recognizing the rotational isomerism mentioned above (p. 4). As a result of the presence of rotational isomers both the stretching vibrations of the NO_2 group are split into two (and in some instances more) maxima differing appreciably:

asymmetric by 1–25 cm^{-1}
symmetric by 10–35 cm^{-1}

No internal hydrogen bond was detected between OH and ONO_2 groups



indeed it seems that ONO_2 inhibits the formation of an intermolecular hydrogen bond between itself and OH groups.

HYDROLYSIS OF NITRIC ESTERS

Nitric esters of monovalent and polyvalent alcohols are hydrolysed by comparatively mild reagents in alkaline or acid media and with slightly more difficulty in a neutral medium. Theoretically, this process might be expressed by the following equation:

$$RONO_2 + H_2O \longrightarrow ROH + HNO_3 \qquad (1)$$

However, the alcohol and acid formed during the hydrolysis of nitric esters are accompanied by a range of other compounds such as aldehydes, ketones, hydroxycarboxylic acids, unsaturated hydrocarbons, nitrous acid, etc. (e.g. reference [107]).

In certain cases the hydrolysis process does not result in the formation of the initial alcohol at all, but a series of other compounds is obtained, by a reaction mechanism which is often unknown. As an example, the hydrolytic reaction of nitroglycerine performed in an aqueous or alcoholic solution of sodium or potassium hydroxide can be quoted. Oxidation and reduction processes take place simultaneously to form organic acids as well as nitrates and nitrites. After Hay [32] the course of the reaction can be summarized by the eqn. (2):

$$C_3H_5(ONO_2)_3 + 5KOH \longrightarrow KNO_3 + 2KNO_2 + CH_3COOK + HCOOK + 3H_2O \qquad (2)$$

This equation does not present a full picture of the chemical changes that occur, before Vignon and Bay [33], Silberrad and Farmer [34] and Berl and Delpy [35] identified the presence of aldehyde resins, oxalic acid and ammonia among the products of hydrolysis performed under similar conditions.

The absence of glycerine among the products of hydrolysis in alkaline medium was also confirmed by Carlson [36].

According to Klason and Carlson [37] glycerol is formed, however, when nitroglycerine is hydrolysed in alkaline media containing readily oxidizable substances, as for instance phenyl mercaptan.

Much experimental work has been carried out in seeking an explanation of the mechanism of the hydrolysis process of nitric esters but a relatively satisfactory theoretical explanation of the phenomenon has been found only recently.

Klason and Carlson were of the opinion that the formation of nitrous acid takes place owing to the peroxy structure of nitric esters, as these, under the influence of a hydrolysing agent, would change their structure and be transformed into peroxy compounds. Simultaneously nitrous acid would be formed:

$$ROONO + H_2O \longrightarrow ROOH + HNO_2 \qquad (3)$$

Now since the chemical structure of nitric esters has already been established, this hypothesis has been abandoned.

However, Matsushima [1b] suggested that peroxides may be formed in the course of hydrolysis of nitric esters (4) as transition products prior to the formation of aldehydes (5):

$$RCH_2ONO_2 + H_2O \longrightarrow RCH_2OOH + HNO_3 \tag{4}$$

$$RCH_2OOH \longrightarrow RCHO + H_2O \tag{5}$$

According to Farmer [38] the first stage of hydrolysis proceeds in accordance with the eqn. (1) (p. 7). Afterwards, the products react with one another to form nitrous acid or nitrites and the series of compounds ennumerated above. Farmer's hypothesis seems unsatisfactory when hydrolysis of nitric esters is carried out in a neutral medium since, for example, if ethyl alcohol is treated with an aqueous solution of potassium nitrate no oxidation of the ethyl alcohol occurs even if the mixture of compounds is boiled.

An instance of the production of olefins has been detected by Lucas and Hammett [39] as the result of hydrolysing the nitric ester of tertiary butyl alcohol. In this case, in addition to the corresponding alcohol a certain quantity of isobutylene is also formed, as shown by eqn. (7):

$$C_4H_9ONO_2 + 2H_2O \longrightarrow C_4H_9OH + H_3O^{\oplus} + NO_3^{\ominus} \tag{6}$$

$$C_4H_9ONO_2 + H_2O \longrightarrow C_4H_8 + H_3O^{\oplus} + NO_3^{\ominus} \tag{7}$$

In experiments with benzyl nitrate the same workers have established that during the hydrolysis of this ester a certain quantity of benzaldehyde is obtained together with benzyl alcohol:

$$C_6H_5CH_2ONO_2 + 2H_2O \longrightarrow C_6H_5CH_2OH + H_3O^{\oplus} + NO_3^{\ominus} \tag{8}$$

$$C_6H_5CH_2ONO_2 \xrightarrow{H_2O} C_6H_5CHO + HNO_2 \tag{9}$$

Experimental data collected by Baker and Easty [40] during a study of the hydroysis of nitric esters has led them to conclude that this reaction can proceed in three directions as shown in the following equations:

$$RCH_2CH_2ONO_2 + Y^{\ominus} \longrightarrow RCH_2CH_2Y + NO_3^{\ominus} \tag{10}$$

$$RCH_2CH_2ONO_2 + Y^{\ominus} \longrightarrow RCH{=}CH_2 + NO_3^{\ominus} + HY \tag{11}$$

$$RCH_2CH_2ONO_2 + Y^{\ominus} \longrightarrow RCH_2CHO + NO_2^{\ominus} + HY \tag{12}$$

Y being a hydrolysing agent.

In the first case (10) a reaction of nucleophilic substitution takes place; the second equation (11) indicates that a hydrogen atom in the β-position can be removed; similarly the removal of an α-hydrogen atom is postulated in eqn. (12).

The experiments mentioned above were performed in aqueous solutions of alcohol containing aliphatic mononitrates. The hypothesis of Baker and Easty is supported by the established fact that methyl nitrate fails to react according to eqn. (11) and that tertiary butyl nitrate is unable to decompose in the way suggested by reaction (12). It is also noteworthy that methyl nitrate reacts according to (12) only in an insignificant degree and that only about 4% of ethyl nitrate takes part in reactions (11) and (12) whereas all the remainder of this compound hydrolyses in accordance with eqn. (10). The rates of the reactions (10), (11) and (12) correspond to ratios of 70:7:1.

Reductive hydrolysis of n-butyl nitrate in an aqueous solution of ethyl alcohol in the presence of sodium hydrosulphide or ammonium hydrosulphide has been carried out by Merrow, Cristol and van Dolah [41]. This is a complicated chemical reaction. As the result of hydrolysing the nitrate in the presence of sodium hydrosulphide (the alkalinity of the solution corresponds to pH 10–11) 93% of nitrite ions and 7% of ammonia are obtained from the ester group nitrogen. When ammonium hydrosulphide is used, the nitrite ions initially produced rise to a maximum concentration and then fall to zero owing to the reducing action of the ammonium hydrosulphide. The reduction process takes place more effectively when the pH is above 10.

The reactions can be represented by the eqns. (13) and (14):

$$C_4H_9ONO_2 + 2NaHS \longrightarrow C_4H_9OH + NaNO_2 + NaHS_2 \tag{13}$$

$$C_4H_9ONO_2 + 4NH_4HS + 3H_2O \longrightarrow C_4H_9OH + 4S + 4NH_4OH \tag{14}$$

Sodium hydrosulphide hydrolysis was commonly applied on an industrial scale in order to regenerate cellulose from nitrocellulose fibre. For this chemical process the following type of reaction can be suggested:

$$C_6H_8O_3(ONO_2)_2 + 2NaHS \longrightarrow C_6H_{10}O_5 + 2NaNO_2 + 2S \tag{15}$$

$$2NaHS + 2S \longrightarrow Na_2S_3 + H_2S \tag{16}$$

Nadai [42] proposed a slightly different mechanism for the hydrolysis of nitrocellulose by hydrosulphides:

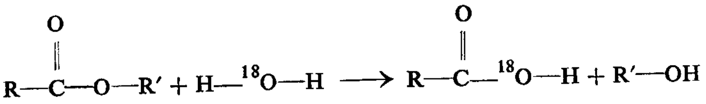
$$RONO_2 + HO^{\ominus} \longrightarrow ROH + NO_3^{\ominus} \tag{17}$$

$$NO_3^{\ominus} + 2HS^{\ominus} \longrightarrow NO_2^{\ominus} + HS_2^{\ominus} + HO^{\ominus} \tag{18}$$

Both the hydrolysis of nitrocellulose by means of hydroxides and the hydrolytic decomposition of butyl nitrate, as established by Merrow *et al.*, proceeds very slowly. For example, if a 0.1 *M* solution of butyl nitrate is hydrolysed at a temperature of 26.9°C by the action of 0.2 *M* sodium hydroxide dissolved in 60% ethanol, then after 16 days, only about 10% has entered into the reaction. With the addition of hydrosulphide, the process is completed within a period of 4 hr.

The above mentioned authors also established that the nitrate ion (in contrast with the nitrite ion) slowly undergoes reduction in the presence of sodium hydrosulphide. This leads to the conclusion that the nitrite ion formed during the hydrolysis of nitric esters cannot be produced by the reduction of a nitrate ion. Hence if the nitrite ion is formed direct during the hydrolysis of nitric esters, then it could only be produced by breaking the linkage between the oxygen and nitrogen atoms.

Since in numerous cases of hydrolysis of nitric esters the presence of a large amount of nitrate ion has been established, which could be liberated only by rupture of the C—O bond, the factors that influence the direction of this process should be discussed. Several investigations have thrown light on this problem, which is more complicated than with carboxylic esters, since during the hydrolysis of the latter compounds whether in acid or in alkaline medium only rupture of the ester bond can take place. This has been established in various ways including the use of water containing an ^{18}O-isotope. In general the hydrolysis of carboxylic esters can be defined by the equation:



$$R—\overset{\overset{O}{\|}}{C}—O—R' + H—^{18}O—H \longrightarrow R—\overset{\overset{O}{\|}}{C}—^{18}O—H + R'—OH \tag{19}$$

This reaction scheme has been confirmed by the hydrolysis of esters containing an optically active alcohol: no racemization of the alcohol occurs during the reaction.

In the investigation with n-butyl nitrate by Merrow, van Dolah and Cristol [41] already cited, neither the presence of the nitrate ion nor of mercaptan was detected. For this reason the following reaction mechanism was proposed for the hydrolysis of nitric acid alcohol esters by means of hydrosulphide:

$$RONO_2 + S_x^{2\ominus} \longrightarrow RO^{\ominus} + NO_2S_x^{\ominus} \tag{20}$$

$$NO_2S_x^{\ominus} + HS^{\ominus}(S^{2\ominus}) \longrightarrow NO_2^{\ominus} + HS_{x+1}^{\ominus} + (S_{x+1}^{2\ominus}) \tag{21}$$

$$HS_{x+1}^{\ominus} + HS^{\ominus} \rightleftarrows HS_x^{\ominus} + HS_2^{\ominus} \tag{22}$$

$$RO^{\ominus} + HS_x^{\ominus} \rightleftarrows ROH + S_x^{2\ominus} \tag{23}$$

$$HO^{\ominus} + HS_x^{\ominus} \rightleftarrows H_2O + S_x^{2\ominus} \tag{24}$$

or

$$RONO_2 + S_x^{2\ominus} \longrightarrow ROS_x^{\ominus} + NO_2^{\ominus} \tag{25}$$

$$ROS_x^{\ominus} + HS^{\ominus} \longrightarrow RO^{\ominus} + HS_{x+1}^{\ominus} \tag{26}$$

$$HS_{x+1}^{\ominus} + HS^{\ominus} \rightleftarrows HS_x^{\ominus} + HS_2^{\ominus} \tag{27}$$

$$RO^{\ominus} + HS_x^{\ominus} \rightleftarrows ROH + S_x^{2\ominus} \tag{28}$$

$$HO^{\ominus} + HS_x^{\ominus} \longrightarrow H_2O + S_x^{2\ominus} \tag{29}$$

As shown by the eqns. (20–24) owing to the activity of the sulphide or polysulphide ion, the O—N linkage is broken to form alkoxide and thionitrate or polythionitrate ions. In the other reactions the influence exerted by sulphide on the oxygen atom, which results in the creation of nitrite ions, has been taken into account. Both schemes indicate that the nitrite ion is not produced by the reduction of the nitrate ion.

Recently the reactivity of nitric esters in the presence of hydrazine has been investigated. These experiments are connected chiefly with the application of hydrazine as a liquid component in rocket fuels. In such fuels, nitric esters can play the part of the oxidizing and explosive component.

As long ago as 1896 Walther [43] observed that as the result of chemical reaction between ethyl nitrate and phenylhydrazine at an elevated temperature, aniline, ammonium nitrate and nitrogen are formed. If the reaction takes place in the presence of sodium ethoxide then, according to Bamberger and Billeter [44] even at room temperature nitrite ions, nitrogen, benzene, phenyl azide, azobenzene, nitrobenzene, aniline, acetic acid and acetaldehyde are formed.

Owing to the influence of hydrazine, at room temperature and in the presence of palladium or platinum as a catalyst, hexyl nitrate is transformed into the corresponding alcohol. Amongst other products nitrous oxide and nitrogen are formed during the same process (L. P. Kuhn [45]):

$$2C_6H_{13}ONO_2 + 2N_2H_4 \longrightarrow 2C_6H_{13}OH + N_2O + 3H_2O + 2N_2 \qquad (30)$$

If in this reaction hydrazine is replaced by methylhydrazine, then the hexyl nitrate forms not methyl hexyl ether but hexyl alcohol.

Merrow and van Dolah [46] investigated the behaviour of nitric esters in the presence of hydrazine and its derivatives. According to these authors nitric esters at room temperature and without catalysts react with phenylhydrazine very slowly even if the concentrations of the components are high.

Analysing the products of reaction between alkyl nitrates and hydrazine they detected nitrate and nitrite ions, a corresponding alcohol, alkyl hydrazine, nitrogen oxides, ammonia and traces of aldehyde. If the reaction is performed without solvents in an excess of hydrazine, reduction occurs. In an aqueous solution of alcohol the process of substitution predominates particularly when the concentrations of reagents are low.

Merrow and van Dolah also established that during the hydrolysis of β-chloroethyl nitrate, 1,3-dichloro-2-propyl nitrate, glycerol trinitrate or glycol dinitrate the gaseous products are evolved more vigorously than during the reaction of unsubstituted aliphatic nitrates.

Investigating the types of reaction between nitric acid esters and hydrazine Merrow and van Dolah endeavoured first of all to solve the problem of how nitric acid is formed since the answer could in effect make it possible to establish the position of the linkage to be broken off in an ester molecule. They have established experimentally that during the reaction between alkyl nitrates and hydrazine the nitrite ion is produced very quickly. Later it dwindles away as reaction proceeds. The creation of $NO_2^{\ominus}$ in this process can never arise from the removal of a hydrogen atom in the α-position, since only an insignificant amount of ester can follow the reaction (31) to form an aldehyde:

$$RCH_2ONO_2 \xrightarrow{N_2H_4} RCHO + H^{\oplus} + NO_2^{\ominus} \qquad (31)$$

Further, the nitrite ion cannot be the reduction product of the nitrate ion formed in consequence of the rupture of the C—O bond since, for example, the NO_3-ion of sodium nitrate does not undergo any change in presence of hydrazine.

The $NO_2^{\ominus}$-ion might be formed from the nitrous acid ester if the latter was present as an impurity in the main reactant. Trials carried out with ethyl nitrite and n-butyl nitrite have demonstrated, however, that when these compounds are treated with an excess of hydrazine they do not undergo any chemical reaction accompanied by the formation of the nitrate ion.

According to Merrow and van Dolah the reaction between a nitric ester and hydrazine is performed in the way outlined below:

$$RONO_2 + H_2NNH_2 \longrightarrow RO^{\ominus} + H_2N{-}\overset{\oplus}{N}H_2{-}NO_2 \rightleftharpoons ROH + H_2N{-}NHNO_2 \tag{32}$$

$$H_2N{-}NH{-}NO_2 + H_2NNH_2 \begin{array}{ll} \nearrow H_2N{-}NH{-}NH{-}NH_2 + HNO_2 & (33) \\ \searrow HN{=}NH + N_2H_4 \cdot HNO_2 & (34) \end{array}$$

$$H_2N{-}NH{-}NH{-}NH_2 \longrightarrow N_2 + 2NH_3 \tag{35}$$

$$2NH{=}NH \begin{array}{ll} \nearrow NH{=}N{-}NH{-}NH_2 \longrightarrow HN_3 + NH_3 & (36) \\ \searrow N_2 + H_2N{-}NH_2 & (37) \end{array}$$

In the first stage of the reaction an alkoxyl anion and the nitrohydrazine cation are formed which afterwards react together to give the corresponding alcohol and nitrohydrazine. Nitrohydrazine reacts with excess hydrazine to produce tetrazene, nitrous acid and di-imid. Then the tetrazene decomposes to form ammonia and nitrogen; from di-imid on the other hand tetrazene, hydrazine and nitrogen are formed. Hydrazoic acid and ammonia are then formed as decomposition products of tetrazene.

Reactions (32–37) take place as a result of breakage of the N—O linkage, in a manner analogous to the breakage of the chemical bond between an acyl radical and an oxygen atom when esters of carboxylic acids are hydrolysed. Generally the linkage is broken off in this way when the n-alkyl esters of nitric acid are hydrolysed in an alkaline medium or when nitration is carried out with nitrates in the presence of bases, e.g. the nitration of aniline by means of ethyl nitrate in the presence of potassium ethoxide to yield phenylnitramine as its final product (Bamberger [47]).

The above reaction scheme between nitric esters and hydrazine or its derivatives is confirmed by the reaction of methylhydrazine and ethyl nitrate which yield methane (not ethane) and nitrogen. This indicates that the unstable monomethyl-di-imid should have been an intermediate product:

$$CH_3HNNH_2 + C_2H_5ONO_2 \longrightarrow CH_3N{=}NH + C_2H_5OH + HNO_2 \tag{38}$$

$$CH_3N{=}NH \longrightarrow CH_4 + N_2 \tag{39}$$

The gradual decreasing concentration of nitrous acid in the mixture of reagents can be explained as the result of the reduction process taking place under the influence of hydrazine:

$$HNO_2 + N_2H_4 \longrightarrow NH_3 + N_2O + H_2O \qquad (40)$$

$$HNO_2 + N_2H_4 \longrightarrow HN_3 + 2H_2O \qquad (41)$$

$$HNO_2 + HN_3 \longrightarrow N_2 + N_2O + H_2O \qquad (42)$$

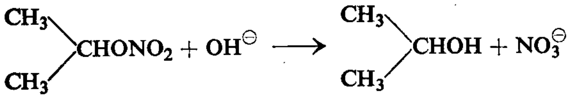
Benzyl nitrate reacts with hydrazine in the presence of solvents or without a solvent to give a range of substitution product: $C_6H_5CH_2HNNH_2$, $(C_6H_5CH_2)_2NNH_2$, $(C_6H_5CH_2)_2NNHCH_2C_6H_5$, $(C_6H_5CH_2)_2NN(CH_2C_6H_5)_2$.

By application of benzylhydrazine, benzaldibenzylhydrazine

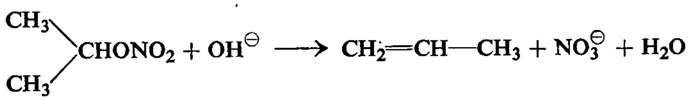
$$(C_6H_5CH_2)_2N{-}N{=}CHC_6H_5$$

has been obtained. It is not certain whether the compound formed was a product of reaction between benzaldehyde (formed by removal of a hydrogen atom in the α-position) and 1,1-dibenzylhydrazine, or an oxidation product of tribenzylhydrazine. Kenner and Wilson [48] have established that tribenzylhydrazine is very likely to be oxidized even by atmospheric oxygen.

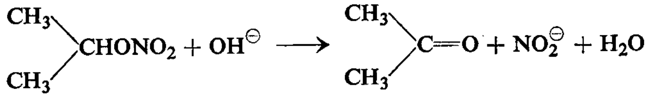
In the presence of hydrazine the C—O linkages of tert-butyl nitrate undergo rupture almost exclusively to form isobutylene and hydrazine nitrate. During this reaction neither the presence of nitrogen nor of its oxides has been detected. By hydrolysing isopropyl nitrate in an alkaline medium, Baker has obtained 70–80% of isopropyl alcohol, 11–14% of propylene and 8–14% of acetone. If the reaction types (10, 11, 12) as suggested by Baker and Easty [40] are accepted, the hydrolysis process can be expressed by the following equations:



$$\begin{array}{l}CH_3\diagdown\\ \qquad CHONO_2\\ CH_3\diagup\end{array} + OH^{\ominus} \longrightarrow \begin{array}{l}CH_3\diagdown\\ \qquad CHOH\\ CH_3\diagup\end{array} + NO_3^{\ominus} \qquad (43)$$



$$\begin{array}{l}CH_3\diagdown\\ \qquad CHONO_2\\ CH_3\diagup\end{array} + OH^{\ominus} \longrightarrow CH_2{=}CH{-}CH_3 + NO_3^{\ominus} + H_2O \qquad (44)$$



$$\begin{array}{l}CH_3\diagdown\\ \qquad CHONO_2\\ CH_3\diagup\end{array} + OH^{\ominus} \longrightarrow \begin{array}{l}CH_3\diagdown\\ \qquad C{=}O\\ CH_3\diagup\end{array} + NO_2^{\ominus} + H_2O \qquad (45)$$

By hydrolysing isopropyl nitrate in a neutral medium only alcohol is formed.

Accepting the reaction (10) suggested by Baker and Easty in order to explain how the alcohol is formed, it must be assumed that the process consists of two successive stages. First a carbonium ion is formed:

$$RONO_2 \longrightarrow R^{\oplus} + ONO_2^{\ominus} \qquad (46)$$

and then an addition-exchange process takes place:

$$R^{\oplus} + H_2O \longrightarrow ROH + H^{\oplus} \qquad (47)$$

No analogous reactions take place with carboxylic acid esters. Cristol and his co-workers [49] therefore suggest that initially an alkoxyl ion is formed and afterwards the corresponding alcohol and nitrate ion are produced:

$$RO{-}NO_2 + OH^{\ominus} \longrightarrow RO^{\ominus} + HONO_2 \longrightarrow ROH + NO_3^{\ominus} \qquad (48)$$

Cristol and his co-workers have carried out the hydrolysis of the optically active 2-octyl nitrate in alkaline and neutral media. The alkaline hydrolysis was performed in the presence of sodium hydroxide both in 92.6% ethanol, where the participation of the ethoxide ion should be taken into account, and in a 64% aqueous solution of dioxane. The neutral hydrolysis was carried out in a 70% acetone solution in the presence of calcium carbonate.

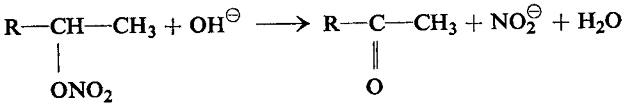
By esterifying (+)2-octanol using a mixture of nitric and sulphuric acid, it was established that the nitrate produced did not undergo inversion. The (+)2-octyl nitrate obtained was heated during a period of 50 hr in a 10% alcoholic solution of sodium hydroxide. The optical rotation of all the reaction products was nil. Analysis by means of Grignard's reagent indicated 45.6% of 2-octanol, 39.8% of ketone and 14.6% of ether (by difference). A sample of the alcohol contained 76% of (+)2-octanol and 24% of racemate, i.e. 88% of (+)2-octanol and 12% of (–)2-octanol.

On the basis of these results and taking into account the effect of the ethoxide ion, the authors propose the following reaction schemes:

$$\mathrm{EtO}^{\ominus} + \mathrm{R{-}ONO_2} \longrightarrow \mathrm{EtOR} + \mathrm{NO_3^{\ominus}} \tag{49}$$

$$\mathrm{EtO}^{\ominus} + \mathrm{RO{-}NO_2} \longrightarrow \mathrm{EtONO_2} + \mathrm{RO}^{\ominus} \tag{50}$$

During the hydrolysis of 2-octyl nitrate according to eqn. (49), ethyl 2-octyl ether is formed which should have a rotation contrary to that of the unreacted nitrate. On the other hand from the reaction (50) which resembles to some extent eqn. (48), an alcohol of the same rotation and a product of transesterification is obtained. Cristol does not explain in detail the mechanism of the reaction of transesterification (ester group exchange reaction). None the less an assumption can be made that it may occur only in the presence of nitronium cation $\mathrm{NO_2^{\oplus}}$. Further, the reaction leading to the formation of ketones has not yet been explained. Most probably it is analogous to the scheme (12) in which a hydrogen atom attached to the α-carbon atom is split off after a O—N linkage is broken:



$$\underset{\displaystyle\mathrm{ONO_2}}{\mathrm{R{-}\underset{|}{C}H{-}CH_3}} + \mathrm{OH}^{\ominus} \longrightarrow \mathrm{R{-}\underset{\displaystyle\overset{\|}{O}}{C}{-}CH_3} + \mathrm{NO_2^{\ominus}} + \mathrm{H_2O} \tag{51}$$

The experiment of hydrolysing 2-octyl nitrate in a dioxane solution has been carried out with a laevo-rotatory ester. In the reaction products 2-octanol forms as the main product with some 2-octanone and a little unchanged 2-octyl nitrate. The rotation of the reaction product amounted to –3.77°, and the alcohol consisted of a mixture containing 42% of (–)2-octanol and 58% of racemate, i.e. 71% (–)2-octanol and 29% (+)2-octanol.

By hydrolysis of a dextro-rotatory 2-octyl nitrate in a neutral medium, this compound has been decomposed to yield a laevo-rotatory product containing 13% of 2-octanone and 87% of 2-octanol, the latter comprising 71% of (–)2-octanol and 29% racemate, i.e. 85.5 parts of laevo-rotatory and 14.5 parts of dextro-rotatory alcohol.

It can be concluded from these experimental results that in alkaline media the 2-octyl nitrate behaves like a typical ester (Day and Ingold [50]). In neutral media, on the other hand, it behaves like an alkyl halogenide or like an ester of sulphuric acid.

Cristol also established in the work cited that the hydrolysis of 2-octyl nitrate cannot be performed with dilute sulphuric acid. In the presence of 10% sulphuric acid as much as 99 parts of alcohol having the same rotation as the original nitrate were formed. With 70–90% sulphuric acid, 2-octanone and nitrogen oxides were formed.

According to Merrow and van Dolah [51] (+)2-octyl nitrate reacts with hydrazine at room temperature to yield 84% (+)2-octanol, whilst by the reaction of the laevo-rotatory nitrate and ammonium polysulphide as much as 99 parts of (−)2-octanol are produced. The fact that to a large extent the original rotation was preserved indicates that in the cases cited the initial step was rupture of the N—O bond.

Further experiments on the hydrolysis of *cis*- and *trans*-cyclohexanediol dinitrates have been carried out by Merrow and van Dolah. The *trans*-1,2-cyclohexanediol dinitrate in the presence of hydrazine is transformed exclusively into *trans*-1,2-cyclohexanediol. Similarly the *cis*-isomer does not change its configuration if treated with ammonium sulphide. All these observations confirm the conclusion mentioned above.

Baker [52], who investigated the influence of nucleophilic reagents on benzyl nitrate in anhydrous alcohol, has established that two parallel reactions proceed simultaneously (Y is a hydrolysing agent):

$$Y^{\ominus} + C_6H_5CH_2ONO_2 \longrightarrow C_6H_5CH_2Y + NO_3^{\ominus} \tag{52}$$

$$Y^{\ominus} + C_6H_5CH_2ONO_2 \longrightarrow C_6H_5CHO + NO_2^{\ominus} + HY \tag{53}$$

The latter reaction takes place via an intermediate stage:

$$C_6H_5CH_2ONO_2 \longrightarrow C_6H_5CH_2O^{\oplus} + NO_2^{\ominus} \tag{54}$$

If the reaction medium contains an aroxide as well as the alkoxide ions, then it is mainly the second of these two ions, which is more nucleophilic, that takes part in the chemical reaction. The way in which both ions are formed from the solvent has been described by Baker according to eqn. (55):

$$Y^{\ominus} + \mathrm{EtOH} \longrightarrow HY + \mathrm{EtO}^{\ominus} \tag{55}$$

Baker controlled the kinetics of the reactions (52) and (53) in the presence of ethyl alcohol, phenol and its mononitro derivative.

On the basis of experiments on the hydrolysis of numerous esters of inorganic acids carried out by Anbar *et al.* [53] this reaction has been defined by means of the three following equations:

$$Y^{\ominus} + \text{—C—O—X} \longrightarrow \text{—CY} + OX^{\ominus} \tag{56}$$

$$Y^{\ominus} + \text{—C—O—X} \longrightarrow \text{—CO}^{\ominus} + XY \tag{57}$$

$$Y^{\ominus} + \text{H—C—O—X} \longrightarrow \text{C=O} + HY + X^{\ominus} \tag{58}$$

According to eqn. (56) a nucleophilic substitution takes place, i.e. the component Y is attached to the α-carbon atom. Similarly in reaction (57) $Y^{\ominus}$ attaches itself to the central atom of the X-group (such as the nitrogen atom in the nitro group). The last equation illustrates a typical oxidation process, producing an aldehyde or ketone with the removal of a hydrogen atom attached to the α-carbon atom.

Equations (56) and (57) are analogous to (10) and (12) proposed by Baker; and (58) resembles (50).

In order to generalize on the conditions that determine the direction of the hydrolysis process and to deduce adequate conclusions, several examples of the hydrolysis of esters of inorganic acids are quoted below together with the probable reaction type. Hydrolysis was performed in an alkaline medium using water labelled with the ^{18}O-isotope.

tert-Butyl hypochlorite	(57)
Triphenylmethyl chlorate, bromate, iodate	(58)
Triphenylmethyl perchlorate	(56)
n-Butyl nitrate	(57)
tert-Butyl nitrate	(57)
Triphenylmethyl nitrate	(57)
n-Butyl nitrate	various reactions
n-Octyl nitrate	various reactions
tert-Butyl nitrate	(56)
Triphenylmethyl nitrate	(56)

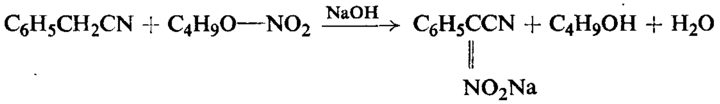
It is clear from this comparison that triphenylmethanol esters of weaker acids undergo the reaction of hydrolysis as shown in the scheme (57). Depending on the kind of radical, during the hydrolysis of strong acid esters either the R—O bond is broken (scheme 56) or a mixture of reaction products is formed as indicated by the schemes mentioned. The reaction goes more readily with esters of weak acids, as the radical's influence is not prominant. With strong acid esters and the more electronegative (iso-) radicals hydrolysis proceeds in accordance with eqn. (56). Esters of strong acids and those which contain less electronegative radicals do not demonstrate any definite direction of hydrolysis.

The above conclusions find further confirmation in the results of hydrolysis of sugar nitrates that have been carried out by Ansell and Honeymann [54], and in experiments to nitrate cyclic ketones by means of optically active nitrates made by Horn and Shirner [55].

Comparing triphenylmethanol esters of hydroxy-acids we can establish that the higher oxidation compounds (being at the same time also stronger acids) are hydrolysed according to the reaction scheme (56), whilst with compounds having a lower degree of oxidation the process follows eqn. (57). For instance, among the following esters: RO—Cl, RO—ClO, RO—ClO_2, RO—ClO_3, the change of reaction type occurs between chloric and perchloric acid esters. Likewise nitric esters react mainly according to the scheme (57). This question has been investigated particularly by Allen [56]. The direction followed by the hydrolysis process depends upon many factors, including the type of radical and the reaction medium.

The above results are supported by Brönsted's theory since with esters of strong acids—owing to their tendency to donate protons—favourable conditions are created for splitting the R—O bond and producing the carbonium ion.

If the reaction formulated in eqn. (56) takes place and if $Y^{\ominus}=RO^{\ominus}$ then primarily ether is formed. If on the other hand $Y^{\ominus}=\;>C^{\ominus}$ or $>N^{\ominus}$ an alkylation process takes place. If the reaction type conforms with the scheme (57) and if $Y=RO^{\ominus}$ then a reaction of transesterification takes place, whilst the presence of $Y^{\ominus}=\;>C^{\ominus}$ or $Y^{\ominus}=\;>N^{\ominus}$ stimulates the nitration process. So, for instance, n-butyl nitrate treated with benzyl cyanide in an alkaline medium produces sodium nitrophenylmethanecarbonitrile in about 70% yield. This provides evidence that the predominating reaction should be defined by the eqn. (57) as shown by the following example:

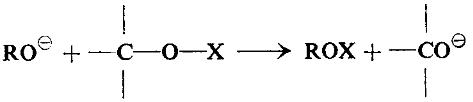


$$C_6H_5CH_2CN + C_4H_9O{-}NO_2 \xrightarrow{NaOH} C_6H_5\underset{\underset{NO_2Na}{\|}}{C}CN + C_4H_9OH + H_2O \qquad (59)$$

In the presence of sodium ethoxide tertiary butyl nitrate reacts with benzyl cyanide to form exclusively butyl ethyl ether and sodium nitrate. In this case no transesterification occurs. Thus the reaction proceeds in accordance with eqn. (56).

With reaction (56) a competing process to form olefins occurs, in which the chemical bond R—O is broken, as outlined in scheme (11). The formation of olefins, as mentioned above, depends primarily on the character of the alkyl group and also on the conditions of reaction.

Tertiary alkyl esters react mainly according to (56) and (57). During hydrolysis performed in accordance with the latter reaction in the presence of $Y^{\ominus}=RO^{\ominus}$ a process of transesterification takes place as shown by the equation below:



$$RO^{\ominus} + -\underset{|}{\overset{|}{C}}-O-X \longrightarrow ROX + -\underset{|}{\overset{|}{C}}O^{\ominus} \qquad (60)$$

Thus in a mixture of a tertiary ester with a secondary or primary alcohol, esters of these alcohols can be produced. Immediately they have been formed, the esters can undergo further chemical combination, as indicated in eqns. (57) and (58). The original ester can be transformed in the manner indicated by eqn. (58) if it possesses a hydrogen atom attached to the α-carbon atom. In any other case alcohol formed as the reaction proceeds cannot be oxidized.

According to reports of Kharasch *et al.* [57] the chemical reaction defined by the scheme (58) occurs when conditions favour the formation of radicals in the solution of an ionizable solvent and when the $X^{\ominus}$-anion thus formed is sufficiently stable.

According to Kharasch, primary and secondary nitrates which have been hydrolysed in accordance with the scheme (57) produce a certain quantity of oxidation product. On the other hand tertiary butyl nitrite can undergo the reaction of transesterification. However, it does not react as suggested by the eqn. (58), since the $NO^{\ominus}$ ion is not sufficiently stable.

REDUCTION OF NITRIC ESTERS

There are various different methods for reducing nitric esters and thereby removing their nitro group. In most cases the original alcohols are recovered as result of the reaction.

The oldest and most popular method is reductive hydrolysis by means of alkaline sulphides or hydrosulphides, for instance sodium or ammonium sulphide or the corresponding hydrosulphide, as discussed above in connection with the question of hydrolysis (pp. 9–10). According to Oehman *et al.* [103] acid hydrolysis of nitroglycerine follows a course similar to that of eqn. (58). Hydrolysis with sulphuric acid (even in the presence of nitric acid) may lead to a transesterification and formation of sulphuric acid esters [104].

As for other methods the following reduction processes are known: in acetic acid by means of iron (Oldham [58]), in acetic acid with iron and zinc (Dewar and Fort [59]), catalytic hydrogenation under pressure over a palladium contact (L. P. Kuhn [60]), or by means of hydrazine in the presence of palladium or platinum. Applying the last method a good yield of alcohol accompanied by NO, N_2 and H_2O has been obtained by L. P. Kuhn [45]. The reduction can be carried out by means of zinc in the presence of acetic anhydride (Hoffman, Bower, Wolfrom [61]).

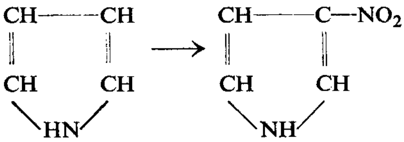
Electrolytic reduction of nitric esters has also been reported (Kaufman, H. J. Cook and S. M. Davis [62]).

A new manner of reducing nitric esters which consists in the application of lithium aluminium hydride has been described by Soffer, Parrotta and di Domenico [63]. The reaction is performed in an ether solution from which alcohol is recovered quantitatively. Among the reaction products in addition to alcohol the presence of NO_2 group and ammonia have been established by these authors. To complete the reaction, 3.3 molecules $LiAlH_4$ are necessary for each ONO_2 group. Simultaneously the same method has been applied by Ansell and Honeyman [54] to reduce the sugar acetal nitrates in a boiling ether solution. This reaction proceeds very slowly. It sometimes takes 50 hr. However, pure acetal alcohol is formed in good yield.

SOME OTHER REACTIONS OF NITRIC ESTERS

In the presence of sodium or potassium ethoxide, nitric esters react with substances containing an active methylene group to form salts of aci-nitro compounds (Wislicenus [64]) as quoted above in eqn. (59). Esters are hydrolysed on this occasion.

Evidently, from these salts pure nitro compounds can be obtained. This property of nitric esters makes it possible to use them as nitrating agents (Vol. I). For instance pyrrole and indole can be nitrated by means of ethyl nitrate. In effect a β-nitro compound is produced:



Like nitrous esters, alkyl esters of nitric acid enter into reaction with a surplus of Grignard's reagent to form N-dialkylhydroxylamine.

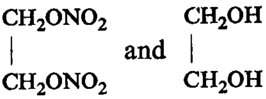
Certain nitric esters are capable of forming addition products with aromatic nitro compounds (see pp. 167, 169), as indicated by T. Urbański [65].

An interesting property of nitric esters, namely their ability to catalyse certain reactions of addition polymerization has been reported recently. Initially this observation was made by Rogovin and Tsaplina [66] while polymerizing styrene and methyl methacrylate in the presence of nitroglycerine. The latter amounted to 5–20 parts by weight corresponding to about 10% of the polymerized substance. As a result of the increased polymerization speed, the molecular weight of the polymer is smaller than if polymerization is carried out slowly.

Hicks [67] confirmed these observations for the methyl methacrylate–glycol dinitrate system. The substances have been used at mole ratios ranging from 0.07 to 5.9. Working at temperatures of 25, 60, 80 and 90°C it was established that from 60 to 90°C partial decomposition of nitroglycol takes place and free radicals initiating polymerization are formed.

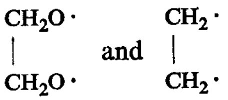
An interesting exception reported by Rogovin and Tsaplina concerns vinyl acetate which when exposed to the influence of nitric esters, polymerizes very slowly. The ester radicals $\cdot NO_2$, $\cdot ONO_2$ and ions $NO_2^{\oplus}$, $ONO_2^{\ominus}$, do not seem to influence appreciably the rate of polymerization and the catalytic action of nitric esters is not produced by the presence of $O-NO_2$ groups.

However, the views of Rogovin and Tsaplina should be revised in the light of recent experiments of Szyc-Lewańska and Syczewski [67a]. They found that glycols and glycerol exhibit the same catalytic action as their nitric esters on the polymerization of styrene and methyl methacrylate. This seems to suggest that the molecules



$$\begin{array}{c}CH_2ONO_2\\ |\\ CH_2ONO_2\end{array} \quad \text{and} \quad \begin{array}{c}CH_2OH\\ |\\ CH_2OH\end{array}$$

behave in an identical way through the formation of the free radicals



$$\begin{array}{c}CH_2O\cdot\\ |\\ CH_2O\cdot\end{array} \quad \text{and} \quad \begin{array}{c}CH_2\cdot\\ |\\ CH_2\cdot\end{array}$$

or through alkoxy $(CH_2O)_2^{2\ominus}$ and alkylene $(CH_2)_2^{2\oplus}$ ions.

FORMATION OF NITRIC ESTERS

The simplest and most commonly used method of preparing nitric esters consists in the "O-nitration" reaction of alcohols with nitric acid, usually in the presence of sulphuric acid. The reaction is accompanied by reversible hydrolysis, which is typical of esterification reactions. It is very likely that the main nitrating agent is the nitronium ion $NO_2^{\oplus}$ (nitryl cation). It acts through electrophilic substitution. The presence of sulphuric and perchloric acids in the esterifying mixed acid favours the esterification, as it increases the concentration of $NO_2^{\oplus}$ ion.

When investigating the O-nitration of glycerol Ingold *et al.* [68] established that primary alcoholic groups are attacked with $NO_2^{\oplus}$ very quickly and the reaction is of zero order. The secondary alcoholic group reacts at a lower rate and the reaction is of the first order.

It was observed that the presence of sulphuric acid promotes the hydrolysis of esters (e.g. [104, 107, 109]). The rate of hydrolysis is for the most part significantly lower than the esterification rate. Moreover, as already discussed above, in addition to the main reaction producing alcohol and nitrating acid, the hydrolysis process is generally accompanied by side reactions. Acids other than sulphuric, or perchloric [104], e.g. acetic [106] or phosphoric, if present in the esterifying mixture, hydrolyse esters to a markedly smaller extent than sulphuric acid. The acid make up of an esterification mixture in industry is established experimentally. Economic factors also plays a part here.

In addition to these chemical reactions outlined above oxidation reactions also take place during the esterification process.

According to certain authors the oxidation reaction is facilitated by the presence of nitrogen dioxide. Since the oxidation reaction is undesirable, attention should be paid to the concentration of nitrogen dioxide in the nitrating acid in order to maintain it as low as possible. Pure nitrogen dioxide is a very strong oxidizing agent.

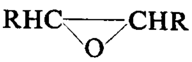
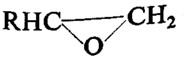
Kaverzneva, Ivanov and Salov [69] found that isopropyl alcohol, under the influence of dinitrogen tetroxide at normal temperature, is transformed into acetone. Ethylene glycol is oxidized rapidly by it to oxalic and glycolic acids.

Owing to oxidation by nitrogen dioxide, 1,2-propanediol is transformed into hydroxyacetone and pyruvic acid. The authors report that no lactic acid is produced, which is evidence that in the first place the secondary alcohol groups are oxidized.

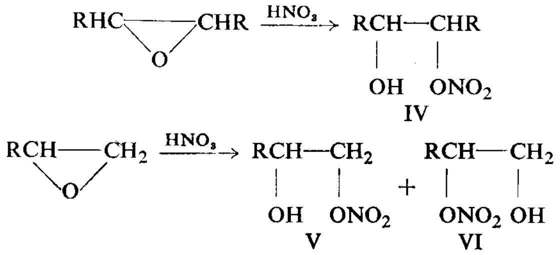
Likewise the primary hydroxy groups of cellulose are oxidized to form the –COOH groups, while the secondary ones give CO-groups (see p. 347).

O-Nitration is an exothermic reaction. Approximate calculations which have been made (Kagawa [70]; Calvet and Dhers-Pession [71]) on the basis of esterifying methyl alcohol and cellulose indicate that the esterification of one hydroxyl group is accompanied by the development of 2±0.2 kcal of heat (see pp. 46, 147).

Nitric esters are produced by the reaction between nitric acid and derivatives of ethylene oxide (Hanriot [72]; L. Smith, Wode, Widhe [73]). According to

Nichols, Magnusson and Ingham [74] oxides having the structure  and  can be nitrated by means of 30% nitric acid in presence of ammonium nitrate, the latter being a component counteracting side reactions of oxidation.

If 1.5 mole of nitric acid for 1 mole of oxide are used then according to the kind of oxide used monoesters (IV), (V) and (VI) will be obtained with 40–60% theoretical yield:



When acting with dinitrogen tetroxide on ethylene oxide and homologues followed by hydrolysis a nitric ester of the type (IV) is formed (Pujo *et al.* [108], Rossmy [75]).

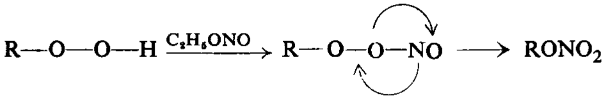
In some cases, in the laboratory a method of indirect introduction of ONO_2 group through the action of silver nitrate upon alkyl halides can be used.

$$RCl + AgNO_3 \longrightarrow RONO_2 \tag{61}$$

Alkyl nitric esters can also be formed by acting on alkylhydroperoxide with ethyl nitrite:

$$R{-}O{-}O{-}H + C_2H_5ONO \longrightarrow RONO_2 + C_2H_5OH \tag{62}$$

The reaction was discovered by Baeyer and Villiger [75a] and studied in a more detailed way by Crigee and Schnorrenberg [1a]. They suggested that the mechanism of the reaction is:



$$R{-}O{-}O{-}H \xrightarrow{C_2H_5ONO} R{-}O{-}O{-}NO \longrightarrow RONO_2$$

NITRIC ESTERS AS EXPLOSIVES

Alkyl esters of nitric acid are very strong explosives. Their oxygen balance is obviously higher than in the case of explosive nitro compounds containing the same number of carbon atoms and nitro groups. Moreover, in many esters the ratio of O-nitro groups to carbon atoms can be more favourable than in aromatic nitro compounds. Many nitric esters possess as many nitro-ester groups as carbon atoms. This is why such esters of nitric acid as e.g. nitroglycerine, nitroglycol and pentaerythritol tetranitrate are among the most powerful explosives, their explosive strength exceeding that of such widely used nitro compounds as TNT. The disadvantage of nitric esters is that they are more sensitive to shock and friction and to high temperature than nitro compounds. Furthermore they can undergo hydrolytic decomposition.

CHEMICAL STABILITY

The stability of an explosive may be regarded as its capacity to remain unchanged during a longer period of storage. The problem of stability is of primary importance with nitric esters, since their structure exposes them to the risk of being hydrolysed. However, the purer the ester, the smaller the danger of hydrolysis. It is of exceptional importance to keep the ester free from acids and strong bases which could cause decomposition. Certain nitric acid alkyl esters exist that are insufficiently stable even in the purest form. Their low stability results, of course, from their chemical structure, as for instance, with methylene glycol dinitrate. For the most part nitric esters of the nitroglycerine, pentaerythritol tetranitrate and nitrocellulose type are characterized by an adequate stability provided they are in a pure form.

Ropuszyński [76] suggests two distinct aspects of stability, namely *chemical* stability—which ought to be understood as the stability of the pure chemical compound; and *practical* stability—that characterizes a product "stabilized" by methods applied in practice.

In accordance with these definitions a substance possessing good chemical stability may still be of insufficient practical stability if it is not fairly pure.

Hydrolytic decomposition has already been discussed. A different type of decomposition of nitric esters occurs at elevated temperatures. More detailed information concerning this type of decomposition will be included in the descriptions of the individual esters properties, in particular those of nitroglycerine and nitrocellulose.

The decomposition of esters at elevated temperatures is of exceptional practical importance, since it has often been responsible for accidents. Investigations of the decomposition of esters at elevated temperatures by laboratory tests serve as a rapid method of estimating their stability.

A number of authors have tried to express the decomposition rate of nitric esters in mathematical formulae. Thus Berthelot [77] expressed the relation between the decomposition rate of nitric esters and the temperature as:

$$V = Kt + C \tag{63}$$

where: V—the rate of reaction in mg of nitrogen produced from 1 g of the substance; t—temperature; K, C—constants, of which C depends on the purity of the substance and its degree of nitration; K depends on the nature of the substance.

Later the relation between the decomposition of alkyl esters of nitric acid and the temperature was formulated (Will [78]) by means of the eqn. (64):

$$\log N = a + b \cdot 0.9932t \tag{64}$$

where: N—the quantity of mg nitrogen evolved from a 2.5 g sample of the substance in 15 min; a, b—constants; t—temperature.

According to Will for guncotton the following constants have been found: $a = 8.8842$, $b = 22.86$.

It is necessary to take into consideration the fact that the decomposition of nitric esters has an autocatalytic character: water and nitrogen dioxide formed during the decomposition lead to the formation of nitric and nitrous acids which accelerate the reaction of decomposition of the nitric ester. The influence of nitric acid on the rate of decomposition of nitroglycerine was studied by Roginskii [79] and is described below.

METHODS OF DETERMINING THE STABILITY OF NITRIC ESTERS

All methods of determining the stability of explosives and particularly of nitric esters consist in examining the behaviour of the substances at an elevated temperature. It is obvious that the most reliable methods of determining stability are those which are carried out at lower temperatures approaching the ordinary room temperature.

It is known and has been demonstrated by several authors (by Sapozhnikov *et al.* [80] for nitrocellulose; by Lukin [81] for nitroglycerine) that change of temperature alters the composition of the reaction products. As the result of numerous experiments, particular temperatures were chosen for definite nitric esters. Thus, owing to the greater ease of decomposition of nitroglycerine as compared with nitrocellulose the high temperature heat test for nitroglycerine is carried out at a temperature lower than that for nitrocellulose (120 and 132° C respectively).

The disadvantage of carrying out a stability test at low temperature is of course the very low rate of the reaction, and hence the very long time required to complete the experiment. Low temperature tests are applied in special cases only, and methods employing elevated temperatures are in general use.

Two main categories are distinguished: (a) qualitative, and (b) quantitative ones.

A full description of the methods of determining the stability of explosives are given in books dealing with analysis of explosives, such as: Kast and Metz [82], Clift and Fedoroff [83], Olsen and Greene [84], and Avanesov [85].

Qualitative tests

The qualitative tests usually consist in determining the heating period necessary to produce a noticeable decomposition of the compound or decomposition of the impurities present in the sample. The higher the stability, the longer the determined time.

Heat test (Abel test). The oldest and the most popular qualitative test is the heat test introduced in Great Britain by Abel in 1865 [86]. It is called the "Abel test" on the Continent of Europe and the "KI starch test" in the U.S.A. It consists in warming a sample of nitroglycerine or nitrocellulose (or dynamite or smokeless powder) in a test tube in which a potassium iodide–starch paper moistened with aqueous glycerol solution is suspended (Fig. 1). Warming is carried out until the test paper acquires a faint brown colour. A thermostatic bath is used for this purpose.

The original British heat test [87] consists in heating the samples: 2 cm^3 of nitroglycerine at 160°F (71.1°C) or 1.3 g of nitrocellulose at 170°F (76.7°C), or 1.6 g of cordite at 180°F (82.2°C). The time the explosive should stand the test is 15 min, 10 min and 30 min respectively.

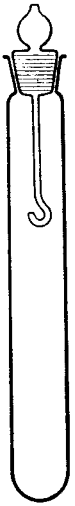


FIG. 1. Test tube for the Abel heat test, Soviet pattern [85].

In various countries different standards are accepted; e.g. in the U.S.S.R. a temperature of 75±0.5°C and in U.S.A. 65.5±1°C is applied. In Germany more sensitive zinc iodide–starch test paper is used (p. 77).

It is obvious that the heat test does not necessarily indicate the beginning of the decomposition of the substance. More often it indicates the presence of unstable impurities (e.g. residual nitrating acid) or unstable by-products more readily decomposed than the substance itself.

The high sensitivity of the test and its simplicity are of great importance and these facts account for the popularity of the method as a test of determining the purity of nitroglycerine and nitrocellulose. The sensitivity of the test is considerably reduced when mercuric salts (e.g. $HgCl_2$) are present in nitrocellulose. This is the result of the reaction of mercuric salts with iodine.

Litmus test (Vieille test). This test introduced by Vieille [88] consists in warming a sample of nitrocellulose (2.5 g) or smokeless powder in a hermetically sealed test tube (Fig. 2) in presence of a band of blue litmus paper inserted within the tube. The tube is kept in a thermostat warmed to 110°C. The temperature inside the test tube is 108.5°C. In U.S.S.R. the temperature of the thermostat is 106.5°C. The blue paper should not turn definitely red in less than 7 hr.

When smokeless powder is tested the sample is warmed to 108.5°C for several

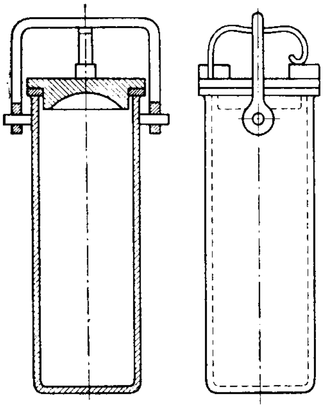


FIG. 2. Tube for litmus test (Vieille test).

days in succession but no longer than 10 hr a day (this is described in detail in Vol. III).

Heat test at 134.5°C. This heat test is in use in the U.S.A. A sample of 2.5 g of nitrocellulose or nitrocellulose powder ("single base powder") is kept in a long test tube in a constant temperature bath regulated to 134.5±0.5°C. A band of methyl violet (rosaniline acetate with crystal violet) test paper is kept over the surface of the sample. The test paper should not change to "salmon" colour before 30 min and no visible NO_2 vapours should be detected before 45 min.

The test is usually continued for a total period of 5 hr, during which no explosion should occur.

Nitroglycerine powder ("double base powder") is tested at 120°C, the duration of the test being the same.

Silvered Vessel test. The so-called "Silvered Vessel test" is a stability test that consists in determining the period of heating necessary to cause exothermic decomposition of the substance. It is usually limited to determining the stability of smokeless powder and is described in Vol. III.

It was suggested by J. B. Taylor [89] as a method for the determination of the stability of nitrocellulose at 135°C. Nitrocellulose can be accepted as stable when, after 45–60 min heating, the temperature of the sample is not higher than the temperature of the thermostat by 1.1°C.

Qualitative tests at lower temperature ("Warmlagermethode") are carried out with powders only and are described in Vol. III.

Quantitative tests

Loss of weight. One of the oldest and simplest quantitative methods is the determination of the loss of weight of a sample heated at a constant temperature. The original Sy-test [90] used in the U.S.A. for determining the stability of nitrocellulose and nitrocellulose powder ("U.S. Ordnance Department 115° Test") consisted in heating a sample of the substance on a watch-glass at 115±0.5°C.

Heating is carried out for 8 hr a day. During the first day the sample should loose only volatile substances (moisture and residual solvent). After that the loss of weight should not be greater than 1% a day during the next six days. A loss of 1% or more should be reached on the eighth day. The total loss of weight should be less than 10%.

In the U.S.S.R. the method was modified by using lower temperatures: 75± ±0.5°C or 95±0.5°C. A sample of 15 g is kept in a 50 ml flask fitted with a cork provided with tubular orifice (Fig. 3). The flask with the sample is weighed every 24 hr and the results are plotted on a diagram. After a certain time an increase in the loss of weight indicates that decomposition has become more rapid. That time is taken as a criterion of the stability of the substance.

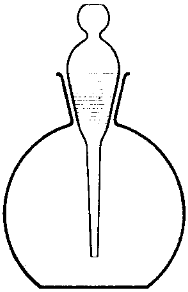


FIG. 3. Flask for determination of loss of weight (Avanesov [85]).

In order to eliminate the necessity of removing the sample from the constant temperature chamber for weighing Guichard [91] introduced the use of an automatic balance which allows the weight of the sample to be recorded continuously.

Will test. Will [78] developed a method which consists in determining the volume of nitrogen evolved from nitrocellulose when kept at 135°C, gaseous products being removed by a stream of CO_2. The nitrogen oxides evolved during decomposition are reduced by hot copper and CO_2 is absorbed by a concentrated solution of potassium hydroxide. The volume of N_2 is recorded every 15 min. The test lasts 4 hr. The method was very useful for research but was difficult to apply as an everyday control of stability. Besides, the fact that nitrogen oxides are removed from the sample by the stream of CO_2 creates conditions which differ from those existing during storage of nitrocellulose or smokeless powder, when all the decomposition products remain in contact with the parent substance.

Bergmann and Junk test. The Bergmann and Junk [92] test consists in determining the quantity of $NO+NO_2$ lost by the sample (2 g of nitrocellulose or 5 g of nitrocellulose powder) when heated at 132°C for 2 hr. The test tube is closed at one end with a hydraulic seal (Fig. 4). The latter may be ball shaped (*a*) or (more frequently) bell shaped (*b*). After the test, the tube is withdrawn from the thermostat and cooled to the room temperature. Water is sucked into the tube, which is then filled up with more water to the 50 ml mark. The solution is either titrated or its NO content determined by the Schulze–Tiemann method, after the solution has been oxidized with potassium permanganate.

One gramme of well stabilized high nitrated nitrocellulose or collodion cotton should not give off more than 2.5 or 2.0 cm^3 of NO, respectively.

The Bergmann and Junk tubes can be used to determine the pH of the solution obtained after heating nitric esters for varying times, e.g. 1, 2, 4 and 6 hr. This makes it possible to draw a curve showing the progress of decomposition of the substance. This method of determining the stability of the esters and smokeless powders was suggested by Hansen [93] and is frequently used for more detailed examination of the stability of nitric esters or powders.

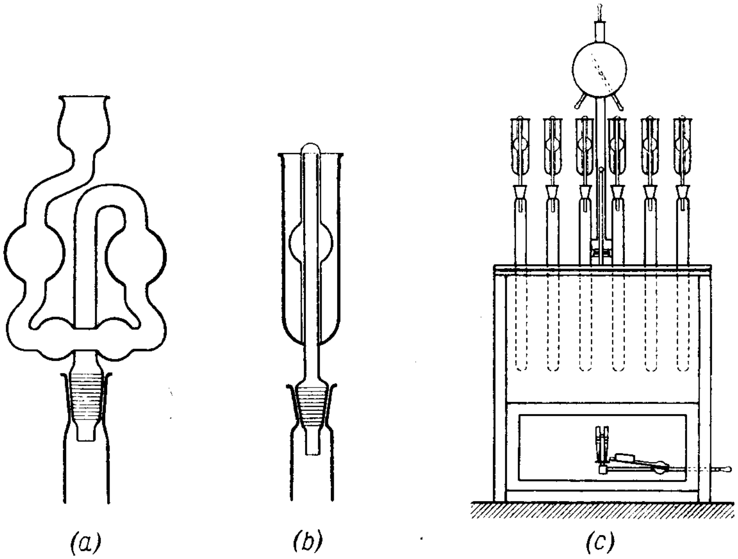


FIG. 4. Tubes for Bergmann and Junk test: (a) with balls, and (b) with tubular ending, (c) thermostat with tubes.

Most nitric esters are subjected to heating at 120–132°C. In the case of nitroglycerine and nitroglycerine-like explosives, and also of nitrostarch, a temperature of 110–120°C is used.

Instead of a pH determination, the conductivity of the aqueous solution of the decomposition products can also be measured (e.g. Phillip [94]; de Bruin and Pauw [95]; Grottanelli [95a]). This, however, is less suitable for routine work.

Manometric test. The idea of measuring the pressure of the gaseous products evolved during decomposition of explosives on storage or heating was known as early as in the middle of the last century. It was mentioned by Abel [96] in his classic work on the stabilization of nitrocellulose. Ph. Hess [97] examined the decomposition of nitrocellulose at 70°C and measured the pressure of the decomposition products by means of a mercury manometer. Mittasch [98] applied the same idea when studying the kinetics of decomposition of nitrocellulose. The first apparatus for routine stability measurement based on this principle was introduced by Obermüller [99] and further improved by Obermüller and Pleus [100].

The main disadvantage of the method consisted in the condensation of some of the products of decomposition in the tubes connecting the container with the manometer. This was overcome by Taliani [101] in his manometric method. The main feature of this method (Fig. 5) consists in warming the sample of 1.3 g (*1*) to 135°C at a constant volume which is maintained by the U-tube (*2*) filled with liquid paraffin. The stopcock (*3*) is closed after the temperature has become uniform and then the pressure is increased by raising the bulb (*4*) to maintain the same level of paraffin oil in both branches of the U-tube (*2*). The experiment is stopped after 300 mm Hg pressure is reached. Goujon [102] modified the method, adopting a pressure of 100 mm Hg as the end of experiment.

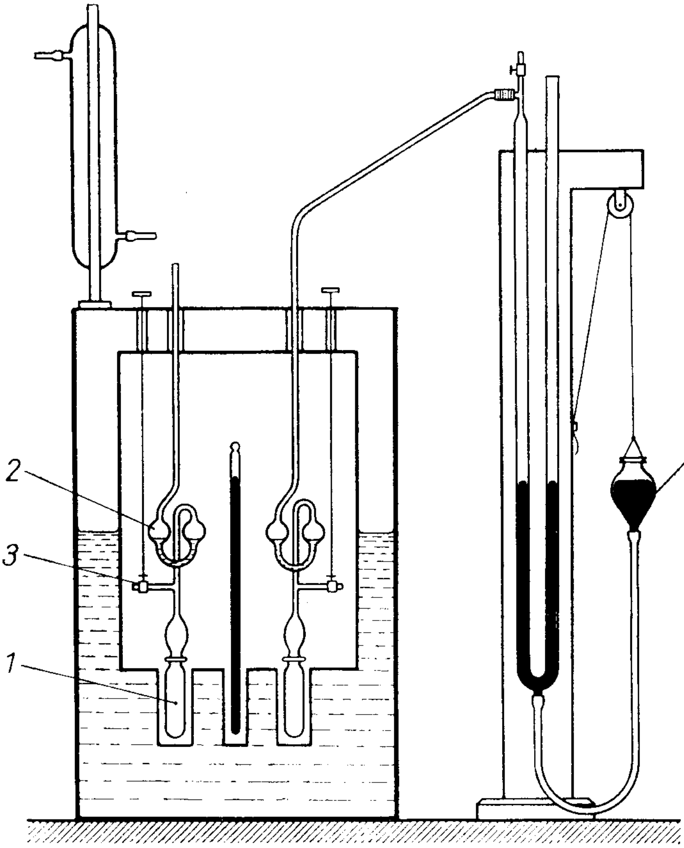


FIG. 5. Taliani test apparatus: *1*—tube with a test sample, *2*—hydraulic closure, *3*—stopcock.

The method of Taliani–Goujon is very useful, although by working under relatively elevated pressure it creates specific conditions which differ from those existing during the storage of explosives.

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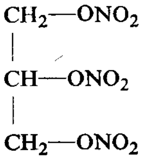
CHAPTER II

GLYCEROL TRINITRATE (NITROGLYCERINE)

ESTERS of monovalent alcohols and nitric acid do not play a large part as explosives. Among the polyvalent alcohol esters most useful for that purpose glycerol nitrates and glycol nitrates are especially important.

NITROGLYCERINE



$$\begin{array}{l} CH_2{-}ONO_2 \\ | \\ CH{-}ONO_2 \\ | \\ CH_2{-}ONO_2 \end{array}$$

Nitroglycerine (NG), strictly glycerol trinitrate is one of the most widely used explosives. It is the main component of high explosives such as dynamites, as well as an ingredient of most mining explosives and it is an essential ingredient of smokeless, so-called double base propellants. Attempts to nitrate glycerine experimentally were begun as long ago as 1830. Glycerine was dissolved in nitric acid without being cooled. The reaction therefore proceeded at a temperature distinctly higher than room temperature, and in these conditions glycerine did not undergo nitration but was oxidized, forming water-soluble hydroxy-keto-acids and hydroxy-acids. It was not until 1847 that nitroglycerine was obtained for the first time by Ascanio Sobrero [1] who used a nitration mixture of nitric and sulphuric acids at a low temperature. Afterwards the whole was poured into water. The oily nitroglycerine sank to the bottom, whence it could be readily separated and freed from acid by careful washing with water. Sobrero recognized the explosive properties of the new substance and named it pyroglycerine. However, although these properties engaged the attention of Sobrero he did not develop the appropriate application, for the danger of manufacturing and handling seemed likely to prohibit its use in practice.

Attempts to make use of nitroglycerine as a high explosive shell filling were carried out in various countries: in Russia they were done by Zinin and his co-worker Pietruszewski in 1854 [2]. However, the trials proved unsuccessful owing to the materials sensitiveness to shock.

The first important steps to develop the manufacture and application of nitroglycerine in mining were taken by a Swedish engineer—Alfred Nobel who learned about nitroglycerine from Zinin 1855, when residing in St. Petersburg [2a]. In 1862 a factory to produce "explosive oil" was built by Nobel in Helleneborg near Stockholm and in 1864–66 he was granted patents [3] for the method of nitrating glycerine by means of a mixed acid composed of nitric and sulphuric acid. At first nitroglycerine was separated from the spent acid by running off the whole into water; afterwards Nobel improved his method so as to get the nitration product as an individual phase.

In spite of numerous failures, as for instance the explosion of his factory in 1864, Nobel introduced the use of "explosive oil" in place of black powder (gunpowder) for mining purposes.

To initiate the nitroglycerine, detonators filled with black powder were used at first. Later, Nobel [4] invented blasting caps (detonators) charged with mercury fulminate for this purpose.

The liquid consistency of nitroglycerine and its sensitiveness to shock are great disadvantages in handling and transporting it.

Nobel endeavoured to diminish the sensitiveness of nitroglycerine to shock by dissolving it in methyl alcohol. The transport of such a solution proved markedly safer than that of nitroglycerine itself. On the spot, in the mine, this solution was treated with water and after decanting the upper aqueous–alcoholic layer above the nitroglycerine, which was precipitated in form of oil, the latter was used as a high explosive. However, this operation was troublesome. Based on an observation that a large quantity of nitroglycerine can be absorbed in diatomaceous earth (kieselguhr) to form a doughy mass, guhr dynamite, consisting of 75 parts by weight nitroglycerine and 25 parts kieselguhr was patented by Nobel in 1867 [5]. This new explosive rapidly become well known and popular. After 1868 about a dozen factories were established in various continents to manufacture nitroglycerine and dynamite.

The manufacture of nitroglycerine was also started in Russia by Pietruszewski, a co-worker of Zinin [2]. Intending to decrease the sensitiveness of nitroglycerine to shock, Pietruszewski mixed the explosive substance with a solid adsorbent, in this case magnesium carbonate. Since about 1867 nitroglycerine has been used in the Upper-Uspienskii district's gold mines in the Trans-Baykal of Siberia [6].

In 1875 Nobel [7] produced the so-called blasting gelatine by dissolving nitrocellulose in nitroglycerine. It is on the basis of this gelatine mixed with oxygen carriers, e.g. ammonium or sodium nitrates, that dynamites ("straight" dynamites) are produced at the present day. It was also Nobel who invented smokeless, "nitroglycerine" powder ("double base" powder), or so-called *ballistite* in 1888 [8]. Nitroglycerine has also found wide application as an ingredient of ammonium nitrate explosives for mining purposes.

The method of manufacturing nitroglycerine introduced by Nobel has been modified and improved. The research work of the authors listed below is cited as containing the most important achievements in this field: Nathan, Thomson and

Rintoul [9], A. Schmid [10], Raczyński [11], Biazzi [12]. A recent improvement in this field was developed in Swedish factory N. A. B. Gyttorp [13].

A broad review of the history of nitroglycerine and dynamite manufacture was published recently by Nauckhoff and Bergström [13].

PHYSICAL PROPERTIES

Nitroglycerine is an oily liquid and in pure form it is colourless and transparent. The commercial product is usually yellowish (of straw yellow colour) or pale brown depending on the purity of the original raw materials and on the conditions of manufacture. Nitroglycerine has a slight "sweetish" smell perceptible after heating to temperatures exceeding 50°C and it has a bitter-sweet and "burning" taste.

Freezing point

There are two modifications of nitroglycerine, differing in freezing point and crystalline forms. With respect to crystal structure the form melting at the lower temperature represents a labile form (Fig. 6) which can be transformed spontaneously into the higher melting stable form of nitroglycerine (Fig. 7).

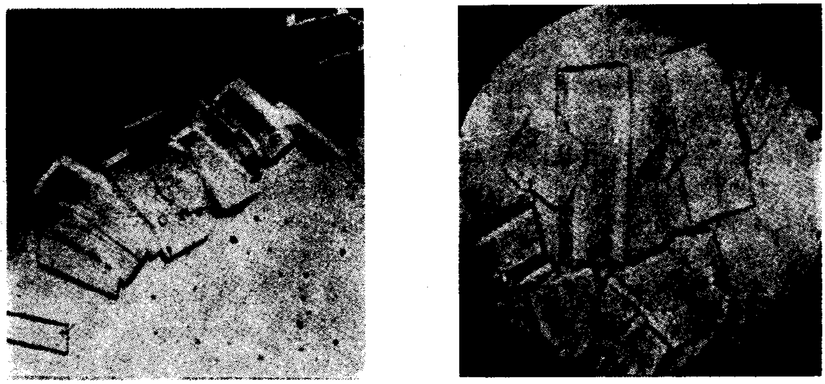


FIG. 6. Crystals of nitroglycerine, labile form (Hibbert [15]).

FIG. 7. Crystals of nitroglycerine, stable form (Hibbert [15]).

The freezing and melting temperatures of these transformations have been established by Kast [14] who also observed that very pure nitroglycerine is transformed on freezing mainly into the labile crystals, whereas a less pure sample often crystallizes in the stable form.

The conditions necessary for the formation of each crystal form were examined by Hibbert [15]. He found that if recently produced nitroglycerine is mixed with wood meal or pulverized glass and cooled to the temperature of −40°C, while being stirred vigorously, the labile form is produced. By introducing a crystal obtained in this way into another portion of cooled nitroglycerine, crystallization of the labile form can be induced.

On the other hand, if nitroglycerine is mixed with wood meal and sodium or ammonium nitrate under the same conditions the stable crystalline form is produced. Nitroglycerine which had been crystallized and afterwards melted readily solidifies again in the same crystalline form it possessed before melting*. However, if nitroglycerine is kept after melting for a longer period at a temperature exceeding 50°C, it is apt to become supercooled and to crystallize like a freshly prepared product again. Hibbert reported that the labile form of nitroglycerine is converted to the stable form after some 1–2 weeks' storage.

Hackel [17] has established that the transformation of the labile into the stable form does not proceed as readily as indicated by Hibbert. Thus, on keeping labile nitroglycerine for a period of 4 months in a thermostat at the temperature of 0°C no traces of conversion to the stable variant were observed. Further, Hackel did not confirm Hibbert's view that molten crystals of the stable form, seeded with labile crystals yielded crystals of the labile form which were unusually inclined to transform into the stable form. Simple, vigorous stirring would be enough to cause this conversion. The cardinal factor determining the stability of either form consists, according to Hackel, in safeguarding the nitroglycerine against being seeded with crystals of the other form.

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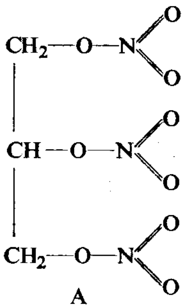
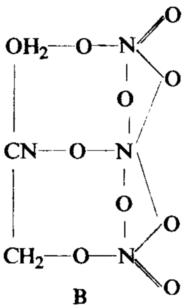
* The capacity of the molten nitroglycerine to crystallize again in its original form was proposed by Hibbert [16] as evidence for the supposition that both variants are isomers (A) and (B) differing in chemical structure:



A



B

Even if the disagreement of these chemical formulae with the accepted method of depicting the nitro group is disregarded, there is no evidence to confirm the existence of two such isomers.

Hackel has extended Hibbert's observations concerning the influence of certain substances on the formation of nitroglycerine crystals of different forms. Thus, adding urethane, phenylurethane, collodion, nitrocotton, cyclonite, tetryl, dinitrobenzene, or centralites I and II promotes the formation of the labile form. Admixtures of siliceous earth, trinitrobenzene, TNT, favour the creation of the stable form.

Freezing points for both variations of nitroglycerine, as published in different papers, are collected in Table 6.

TABLE 6

FREEZING TEMPERATURES OF NITROGLYCERINE MODIFICATIONS, °C

Modification	Nauckhoff [18]	Kast [14]	Hibbert [15]	Hackel [17]
Labile	—	2.1–2.2	1.9	1.9
Stable	12.4	13.2	13.0	13.0

Hibbert [15] assumed that the labile form of nitroglycerine belongs to the triclinic system, while according to Flink [19] the stable form has orthorhombic bipyramidal crystals.

On the basis of the dipole moment values and viscosity measurements of the two forms of nitroglycerine, de Kreuk [20] considered that the difference between the two forms is produced by rotational isomerism. According to this hypothesis the labile and stable forms would correspond to *cis-* and *trans*-isomers respectively. In a non-polar solvent the *trans* form predominates. In a polar solvent the content of the *cis* form increases and reaches a maximum in liquid nitroglycerine.

This can be seen from the figures for dipole moments in various solvents given below (p. 45).

The heat developed during the transformation of one form of nitroglycerine into the other is given on p. 46. The linear crystallization rate of nitroglycerine to form the stable modification at different temperatures was investigated by Nauckhoff [18] who found the following figures:

temperature, °C	rate, mm/min
+5	0.145
0	1.183
−5	0.267
−17	0.125

Solubility

Nitroglycerine is hardly miscible with water. One litre of water dissolves (according to Will [21], Naoúm [22] and Oehman [108]):

at 15°C	1.6 g nitroglycerine
20°C	1.8 g nitroglycerine
50°C	2.5 g nitroglycerine

The solubility of nitroglycerine in aqueous (1–10%) sodium carbonate is still lower (of the order of 1.0 g) [108].

Nitroglycerine is readily dissolved in most organic solvents and itself behaves as a good solvent. Thus, it is completely miscible in all proportions at room temperature with the following liquids: methyl alcohol, ethyl acetate, anhydrous acetic acid, benzene, toluene, xylenes, phenol, nitrobenzene, nitrotoluenes, pyridine, chloroform, dichloroethane, dichloroethylene, and the like.

Further, nitroglycerine can be blended in all proportions with other liquid nitric esters, such as methyl nitrate, the so-called nitroglycol—ethylene glycol dinitrate, diethylene glycol dinitrate, dinitroglycerine, trimethylolnitromethane trinitrate (nitroisobutylglycerine trinitrate), etc.

The solubility of nitroglycerine in halogeno derivatives of hydrocarbons depends on their chlorine content. Thus, nitroglycerine can be mixed with dichloroethylene in all proportions but with 100 parts of trichloroethylene at room temperature only 20 parts of nitroglycerine are miscible, whilst nitroglycerine dissolves with difficulty in tetrachloroethylene and pentachloroethane.

To an appreciable extent the solubility of nitroglycerine in ethyl alcohol depends on the temperature of the solvent and its water content. In the cold a limited quantity of nitroglycerine is dissolved in absolute alcohol, whereas at temperatures of about 50°C it mixes with absolute or 96% alcohol in all proportions. The solubility of nitroglycerine decreases as water is added to the ethanol. In consequence, when water is poured into an alcoholic solution, nitroglycerine is precipitated step by step. This precipitation becomes very considerable after the alcohol has been diluted from 50 to 25% concentration.

To characterize the solubility of nitroglycerine in ethyl alcohol the data quoted by Naoúm [22] are given below, in Table 7.

TABLE 7

THE SOLUBILITY OF NITROGLYCERINE IN ETHYL ALCOHOL

Ethyl alcohol	Temperature °C	Grammes nitroglycerine dissolved in 100 cm³ ethyl alcohol
Absolute	0	*ca.* 30
Absolute	20	*ca.* 43
96%	20	31.6
50%	20	1.8
25%	20	0.7

Similarly other alcohols, such as propyl, isopropyl and amyl alcohols dissolve nitroglycerine at room temperature to a limited extent only. However, they are miscible in all proportions at 90–100°C.

In polyhydroxy alcohols nitroglycerine is still less soluble. The best of these solvents is ethylene glycol. Thus 100 g of ethylene glycol dissolve 12 and 20 g of nitroglycerine at 20 and 80°C respectively. The solubility of nitroglycerine in glycerol is very low.

For analytical purposes, attention must be paid to the solubility of nitroglycerine in acetic acid and in carbon disulphide, since these solvents can be used to separate nitroglycerine from aromatic nitro compounds. Thus nitroglycerine dissolves readily in 65% acetic acid which does not dissolve nitro compounds. In carbon disulphide, nitroglycerine dissolves with difficulty. At room temperature, 100 ml of this solvent dissolve about 1.25 g nitroglycerine. Nitro compounds, on the other hand, are readily dissolved in carbon disulphide.

Both in the cold and in the warm nitroglycerine is slightly soluble in aliphatic hydrocarbons, for example petrol, ligroine, kerosene, paraffin oil, lubricating oils, vaseline oil (Table 8).

TABLE 8

SOLUBILITY OF NITROGLYCERINE IN ALIPHATIC HYDROCARBONS (AFTER NAOÚM [22])

Solvent	Temperature °C	Grammes nitroglycerine dissolved in 100 g solvent
Ligroine	20	about 1.5
	80	about 6.0
Petrol	20	about 2
	80	about 6
Purified oil	20	about 4
	80	about 9

A comparatively high proportion of nitroglycerine can be blended with vegetable oils. For instance, at 20°C 100 g olive oil dissolve 20 g nitroglycerine and at 100°C about 25 g nitroglycerine are dissolved. Nitroglycerine is also relatively soluble in castor oil. Nitroglycerine is only very slightly soluble in an aqueous solution of ammonia, sodium hydroxide and potassium hydroxide. When hot it undergoes the process of hydrolysis (for more details see p. 7).

From the manufacturing point of view the solubility of nitroglycerine in sulphuric acid, nitric acid and in their mixtures is most important, hence great attention has been paid to this question.

Concentrated sulphuric acid readily dissolves nitroglycerine. It has been reported by Naoúm [22] that 100 g of 98% sulphuric acid at 20°C dissolve about 26 g nitroglycerine and 100 g of 70–80% sulphuric acid are capable of dissolving 7.5 g of nitroglycerine.

In the presence of concentrated sulphuric acid, nitroglycerine is hydrolysed to form HNO_3. According to the concentration of the sulphuric acid the products are either esters containing a smaller number of nitrate groups or mixed esters of nitric and sulphuric acids, for instance glyceryl–sulphuric nitrates. At room temperature anhydrous nitric acid mixes with nitroglycerine in all proportions. The solubility decreases step by step as the concentration of acid is diminished. Thus a 100 g portion of 65% nitric acid at 20°C dissolves 8 g nitroglycerine. Solutions of nitroglycerine in nitric acid are unstable since on storage they begin to decompose as a result of oxidation caused by the nitric acid, and nitric oxides are evolved.

Nathan and Rintoul [23], when studying the solubility of nitroglycerine in mixed acids, found that compositions with the ratio $H_2O : HNO_3 = 1.1$ and sulphuric acid content from 0 to 60% are particularly dangerous in this respect: they readily produce an uncontrollable reaction, and no acid of a composition in or near this zone should ever be allowed to come in contact with nitroglycerine in a manufacturing operation. This extremely important observation was recently studied in detail by Oehman *et al.* [110], (see Fig. 26, p. 84).

Nathan and Rintoul also examined the solubility of nitroglycerine in acid mixtures with $H_2SO_4 : H_2O$ and $H_2SO_4 : HNO_3$ ratios having the constant values: 5.8 and 10.4 respectively.

Their figures were used by Pascal [24] to construct a triangular diagram—Fig. 8 (Table 9).

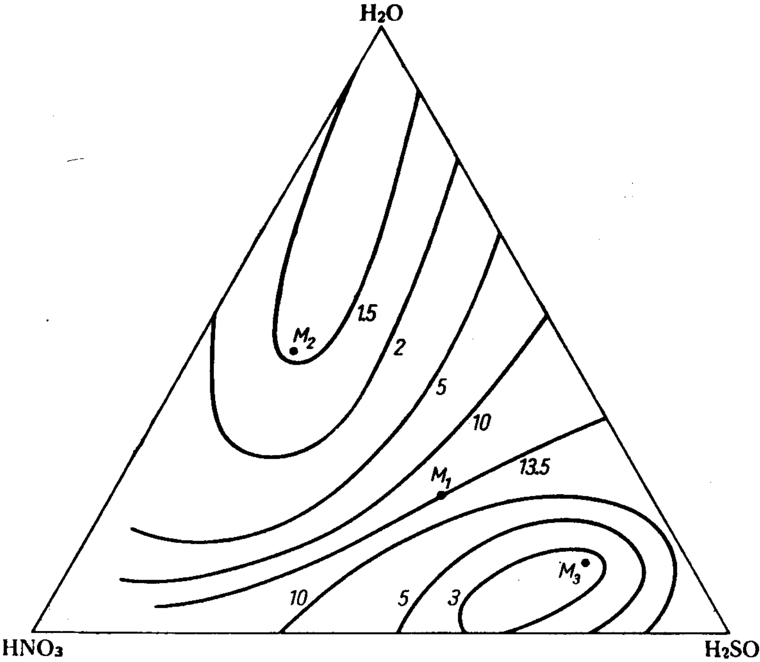


Fig. 8. Solubility (in %) of nitroglycerine in mixtures of nitric acid, sulphuric acid and water, according to Pascal [24].

Table 9

Solubility of nitroglycerine in mixtures of HNO_3 and H_2SO_4

Designation of mixture	Composition of mixture, %			Quantity of dissolved nitroglycerine, %
	HNO_3	H_2SO_4	H_2O	
M_1	24	50	26	13.5
M_2	38	20	42	1.6
M_3	13	75	12	2.5

More recently investigations of the solubility of nitroglycerine in mixed acids (spent acids) have been made by Oehman [108], Klassen and Humphrys [25] (Fig. 9).

In practice the nitrating conditions most frequently applied are those which permit the composition of the spent acids after nitration to approximate to the mixture M_3.

Naoúm [22] has established the solubility of nitroglycerine in mixed acids composed of ingredients resembling approximately the mixture M_3 (Table 10).

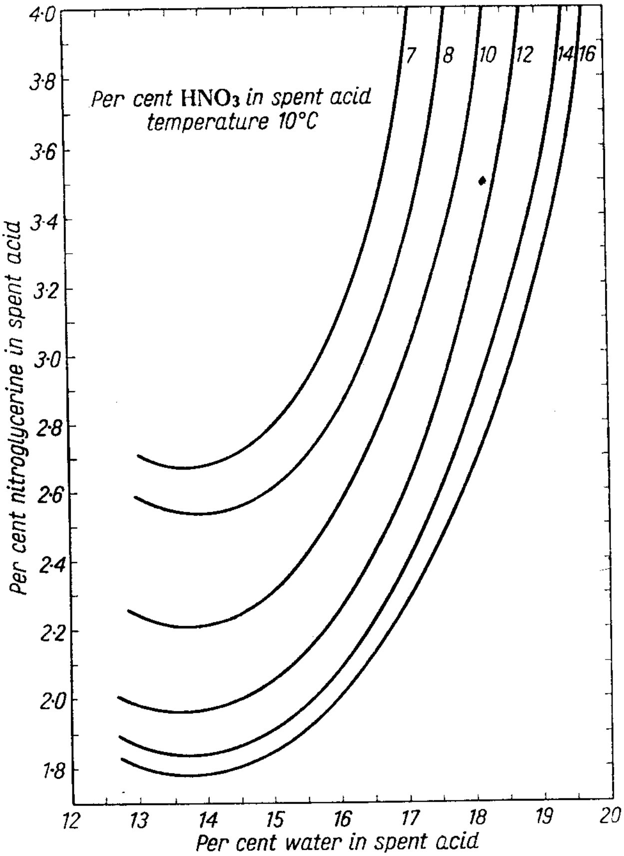


FIG. 9. Solubility of nitroglycerine in spent acid, according to Klassen and Humphrys [25].

TABLE 10

SOLUBILITY OF NITROGLYCERINE IN MIXTURES OF HNO_3 AND H_2SO_4

Composition of mixture, %	I	II	III	IV	V	VI
Nitric acid, HNO_3	10	10	10	15	15	15
Sulphuric acid, H_2SO_4	70	75	80	80	75	75
Water, H_2O	20	15	10	5	10	15
Quantity of nitroglycerine soluble in 100 parts by weight of mixed acid	6.00	3.55	3.33	4.37	2.60	2.36

Part of the nitroglycerine dissolved in this mixture of acids undergoes hydrolysis.

Concentrated hydrochloric acid does not dissolve nitroglycerine. On heating, a gradual decomposition occurs accompanied by a dark yellow colour due to hydrolysis and the production of nitrosyl chloride.

Nitroglycerine as a solvent. The capacity of nitroglycerine to dissolve aromatic nitro compounds has been studied for its practical importance, since blends of nitroglycerine with nitro compounds often form the base components of high explosives, as for example dynamites and smokeless powders. Investigating systems which contain nitroglycerine makes it possible for instance to find substances which decrease the freezing point of nitroglycerine. The first experiments of this kind were performed by Mikołajczak [26]. In order to lower the freezing point of nitroglycerine, dinitroglycerine was added. Afterwards Herlin [27] investigated the effect of adding nitro compounds. The influence of nitroglycol, dinitrochlorohydrin, and diglycerol tetranitrate was determined by Sapozhnikov and Snitko [28]·

Hackel [29] carried out extensive research by means of thermal analysis to establish the eutectic composition of both the labile and stable modification of nitroglycerine with aromatic nitro compounds and with substances used in manufacturing smokeless powders such as centralites, urethanes and others listed in Table 11 and Fig. 10.

TABLE 11

COMPOSITION OF EUTECTICS FORMED FROM NITROGLYCERINE

	Stable form		Labile form	
	Nitroglycerine percentage in eutectic	Freezing temperature of eutectic °C	Nitroglycerine percentage in eutectic	Freezing temperature of eutectic °C
Nitrobenzene	45.5	−15.2	57.5	−22.9
m-Dinitrobenzene	82.5	5.0	88.0	− 5.4
2,4-Dinitrotoluene	72.7	6.1	89.0	− 4.1
2,4,6-Trinitrotoluene	82.9	6.3	90.0	− 4.0
Tetryl	90.0	9.8	94.0	− 0.6
Cyclonite	99.5	12.3	99.7	1.2
Nitroglycol	*ca.* 20	*ca.* −30	*ca.* 40	*ca.* −40
Pentaerythritol tetranitrate	98.5	12.3	98.9	1.3
Phenyl urethane	90.0	9.6	93.0	− 0.8
Phthalide	76.5	0.8	8.10	− 8.2
Methyl centralite	96.5	10.6	98.0	0.8
Diphenylamine	93.0	9.8	96.0	− 0.4

The freezing points of blends of nitroglycerine and nitroglycol have been investigated by Avogadro di Cerrione [30] who established experimentally that both substances can be dissolved in any quantitative ratio to form the following eutectic mixtures:

(1) 29% stable form of nitroglycerine,
71% nitroglycol,
melting point −29°C;
(2) 39% labile form of nitroglycerine,
61% nitroglycol,
melting point −23°C.

Nitroglycerine is able to dissolve nitrocellulose containing a comparatively low percentage of nitrogen, namely collodion cotton ("soluble nitrocellulose"). Solution takes place slowly at room temperature, whereas at 60–65°C it is complete in some 15–20 min. The consistency of the solution obtained depends on the concentration of nitrocellulose in the nitroglycerine and on the viscosity of the nitrocellulose. For practical purposes, for instance, in the manufacture of blasting gelatine, collodion cotton that gives high viscosity solutions of jelly consistency should be used even if they contain only a small quantity of nitrocellulose.

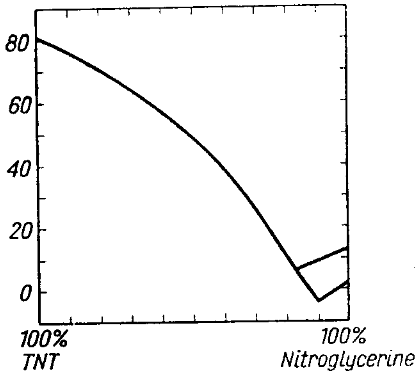


FIG. 10. Eutectic of nitroglycerine with TNT (Hackel [17]).

Nitroglycerine can also dissolve a certain amount of inorganic acid. It has been established by Wallerius [31] that the higher the concentration of nitric acid in the spent acid, the higher is the residue of nitric acid in the nitroglycerine after it has been separated. If for instance the HNO_3 concentration in the spent acid amounts 10% then the quantity of HNO_3 left in the nitroglycerine amounts to 6.15%. A concentration of nitric acid in the spent acid amounting to 14% corresponds with as much as 8.6% of HNO_3 retained in the nitroglycerine. As for the content of sulphuric acid in the nitroglycerine, it remains the same in both cases and amounts only to 0.3% of H_2SO_4. According to Oehman [32] the acid (unwashed) nitroglycerine contains about 8% of nitric acid; of the sulphuric acid it contains, 0.1% is dissolved and 0.5% is emulsified.

In the system nitric acid–nitroglycerine–water, a labile equilibrium is established, determined by the coefficient of phase separation. Thus under certain conditions as much as 8% nitric acid passes into the water phase whereas the nitroglycerine does not contain more than 0.01% HNO_3. A thorough study of the partition of HNO_3 and dinitroglycerine between nitroglycerine and aqueous solutions was made by Oehman [108].

These data are very important for practical purposes, namely for the problem of purifying nitroglycerine by washing. This problem is discussed in detail later (see p. 74).

Very recently Ropuszyński [33] has proved that nitrating glycerine at an elevated temperature exerts a propitious influence upon the stability of the product. This is due to the fact that nitroglycerine obtained at a higher temperature before being stabilized by the usual methods i.e. is washed by means of water and of sodium carbonate solution, contains less residual acid.

The data in question are collected in Table 12.

TABLE 12

THE RELATION BETWEEN THE NITRATING TEMPERATURE AND RESIDUAL ACID CONTENT

Nitrating temperature °C	Residual acid content		Heat test min
	$\%HNO_3$	$\%H_2SO_4$	
15	0.0132	0.0024	15
25	0.0057	0.0017	24
40	0.0052	0.0008	30

Boiling point and vapour pressure

Nitroglycerine begins to boil at a temperature above 180°C. At the same time decomposition takes place accompanied by the evolution of nitric oxides and water vapour. In the distillate, dilute nitric acid and some nitroglycerine is present, probably carried over with the water vapour. The water is formed as a result of the partial decomposition of nitroglycerine which occurs when it is heated to high temperature (see. p. 47).

Owing to decomposition, it is impossible to determine the precise boiling point, though Belayev and Yuzefovich [34] reported that at a pressure of 50 mm Hg the boiling point of nitroglycerine is 180°C, whereas under a pressure of 2 mm Hg it is 125°C.

For the vapour pressure of nitroglycerine different data are to be found in the literature which are incompatible and depend to an appreciable extent upon the method of measurement chosen. Thus the vapour pressure of nitroglycerine at 25°C was found by Chiaraviglio and Corbino [35] to be below 0.00012 mm Hg.

The values found by Marshall and Peace [36] are of the same order:

at 20°C	0.00025 mm Hg	at 60°C	0.0188 mm Hg
30°C	0.00038 mm Hg	70°C	0.043 mm Hg
40°C	0.0024 mm Hg	80°C	0.098 mm Hg
50°C	0.0072 mm Hg	93.3°C	0.29 mm Hg

Naoúm and Meyer [37], on the other hand, published significantly higher figures.

By means of the dynamic method they found the following data:

at 20°C 0.011 mm Hg
at 60°C 0.036 mm Hg

Applying the statistical method they have calculated that at 20°C the vapour pressure of nitroglycerine is 0.0009 mm Hg.

According to Rinkenbach [38] the vapour pressure of nitroglycerine is:

at 20°C 0.0015 mm Hg
at 60°C 0.060 mm Hg

The vapour pressure of nitroglycerine has also been determined by Crater [39] and Brandner [40]. The latter attempted to remove the discrepancies which exist between the values published by different investigators. Thus the data of Brandner are:

temperature, °C	pressure, mm Hg
30	0.0012
35	0.0020
40	0.0030
45	0.0047
50	0.0081

The results of these researches are not in line with the data found by Naoúm and Meyer, nor with those of Crater. These differences seem to be explicable by suggesting that Naoúm, Meyer and Crater did not use absolutely dry nitroglycerine. The data of Brandner approximate to the results quoted by Rinkenbach [38] and Marshall and Peace [36] (at higher temperatures).

Using the Marshall data, Roginskii and L. M. Sapozhnikov [41] calculated the heat of evaporation of nitroglycerine ΔH_v to be:

at $T = 100°K$ 20.64 kcal/mole
at $T = 140°K$ 20.38 kcal/mole
at $T = 180°K$ 20.11 kcal/mole

Using his own data, Brandner has calculated the heat of evaporation of nitroglycerine to be $\Delta H_v = 19.17$ kcal/mole. The same author has investigated the vapour pressure of nitroglycol (see p. 143) and calculated that of nitroglycerine–nitroglycol mixed solutions. The results are collected in Table 13.

TABLE 13

VAPOUR PRESSURE OF THE NITROGLYCERINE–NITROGLYCOL BLENDS

Percentage of nitroglycol	Total vapour pressure, mm Hg			
	10°C	30°C	40°C	50°C
10	0.0027	0.186	0.0433	0.1002
20	0.0051	0.0345	0.1159	0.1841
40	0.0093	0.0624	0.1475	0.3314

Häussermann [42] reported that a small quantity of nitroglycerine distils with steam. With the saturated steam produced from 1 l. of water, 8 g of nitroglycerine are carried over at a temperature of 100°C.

Naoúm [22] reported that on exposure of a 20-g sample of nitroglycerine on a 70 mm dia. watch glass for a period of 24 hr the following weight decrease occurred:

at 50°C	0.04 g (0.2%)
at 75°C	0.32 g (1.6%)
at 100°C about	2 g (about 10%)

In agreement with reports of Rinkenbach [38] the weight loss of a nitroglycerine specimen at a temperature of 60°C amounts 0.11 mg/cm^2/hr.

Specific gravity and other physical constants

According to Perkin [43] the specific gravity of nitroglycerine is:

at 4°C	1.614 g/cm^3
at 15°C	1.600 g/cm^3
at 25°C	1.591 g/cm^3

Kast determined the value as 1.5995 g/cm^3 at a temperature of 15°C.

On freezing nitroglycerine contracts in volume by as much as 8.3%. The specific gravity of the stable modification at 10°C is 1.735 g/cm^3 (Beckerhinn, [44]).

The refractive index of nitroglycerine is $n_{\mathrm{D}}^{20} = 1.4732$.

The viscosity of nitroglycerine is higher than that of water but many times less than that of glycerine. The following results have been published by Naoúm:

The time of discharge from a 20-ml pipette is 6 sec for water, 15 sec for nitroglycerine, and 540 sec for glycerine.

According to de Kreuk [20] the viscosity of nitroglycerine at 20°C is 37.8 cP. Rinkenbach [38] gives the figure 35.5 cP. See also Table 3 (p. 3).

Dielectric constant $\varepsilon_{20} = 19.25$ and dipole moments μ of nitroglycerine were determined by de Kreuk [20]:

nitroglycerine (pure, liquid)	$\mu = 3.82$ D
nitroglycerine in hexane	$\mu = 2.56$ D
nitroglycerine in carbon tetrachloride	$\mu = 2.88$ D
nitroglycerine in benzene	$\mu = 3.16$ D

According to this author different values of μ are due to rotational isomers present in various proportions. Solutions in non-polar solvents would contain a high proportion of *trans*-isomer, whose dipole moment is very low.

Absorption spectra

T. Urbański and Witanowski [109] found that the infra-red absorption spectrum contains the bands:

NO_2 asymmetrical stretching vibrations: 1675, 1654, 1645 cm^{-1}
NO_2 symmetrical stretching vibrations: 1293, 1276 cm^{-1}

Various frequencies are most likely due to rotational isomers (see above).

THERMOCHEMICAL PROPERTIES

The specific heat of nitroglycerine was determined by Nauckhoff [18] as 0.356 cal/g and that of the crystalline substance (stable form) as 0.315 cal/g. For liquid nitroglycerine Belayev [45] published the value 0.4 cal/g.

The heat of crystallization (freezing) of nitroglycerine has been determined by many authors (Nauckhoff [18], Beckerhinn [44]). The most complete investigations were those performed by Hibbert and Fuller [46] who have established the following data:

heat of crystallization of the stable form	33.2 cal/g
heat of crystallization of the labile form	5.2 cal/g

Hence, the heat of transforming the labile variation into the stable one is 28 cal/g.

Heat of combustion and heat of formation of nitroglycerine. It has been reported by Rinkenbach [47] that the heat of combustion $-\Delta H_c$ at constant volume should be 368.4 kcal/mole, which corresponds to 1623 kcal/kg. Thus the heat of formation $-\Delta H_f$ is $+85.3$ kcal/mole ($+374$ kcal/kg).

Values for the heat of formation of nitroglycerine published by other authors are listed below:

415 kcal/kg	(Brunswig [48])
416 kcal/kg	(Kast [49])
370 kcal/kg	(J. Taylor and Hall [50])

According to information from different sources the heat of nitration of glycerol to nitroglycerine varies from 120 to 170 kcal per 1 kg of glycerine.

CHEMICAL PROPERTIES

In the presence of reducing agents such as tin and hydrochloric acid, zinc and acetic acid, alkaline sulphides and hydrosulphides, nitroglycerine is reduced to form glycerine and ammonia. This is evidence that there are no nitro groups attached directly to a carbon atom, otherwise amines would be obtained. Like every ester, nitroglycerine undergoes the reaction of hydrolysis. On heating in a solution of sodium or potassium hydroxide in water or alcohol, not only is the hydrolytic process stimulated, but also oxidation and reduction processes accompanied by the formation of organic acids and of nitrates and nitrites. In consequence the reaction products are more complicated than might be expected. According to Hay [51, 52] the reaction proceeds according to eqn. (2), p. 7.

This equation does not comprise the whole complex of simultaneous chemical reactions, which have already been discussed (p. 7). Later investigators (Vignon and Bay [53]; Silberrad and Farmer [54], Berl and Delpy [55]) also found such products as aldehyde resins, oxalic acid and ammonia. It is characteristic that from nitroglycerine hydrolysed in an alkaline medium no glycerine is recovered. Glycerine can however be obtained again when the hydrolysis is carried out in the presence of readily oxidizable substances. Thus it was established by Klason and Carlson [56] that as a result of hydrolysing nitroglycerine by means of NaOH in the presence of phenyl mercaptan, glycerine was produced together with diphenyl sulphide.

The action of concentrated sulphuric acid and the formation of mixed sulphuric–nitric esters, as well as the action of nitric acid and mixtures of nitric–sulphuric acid and water and of hydrochloric acid have been discussed above. Concentrated hydriodic acid of 1.5 density decomposes nitroglycerine to glycerol and nitric oxides.

Dimethyldiphenyl urea ("Carbamite") and nitroglycerine form a non-homogenously melting addition product of 1:1 molecular composition according to Hackel [29].

STABILITY

Heating nitroglycerine (particularly moist samples) at a temperature of 75°C brings about an apparent decomposition within 3–4 days characterized by the development of acid products. After 6 days the presence of HNO_3 is clearly distinguishable. If the volatile products of decomposition are removed, e.g. by blowing with air, as quickly as they are developed, then only very slow decomposition of the nitroglycerine takes place.

Nitroglycerine contaminated with acid as the result of insufficient washing or due to thermal decomposition undergoes decomposition. Small samples undergo gentle decomposition to produce oxides of nitrogen, nitric acid and organic acids, including among others oxalic acid. Naoúm reported that 10 g of nitroglycerine decomposed to form 2 g of oxalic acid and 2.3 g of other crystalline acids and oxidation products. The products are slightly different if the specimen to be decomposed is kept at a temperature higher than 50°C. The residue is a viscous syrup containing glyceric acid and other organic acids. A valuable investigation into the relation between the composition of spent acid and the stability of nitroglycerine was recently carried out by Oehman *et al.* [110] (Fig. 26, p. 84).

Decomposition of small unconfined samples of nitroglycerine is not dangerous. On confinement, however, the reaction takes a different course, since as decomposition proceeds increasing quantities of gaseous reaction products cause a high pressure to develop and this stimulates further decomposition of the nitroglycerine. The decomposition of large quantities of nitroglycerine can be dangerous. Eventually the heat caused by decomposition is not removed quickly enough and an explosion may take place. It has been proved by Roginskii [57] that such an explosion is not necessarily due to the elevation of temperature to the point of initiation (i.e. to a temperature over 180°C). Slow decomposition at a lower temperature in the presence of the nitric acid, which exerts a catalytic effect, is accompanied by development of branched reaction chains and an explosion can occur. Owing to this an explosion is possible even at a temperature considerably lower than 180°C.

Test specimens of 0.3 g nitroglycerine with an admixture of 5% HNO_3 in sealed ampoules were kept by Roginskii in a thermostat at a temperature of 41°C. Explosion took place after an interval of 320 min, by which time the temperature of the sample exceeded that of the thermostat by only a few centigrade degrees (Fig. 11).

The decomposition of nitroglycerine is also accelerated in the presence of other substances produced during the course of reaction. Attention was paid to that phenomenon by several earlier authors, like e.g. Sapozhnikov [58]. It has been confirmed by more recent investigations. For instance Lukin [59] has established that the chief accelerating agents are NO_2 and water. Nitrogen, NO, CO and CO_2, on the other hand, exert no accelerating effect. Andreyev *et al.* [60] have shown that water has the same influence upon nitroglycol.

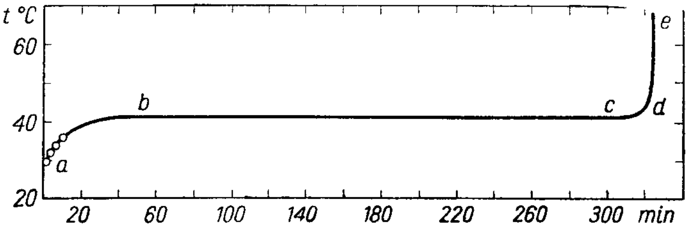


FIG. 11. Decomposition of nitroglycerine with 5% HNO_3 at 41°C according to Roginskii [57]: *ab*—warming up the sample in a thermostate, *cde*—self heating of the sample, *e*—point of explosion.

According to results obtained by Andreyev and Bezpalov [61] dry nitroglycerine starts to undergo an autocatalytic decomposition after having been heated for a period of 40 hr at 100°C, whilst with nitroglycerine containing 0.01% of water the interval is shortened to 30 hr. In the presence of 1.5% water the time is as short as 2 hr.

R. Robertson [62] examined the decomposition of nitroglycerine at temperatures from 90 to 135°C, using a carbon dioxide stream to remove volatile decomposition products. The concentration of nitrogen oxides in the jet of carbon dioxide was established spectrographically. He found in this way that nitroglycerine decomposed in a manner similar to that of fairly well stabilized nitrocellulose, but more rapidly. In the temperature range of 95–125°C, every 5° elevation of temperature doubled the decomposition rate in these conditions.

T. Urbański, Kwiatkowski and Miładowski [63] examined the decomposition of nitroglycerine at 110°C and found the following figures for the pH of the aqueous extracts (Table 14):

TABLE 14

Samples	pH after heating at 100°C for		
	1 hr	2 hr	3 hr
2.0 g	3.05	2.77	2.57
2.5 g	2.94	2.70	2.45

The characteristic shape of the curve of pH as a function of time is given in Fig. 12.

Addition of nitro compounds (such as nitro derivatives of benzene and toluene) neither changes the pH nor the shape of the curve.

The decomposition of nitroglycerine at higher temperatures was investigated by Snelling and Storm [64] who established that at a temperature of 135°C the decomposition is sharply distinct from the lower temperature decomposition and the substance becomes red coloured owing to absorption of the decomposition products. At 145°C decomposition is accompanied by development of gaseous products and becomes very energetic. At 165°C the process is still more vigorous: dilute nitric acid and glycerol nitrates are distilled simultaneously. The remainder is a liquid containing glycerol, its mono- and dinitrates as well as other products difficult to identify. At a temperature of 180–185°C the nitroglycerine becomes highly viscous and at 215–218°C detonation occurs.

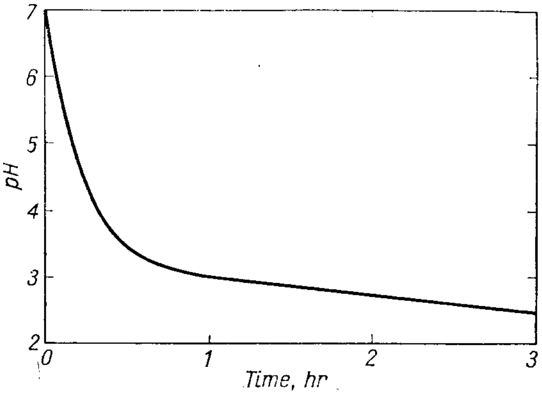


FIG. 12. Change of pH of aqueous extract of nitroglycerine heated at 110°C (T. Urbański, Kwiatkowski, Miładowski [63]).

Temperature of initiation of nitroglycerine is 200–205°C (bath temperature), the rate of the temperature increase being 20° per min. Above 180°C a distinct exothermic decomposition of the substance begins, and hence at the moment of explosion the temperature of the nitroglycerine is higher than that of the bath, i.e. 215–218°C (Snelling and Storm [64]).

The behaviour of nitroglycerine on a heated metallic surface has been studied by T. Urbański and Rychter [65]. A drop of nitroglycerine allowed to fall on a metal plate heated to a temperature between 215 and 250°C exploded with violence to deform the plate. These observations suggest that the phenomenon is to be regarded as detonation or an effect resembling detonation. If the plate is heated to a temperature exceeding 420°C the drop of nitroglycerine acquires a spherical form and burns gently. At 470°C the slowest burning, lasting 2.0 sec, was observed.

This phenomenon is illustrated in Fig. 13.

The activation energy E needed for the thermal decomposition of nitroglycerine was calculated by T. Urbański and Rychter to be:

for temperature ranging from 215 to 250°C $E = 37.40$ kcal/mole
at temperatures over 470°C $E = 4.975$ kcal/mole

The first of those values is of the same order as those obtained by other authors. Thus considering the numeral data of Robertson [62] and Will [66] the following values of the activation energy necessary to decompose nitroglycerine were reported by Semenov [67]:

150–190°C	$E = 50.0$ kcal/mole
125–150°C	$E = 45.0$ kcal/mole
20–125°C	$E = 42.6$ kcal/mole

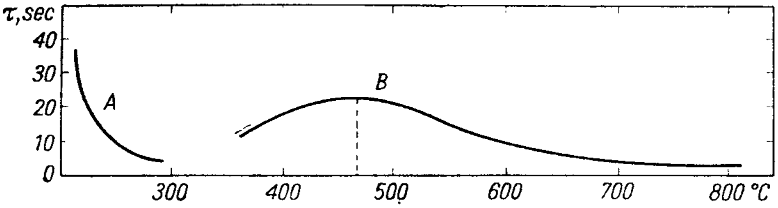


Fig. 13. Decomposition of nitroglycerine on a hot metal plate: A—violent decomposition, B—quiet decomposition of spheroid (T. Urbański and Rychter [65]).

Attention was drawn by Semenov to the fact that explosive substances are characterized by a high value of the activation energy E, as well as of the temperature-independent factor B.

This has been confirmed in a recent reports by Andreyev, Glaskova, Maurina and Svetlov [60]. According to these authors the activation energy of nitroglycerine decomposition at 140–150°C is $E = 45.0$ kcal/mole ($\log_{10} B = 20$).

It follows from the calculations of T. Urbański and Rychter that a non-explosive decomposition of nitroglycerine is characterized by a low E value which agrees with the above considerations of Semenov.

The ability of nitroglycerine to decompose readily when heated to a relatively low temperature (from 50°C upwards) long ago aroused suspicions that the chemical stability of this substance is low and that in the course of time it gradually undergoes spontaneous decomposition at room temperature. Well purified nitroglycerine, however, does not undergo decomposition during storage as has been realized from many years experience. Thus for instance, a sample of nitroglycerine obtained by Sobrero in 1847, preserved in the factory at Avigliana for over 70 years and regularly examined in the laboratory there has shown no signs of any change in stability. At 1912 a bore hole filled with nitroglycerine was found in a Swedish mine which had not been worked for a 38 years. The hole was a relic from the time when nitroglycerine was used alone as "blasting oil". The average annual temperature in this area is +8°C yet no changes in properties have been established in the nitroglycerine [22].

It was also noted that samples of blasting gelatine and dynamite which had been manufactured in Europe and delivered to Africa, and then sent back to Europe after several years showed no marks of decomposition [22]. Actually it is now agreed that very pure nitroglycerine is sufficiently stable at a temperature corresponding to the mean climatic temperature experienced in Europe. However, it should be protected from higher temperatures, and those approaching 50°C must be considered as dangerous. Nitroglycerine which has been heated to this temperature should be carefully checked. Similarly nitroglycerine which has been exposed to a direct sunlight should be tested (see below).

In this connection special attention should be paid to the control of nitroglycerine purity by means of the heat test (also called Abel test) which was described earlier (p. 23).

In the U.S.A. and some other countries an examination of the acidity of nitroglycerine by means of litmus paper is obligatory as well in addition to the Abel test.

The action of light. The opinion is expressed in the literature (e.g. Naoúm [22]) that diffused daylight has no adverse effect on nitroglycerine. Nevertheless in plants manufacturing or using nitroglycerine the latter is protected from direct sunlight.

T. Urbański, Malendowicz and Dybowicz [68] examined the behaviour of nitroglycerine (and of other nitric esters) exposed to ultra-violet rays and established that nitroglycerine irradiated once for a short period with a quartz lamp started to undergo slow decomposition which stopped only after an interval of 2–3 days. A sample of 3 g nitroglycerine was irradiated for 1 hr with rays from quartz lamp passing through a filter permeable to rays of 3200–4100 Å whilst maintained at a temperature of 15°C. In order to test the decomposition of the specimen, from time to time 0.25–0.5 g sample of the substance were removed, shaken with water and the pH values determined. The following results have been obtained: immediately after irradiation pH = 6.86; after 6, 24, 48 and 72 hr—6.12, 4.66, 4.48 and 5.22 respectively.

The decomposition of a sample irradiated for 10 min without any filter was similar.

By means of the Taliani–Goujon stability test it has been demonstrated that nitroglycerine which has previously been irradiated decomposes distinctly more quickly than non-irradiated nitroglycerine.

According to experiments by Deb [69] explosion of nitroglycerine can be provoked by intensive irradiation with ultra-violet rays (of 900 J strength), if the substance was previously heated to 100°C.

Kaufman [111] found that nitroglycerine is quite susceptible to γ-radiation, N_2, nitrogen oxides, H_2, CO_2 and CO being evolved.

EXPLOSIVE PROPERTIES

The explosive decomposition of nitroglycerine is generally expressed by the following equation:

$$4C_3H_5(ONO_2)_3 \longrightarrow 12CO_2 + 10H_2O + 6N_2 + O_2 \qquad (2)$$

According to Naoúm's [22] calculations the heat of explosion ought to amount in this case to 1485 kcal/kg, the volume of gases $V_0 = 715.7$ l./kg (or after condensation of water 469 l./kg), the temperature 3185°C (this number is repeated by the author after Hess [70]); thence the "force" $f = 9292$ m.

It has been established experimentally by Sarrau and Vieille [71] that the volume of gases, after the water vapour had been condensed, is 465 l./kg, i.e. a value very close to the value obtained by calculation. However, the composition of the gases found by these authors is different, probably in consequence of the incomplete explosive decomposition of nitroglycerine under the conditions of the experiment (calorimeter bomb).

After condensation of water vapour, the following composition has been established for the gases:

CO	35.9%
CO_2	12.8%
NO	48.2%
N_2	1.3%
H_2	1.6%
CH_4	0.2%

As reported by Bowden and Yoffe [72] the composition of the gaseous products evolved during explosion of nitroglycerine depends on the method of initiating the substance (composition of products in per cent):

	NO	N_2O	N_2	CO_2	CO	H_2	O_2
Initiated by detonation	—	—	32.0	63.1	—	—	4.9
Initiated by shock	29.7	2.3	11.7	28.8	25.5	5.0	—
Initiated by heating to 180°C	50.3	1.0	2.1	17.2	28.9	0.5	—

A different equation for the decomposition of nitroglycerine based partly on the data of Sarrau and Vieille [71] and partly on his own experiments was published by Kast [49]

$$32C_3H_5(ONO_2)_3 \longrightarrow 96CO_2 + 80H_2O + 6NO + 45N_2 + 5O_2 \qquad (3)$$

together with the following figures: heat of explosion 1455 kcal/kg, volume of gases $V = 715$ l./kg, temperature 4250°C, "force" $f = 12{,}240$ m.

Other sources quote the values listed below (heat of formation—see p. 46):

heat of explosion	temperature
1470 kcal/kg (Escales [73])	3153°C (Gody [75])
1478 kcal/kg (Berthèlot [74])	3005°C (Wuich [76])

Sensitiveness to shock. It was Nobel [77] who first established in 1869 that crystalline nitroglycerine is significantly less sensitive to shock than the liquid. Advantage was taken of this property (Mowbrey [78]), in transport. The sensitiveness of nitroglycerine has been examined in detail by Hackel [17]. He found that the stable modification was slightly more sensitive than the labile form. The results of his experiments are collected below:

liquid nitroglycerine gives	10% explosions due to a shock of 0.08 kgm/cm²
	50% explosions due to a shock of 0.11 kgm/cm²
crystalline nitroglycerine, stable form	10% explosions due to a shock of 0.51 kgm/cm²
	50% explosions due to a shock of 0.65 kgm/cm²
crystalline nitroglycerine, labile form	10% explosions due to a shock of 0.63 kgm/cm²
	50% explosions due to a shock of 0.78 kgm/cm²

In the earlier experiments of Beckerhinn [79], Hess [70] and Will [80] it was reported that in order to bring about an explosion of solid nitroglycerine a 3–4 times more powerful shock was needed than in the case of liquid nitroglycerine.

Cronquist [81] has found that a mixture containing both liquid and crystalline nitroglycerine is more sensitive to shock than either of them alone. This is thought to be the result of friction between the sensitive liquid and the crystals. Nitroglycerine readily explodes on impact with a rifle bullet.

Although nitroglycerine is very sensitive to shock and explodes readily if stimulated in various ways—both mechanical and thermal, it can often undergo incomplete explosion.

The following data for nitroglycerine for the net expansion in the lead block (with water tamping), obtained when detonators of different initiating strength were used, have been reported by Naoúm [22]:

detonator No. 1	190 cm³
detonator No. 2	225 cm³
detonator No. 6	460 cm³
detonator No. 8	590 cm³

In these experiments, Naoúm showed that weak initiation with the No. 1 detonator produced only 32% of the effect obtainable by means of the No. 8 detonator. Nitroglycol and methyl nitrate explode more completely even if initiated with weak initiation differing in this respect from nitroglycerine.

A certain difficulty in detonating nitroglycerine is to some extent explicable by its high viscosity and the fact that it is a liquid. If on the other hand nitroglycerine is mixed with diatomaceous earth in the ratio of 75 parts of nitroglycerine to 25 parts of kieselguhr the detonating capacity of nitroglycerine is increased. Under these conditions on initiation with a No. 1 detonator the expansion recorded in the lead block test is 285 cm^3, whilst with a No. 8 detonator it is 305 cm^3. The insignificant difference between these two values is due to the difference in the detonation strength of the initiators themselves and if a correction is applied, the values are approximately the same. Undoubtedly both the dispersion of the nitroglycerine over a large surface area on the particles of kieselguhr and its extensive contact with air contained in the absorbent facilitate explosion.

These considerations would suggest that solid nitroglycerine is likely to explode more readily than the liquid nitroglycerine as, indeed, it does, as confirmed experimentally by Gorst and Andreyev [82] and by Hackel [29]. The results of Hackel's investigations are quoted in Table 15.

TABLE 15

THE LEAD BLOCK EXPANSION* BROUGHT ABOUT BY DETONATION OF NITROGLYCERINE

Type of nitroglycerine	Sand tamping cm^3	Water tamping (with admixture of glycerine) cm^3
Crystalline nitroglycerine (both modifications)	390	630
Liquid nitroglycerine	390	510

* The experiments were performed with blocks cooled to a temperature between −2 and −5°C. This is why the resultant values are lower when compared with the data quoted by other authors.

Sensitiveness to friction. Nitroglycerine is sensitive to friction. Thus, for instance, an explosion can take place simply as the result of rubbing it in a porcelain mortar with a rough surface.

Rate of detonation. The rate of explosion of a liquid explosive may vary within wide limits. Thus, according to numerous experiments it has been established that for liquid nitroglycerine the order of the explosion rate is 1000–8000 m/sec. The detonation rate of solid nitroglycerine, on the other side, does not vary in this way. It amounts 8000 m/sec at the maximum density of loading.

The explosion rates of liquid and crystalline nitroglycerine found by different authors are collected in Tables 16 and 17.

It follows from the data quoted that liquid nitroglycerine explodes with a moderate velocity of the order 1000–2000 m/sec, if the initiation of explosion is insufficiently strong.

A small diameter of the tube to be filled with the explosive favours a low rate of explosion. If this is very small, (a few millimetres) the velocity of propagation of explosive decomposition may be reduced to 700 m/sec, and is variable, so that the process cannot be regarded as detonation.

Nitroglycerine emulsified with a sufficiently large amount of water does not detonate. An emulsion of nitroglycerine can, however, detonate if it is composed of 150 parts (or less) of water and 100 parts of nitroglycerine, as reported by Médard [96]. The detonation rates of emulsions, when initiated with a No. 8 detonator are as follows:

water to nitroglycerine ratio	rate of detonation
75:100	6400 m/sec
100:100	5530 m/sec
150:100	5250 m/sec

TABLE 16

THE EXPLOSION AND DETONATION RATES OF NITROGLYCERINE

Conditions of loading and initiation	Rate of explosion m/sec	Author
Liquid		
Explosion		
Lead tube, 30 mm dia.	1525	Abel [83]
Narrow lead or tin tube, 3–6 mm dia.	1100	Berthelot and Vieille [84]
Iron tube 30 mm dia.	2050	Mettegang [85]
	1525	Blochmann [86]
Glass tube 22 mm dia. initiated by No. 8	1165	Andreyev and Dzerzhkovich [87]
detonator	*ca.* 700	Ratner and Khariton [88]
Detonation		
Glass tube 24 mm dia. initiated by No. 8 detonator	8000	Hackel [17]
	7800	Cook [93]
Iron tube 25–37.5 mm dia. initiated by 1.5 g mercury fulminate	8525	Comey and Holmes [89]
Gas pipe, initiated by 50 g tetryl	7430	Günther [90]
Glass tube 22 mm dia. initiated by 10–15 g crystalline nitroglycerine	9100	Andreyev and Dzerzhkovich [87]
Steel tube 22 mm dia. initiated by 75 g PETN	7760–8240	Friedrich [91]
Tube 35 mm dia. initiated by No. 8 detonator	6500	Naoúm and Berthmann [92]
Tube as above, initiated by 50 g of picric acid	8580	Naoúm and Berthmann [92]
Crystalline		
Glass tube 21 mm dia. initiated by No. 10 detonator	8100	Chemisch-technische Reichsanstalt [94]
Iron crucible, initiated by No. 8 detonator	*ca.* 8000	Stettbacher [95]
Glass tube 22 mm dia. initiated by No. 8 detonator stable form	9150	Andreyev and Dzerzhkovich [87]
labile form	did not detonate	Andreyev and Dzerzhkovich [87]
labile form, initiated by 20 g tetryl	9100	Andreyev and Dzerzhkovich [87]
Glass tube, 24 mm dia., stable form initiated by No. 8 detonator	8220	Hackel [17]
labile form initiated by No. 8 detonator	*ca.* 8190	Hackel [17]

An emulsion composed of 200 parts of water and 100 parts of nitroglycerine is incapable of being initiated. In order to achieve complete safety, however, a ratio of 300 parts of water to 100 parts of nitroglycerine should be chosen.

In experiments designed to find the difference in the rates of explosion between the labile and the stable forms of crystalline nitroglycerine Hackel found that both detonate with the same rate.

The occurrence of various explosion rates for liquid nitroglycerine has been explained by Audibert [97] by postulating two successive reaction stages. First a slightly exothermic chemical reaction (4a) would occur:

$$C_3H_5(ONO_2)_3 \longrightarrow 2\,CO + CO_2 + 2\tfrac{1}{2}H_2 + 1\tfrac{1}{2}N_2O + 1\tfrac{3}{4}O_2 + 21\ \text{kcal} \tag{4a}$$

The decomposition of nitroglycerine can stop at this reaction stage if an initiation is weak and if the nitroglycerine is not confined. In these circumstances large quantities of N_2O are developed as the nitroglycerine decomposes. If initiation is strong enough and the nitroglycerine is confined, (e.g. in a tube) then a second reaction stage (4b) of distinctively exothermic character can follow:

$$C_3H_5(ONO_2)_3 \longrightarrow 3\,CO_2 + 2\tfrac{1}{2}H_2O + 1\tfrac{1}{2}N_2 + \tfrac{1}{4}O_2 + 319\ \text{kcal} \tag{4b}$$

Audibert's theory seems to be correct only in certain cases. After a very vigorous initiation the final reaction probably takes place immediately and the maximum heat energy is developed.

Sensitiveness to flame. Attention has been paid recently (Andreyev [98]) to the fact that there is little precise information available concerning the sensitiveness of nitroglycerine to flame and its ability to burn. Naoúm states in his book [22] that nitroglycerine is difficult to ignite, yet burns readily. Unquestionably nitroglycerine burns without difficulty in the open air. However, it behaves otherwise when confined.

It was demonstrated by Andreyev that nitroglycerine placed in a glass tube of 5.18 or 22 mm dia. can be ignited with a gas flame or with a glowing wire. Burning is limited, however, to local decomposition and is not transferred to further layers. This phenomenon occurs both at room temperature and at 80°C. None the less an explosion can be brought about without preliminary burning if ignition of nitroglycerine is repeated on the same spot.

In Andreyev's experiments nitroglycerine burned in a vessel where the pressure had been reduced below the atmospheric pressure. The flame died out, however, when the pressure was increased beyond a certain limit, owing to the evolution of gaseous decomposition products. In the neighbourhood of that pressure, burning was very irregular. The critical pressure, when the flame of nitroglycerine is about to expire, depends upon the conditions of experiment, and varies between 234 and 375 mm Hg. The linear burning rate was estimated as 0.075 cm/sec.

At a temperature of 98°C the critical pressure was similar, while burning the rate increased significantly, to about 0.13 cm/sec.

Generalizing, Andreyev reported that nitroglycerine burns steadily at pressures below 400 mm Hg; the rate of burning depends on the pressure (Fig. 14) according to the equation:

$$U = 0.0067 + 0.216p^{0.831}$$

Among the products of burning, substances characteristic of incomplete decomposition of nitroglycerine, such as formaldehyde, can be detected. Extrapolating the curve in Fig. 14, Andreyev has determined the rate of burning for nitroglycerine at atmospheric pressure to be of about 0.23 g/cm/sec. Crystallized (frozen) nitroglycerine behaves the same as the liquid. Nitroglycerine with nitrocellulose dissolved in it (as for instance blasting gelatine) burns distinctly more readily than pure nitroglycerine and will burn under atmospheric pressure. Andreyev made the interesting observation that the higher the viscosity of the solution, the higher is the pressure at which marked increase of the burning rate occurs. A more detailed discussion of this is included in Vol. III.

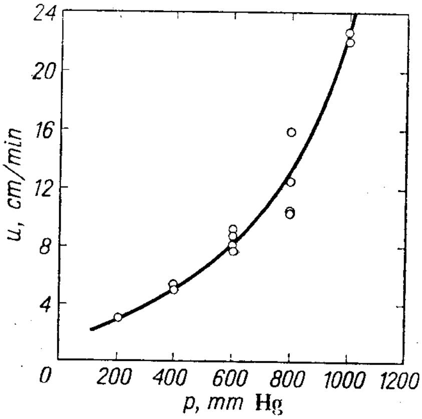


FIG. 14. Rate of burning of nitroglycerine as a function of pressure (Andreyev [60, 61]).

Nitroglycol burns more readily than nitroglycerine, whereas dinitrodiglycol burns distinctly less so.

TOXICITY

References to the extremely powerful physiological activity of nitroglycerine were made as early as 1848 by Sobrero [1].

Nitroglycerine is a highly toxic substance. Its effect consists in dilating the blood vessels and thereby lowering the blood pressure.

Poisoning can take place either from inhalation of the vapour of nitroglycerine (the very low concentration corresponding with the vapour pressure at room temperature is sufficient) or as the result of penetration through the skin or through the mucous membranes (the latter occurs with particular ease).

The degree of sensitivity to the action of nitroglycerine varies to a large extent among different people. The chief symptom of nitroglycerine poisoning is a very severe headache which gives the impression that the head is being squeezed. Consumption of alcoholic drinks increases the toxic effect. The human body quickly becomes accustomed to the presence of nitroglycerine; often this accommodation is complete after a few days work with it. However, the immunity is lost when the contact with nitroglycerine ceases and the worker's system must re-adapt itself when contact is resumed. Workers accustomed to close contact with nitroglycerine manage to knead dynamite dough with bare hands and to pass in through a sieve, without suffering any harmful consequences. Review of the medical literature (Schuchard [99], Evans [100], Ebright [101], Hudson [102]) indicates from many years of work that nitroglycerine produces no symptoms of chronic poisoning and that the substance should not be regarded as an industrial poison. It is exceptionally rare that individuals are found who cannot grow accustomed to handling nitroglycerine. Obviously any worker who fails to develop immunity should be transferred to other work. In cases of accidental poisoning (reported in the medical press) pain, vomiting, cyanosis, disturbances of the sight, swelling of extremities and paralysis have been observed. Rare cases of fatal poisoning have been reported. Antidotes include caffeine and analgesics (pain-relieving remedies) but the first step is to expose the patient to fresh air. In the case of slight poisoning the symptoms can be relieved simply by the latter treatment. Nitroglycerine headaches can be relieved by intramuscular injection of caffeine, sodium benzoate and oral administration of amphetamine sulphate (Rabinovitch [103]; Schwartz [104]).

After each shift, workers in the nitroglycerine department should change their clothing and have a bath, since accidents have been reported in which a worker returning home in his working clothes has caused his family to suffer from nitroglycerine poisoning (Lazarev [105]).

According to Weinberg [106] in the human system nitroglycerine is reduced to nitrous esters.

For many years the physiological effect of nitroglycerine in promptly decreasing the blood pressure has been used medically. It was used for the first time in about 1850 under the name glonoinum. For this purposes nitroglycerine is prepared in the form of a 1% alcoholic solution, which is given orally in doses of one or a few drops. The maximum single dose is 0.1 mg [107]. The present trend is to use other esters of nitric acid, namely erithritol tetranitrate (see p. 167), pentaerithritol tetranitrate (see p. 183), mannitol hexanitrate (see p. 171) and other similar derivatives instead of nitroglycerine to reduce the blood pressure. Being crystalline these substances are not so readily assimilated and therefore act more slowly and produce a longer lasting effect.

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CHAPTER III

PRODUCTION OF NITROGLYCERINE

TECHNOLOGICAL PRINCIPLES OF NITROGLYCERINE MANUFACTURE

THE O-nitration of glycerine and similar alcohols is a chemical reaction which is applicable on a large scale only by special technical methods. The technological processes used for manufacturing nitroglycerine and other similar nitric esters differ considerably from the current methods usually applied in the commercial production of organic compounds. These differences primarily concern the plant and are due to a large extent to the danger of the nitration process itself and also to the risks involved in handling both the product and the spent acids. In the manufacture of other organic chemicals the danger factor either does not exist or exists in a considerably smaller degree.

From experience gained over many years, special equipment and methods of nitration and purification of nitroglycerine have been developed and certain traditions established. Recently, however, changes have occurred in this field. Continuous methods of nitroglycerine manufacture have been introduced. In many cases they have revolutionized traditional techniques and led to new manufacturing processes.

Before describing individual production processes certain general principles will be outlined.

MIXED ACID COMPOSITION AND YIELD OF THE PROCESS

Theoretical calculation based on the equation of nitration shows that when 100 parts of glycerine are added to 205.4 parts of HNO_3 the yield is 246.7 parts of nitroglycerine. At the same time 58.7 parts of water are formed. In practice this yield cannot be obtained because the nitration of glycerine, like every esterification reaction, is in principle a reversible one. The yield is partly defined by the number of O-nitro groups introduced into the molecule of glycerol.

The stronger the acid concentration, the higher the degree of nitration and the larger is the yield. An excess of acids establishes equilibria that favour a more complete reaction. The surplus must not be too large, however, since nitroglycerine is slightly soluble in spent acid and this may considerably decrease the yield of final product. For this reason it is necessary to formulate the nitrating acid so as to achieve as complete a nitration as possible while at the same time minimizing the loss of product due to its solubility in the spent acid.

Nitroglycerine can be obtained if nitric acid alone is used as a nitrating agent. In this case a large excess of acid should be used. One part by weight of glycerine mixed with 10 parts by weight of the strongest nitric acid (99%) below room temperature and afterwards diluted with 30 parts weight of water and ice yields 1.765 parts of nitroglycerine. From the separated spent acid a further quantity (0.307 parts by weight) of the substance can be extracted by means of chloroform. The total yield therefore amounts to 2.072 parts of nitroglycerine, containing a small admixture of "dinitroglycerine" (glycerol dinitrate), i.e. about 84% of theoretical yield.

If a smaller quantity of nitric acid is used in the process, e.g. 5 parts of acid with 1 part of glycerine, the yield decreases and the product represents a mixture of nitroglycerine and dinitroglycerine in the ratio of 1:3. Clearly an uneconomic procedure of this kind cannot have any practical application. Therefore even in the earliest experiments on nitroglycerine manufacture (Sobrero, Nobel, Zinin) a mixture of nitric acid and sulphuric acid was used for nitrating the glycerine. It was proved that for 1 part of glycerine a strong mixed acid containing 3 parts of nitric acid 90% and 4.5 parts of concentrated sulphuric acid could be used instead of 10 parts of anhydrous nitric acid, the yield being significantly higher, namely from 100 parts glycerine 215 parts of nitroglycerine, corresponding to 87% of the theoretical yield. The quantity of water should be below this required for $H_2SO_4{\cdot}H_2O$ [53, 54].

Experiments on the use of mixtures of nitric acid with phosphoric anhydride showed this to be impracticable, since separate layers were formed with the phosphoric acid at the bottom and nitroglycerine remaining dissolved in the nitric acid layer from which it had to be separated by adding water. Nor was replacement of sulphuric acid by anhydrous calcium nitrate of any practical value, as precipitation of nitroglycerine by the addition of water was necessary. The yield attained by application of both these methods does not exceed 2 parts of nitroglycerine from 1 part of glycerol. At the time when concentrated nitric acid was very expensive, attempts were made to nitrate glycerine with a mixture of sulphuric acid and sodium nitrate (Huntley and Kessel [1]). However, this method found no practical use.

Considerable progress in the field of nitrating glycerine was achieved by Nathan, Thomson and Rintoul [2] who introduced oleum as a component of the nitrating acid, thus formulating an anhydrous mixed acid for the nitration process. Its application gave larger yields than nitration with acids containing about 5% of water. For example 100 parts of glycerine react with a mixed acid prepared from 280 parts of nitric acid 90% and 360 parts of oleum 20% to yield 225 parts nitroglycerine which corresponds with 91% of the theoretical yield. The development of improved equipment in full scale plant makes it possible to obtain 234 parts of nitroglycerine from 100 parts of glycerine, i. e. 95% of theory.

At present the most commonly used nitrating agent is the anhydrous mixed acid containing:

45–50% HNO_3
50–55% H_2SO_4

Mixed acid for nitration should be prepared from pure acids. The waste acids remaining after nitrating glycerine are not re-used in the nitration. They are subjected to a denitration process (more details are given on p. 84). In some factories nitrating acid is produced by mixing nitric acid with the spent acid which remains after the trinitration of toluene, afterwards concentrating the mixture by the addition of oleum. However such acid includes certain impurities, e.g. tetranitromethane, traces of which in nitroglycerine may exert a negative influence on the result of the starch–iodide paper test (heat test [3]). Where this procedure is adopted, during the final washing of nitroglycerine with sodium carbonate solution a small quantity of sodium sulphite should be added, since this combines with tetranitromethane to form a soluble sodium salt of trinitromethanesulphonic acid which can be removed with ease (see Vol. I, p. 589). In general, however, the use of spent acids in the preparation of mixed acid for the manufacture of nitroglycerine should be considered as improper. Indeed the use of spent acids for this purpose is forbidden, for instance, in the U.S.S.R. because despite special stabilizing methods (described above) nitroglycerine of satisfactory stability cannot be obtained.

Further, attention should be paid to the composition of the nitrating acid, for it is not without influence upon the stability of nitroglycerine and similar esters.

It has been demonstrated experimentally (L. P. Kuhn, W. J. Taylor and Groggins [4]) that increasing the D.V.S. (Vol. I, p. 139) favours high stability of the nitrator charge, while decreasing it results in reduced stability. This is explained by the fact that increasing the D.V.S. tends to shift the nitration or esterification further towards completion, whereas too low a D.V.S. would permit accumulation of incompletely nitrated material, along with increased dilution, and this would be favourable to oxidation reactions. It is also of interest to follow the changes in the value of the D.V.S. ratio during the course of nitration when glycerine is fed into the mixed acid. Since the amount of sulphuric acid is constant throughout the nitration and there is no water at the beginning of the nitration, the D.V.S. ratio is infinity until enough water has been formed to balance the initial negative water content. In a typical glycerine nitration this takes place after about 18% of the nitration has been completed. The D.V.S. ratio falls rapidly at first and then more slowly approaches the specified value which is reached at the end of the nitration.

One of the important factors in maintaining safety during nitration is the necessity for keeping the correct acid to glycerine ratio. In general too large a charge of glycerine in relation to the amount of acid present may lead to decomposition with a temperature rise accompanied by oxidation that is very often difficult to control.

The ratio mixed acid/glycerine should be such as to maintain an excess (*ca.* 20%) over the theoretical quantity of required nitric acid. The weight ratio mixed acid/glycerine is usually 5.5–6.5.

EQUIPMENT FOR PRODUCTION OF NITROGLYCERINE

For production of nitroglycerine a variety of equipment can be applied, depending on the method of manufacture to be used, that is either batch or continuous. In Europe the batch process of nitrating glycerine is performed in nitrators holding 150–250 kg glycerine, in South Africa 400 kg glycerine and in the U.S.A. 600 kg glycerine. According to MacNab [5] batch nitration was carried out with up to 1400 lb (635 kg) of glycerine. Continuous processes are much more efficient and safer in principle. Formerly the most commonly used construction material for nitrators (Fig. 15) was lead. This substance, used as long ago as the 1870's by Nobel, has many advantages.

(1) In the event of an explosion lead does not break into dangerous small fragments, but being a soft metal it is readily disintegrated or remains at the site of the explosion or in its neighbourhood as a lumpy mass. Iron vessels, on the other hand, break up if an explosion occurs and their destructive range may be considerable.

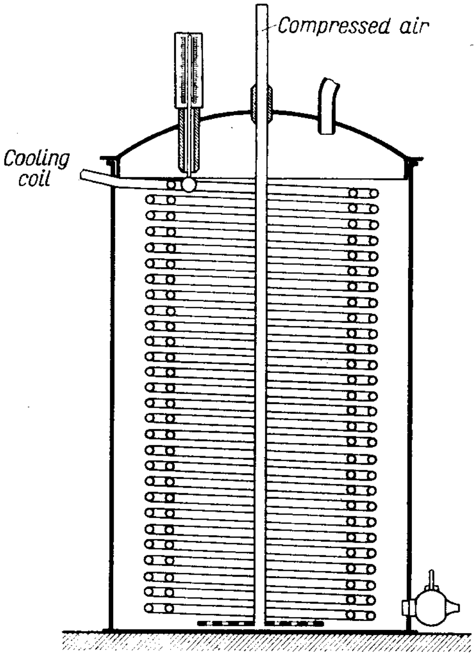

FIG. 15. Diagram of Nobel nitrator made of lead (Nobel, U.S. Pat. 57175 (1866), after Nauckhoff and Bergström [7]).

(2) Lead is an acid-resistant material and the lead sulphate formed on the surface does not contaminate the product of nitration, merely forming a permanent protective layer against the corrosive effects of the nitrating acids. However, the cover of lead sulphate acts as a thermal insulator, which is undersirable since it lowers efficiency of operation, e.g. when leaden cooling coils are used.

(3) Due to its softness lead can be struck or rubbed with less danger than that caused by striking or rubbing other materials, e.g. iron.

(4) Since it is a soft material, melting at a low temperature, lead is easily welded. In nitroglycerine plants, parts of equipment of lead can be constructed without difficulty in the factory's own workshops from sheet lead 10–15 mm thick.

Cast iron nitrators (Fig. 16) were used [6] more often than lead ones for nitrating nitroglycerine in the U.S.A.

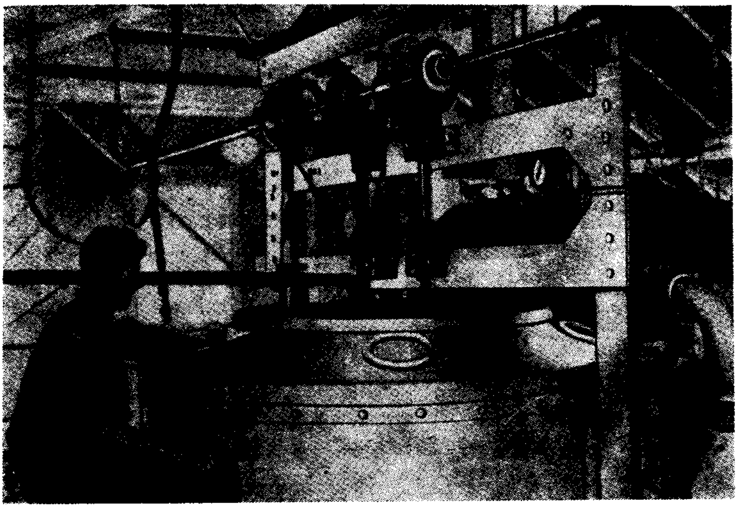

FIG. 16. U. S. nitroglycerine nitrator with two mechanical stirrers (*ca.* 1½ ton of nitroglycerine produced in one batch; Symmes [6]).

In the recently introduced continuous methods of nitroglycerine manufacture nitrators made from acid resistant steel are used since the art of welding stainless steel had progressed remarkably by the 1930's. The design and construction of nitrators for nitrating glycerine are included in the descriptions of individual methods of nitration.

Stirring

Good stirring of the mixture in the nitrator is a major safety factor and also important in securing a good yield. Lead nitrators have been equipped since Nobel's times with compressed air stirring, the pressure applied being usually 4 atm. Air nozzles are situated in the bottom of the nitrator in such way that no dead spaces remain. The efficiency of stirring is checked by putting corks on the surface of water led into the nitrator for test purposes.

If compressed air stirring is used, attention should be paid to the purity of air. Usually the air coming from the compressor contains a certain amount of lubricating oil. If this oil were to enter the nitrator it would react with the mixed acid and produce a dangerous rise in temperature. Thus the air must be purified before entering the nitrator. Generally a filter filled with coke or pumice is used.

Between the filter and the nitrator a reservoir of compressed air, fitted with a safety valve set for 4 atm pressure, should be installed. In the event of any breakdown in the compressor and any pause in the in-flow of compressed air, a steel cylinder filled with compressed nitrogen (or carbon dioxide) kept ready for this emergency should be used to supply gas to the stirrer pipe. While stirring is interrupted the supply of glycerine to the nitrator must be stopped.

Stirring by means of compressed air has a drawback, in that a certain quantity of nitric acid which is volatile is carried out of the nitrator and thus by decreasing the nitric acid content in the nitrator, can contribute to a diminished yield of the whole process. Experience has indeed shown that with mechanical stirring the output is usually higher by about 2% as compared with compressed air stirring.

The cast iron nitrators used in the U.S.A. are equipped with mechanical stirrers (Fig. 16).

According to Nauckhoff and Bergström [7] a nitrator with mechanical stirring was used as long ago as the 1870's: in 1872 in the British Dynamite Co. in Ardeer and in 1879 by A. Liedbeck at Isleton in Switzerland, Paulilles in France and Avigliana in Italy.

Nowadays nitrators for continuous nitration made from stainless steel are fitted with high-speed mechanical stirrers operating at up to 600 r.p.m.

The method by which glycerine addition is carried out also exerts an influence on the uniformity of the nitration process. There exist several arrangements by means of which the nitrator can be supplied with glycerine, in the form of a few up to about twenty thin streams or in a finely divided state. On the basis of long years' experience it has been found, however, that the method of adding the glycerine to the acid is a secondary factor in comparison with stirring. Hence glycerine can be added as a 1–1.5 cm stream without any trouble, if the contents of nitrator are well stirred.

Since the viscosity of glycerine is high, especially at low temperatures, it must be warmed before it is introduced into the nitrator. In practice glycerine is warmed to 25–40°C. At a lower temperature its viscosity is too high, and at a more elevated temperature there is a danger that the temperature could be too high at the moment of contacting glycerine with the nitrating mixture and that decomposition of the nitroglycerine formed thus could take place. Because of its low viscosity at temperatures between 25 and 40°C the stream of glycerine is easily dispersed in the nitrating acid by stirring.

There are special devices which make it possible to introduce glycerine to the nitrator by means of compressed air if a convenient inlet valve is opened manually by pressing with the hand. Then, if there is any danger of an explosion (e.g. if the temperature is too high, and brown fumes are formed), the glycerine supply must be stopped quickly. The workman in change of the nitration can do this easily for simply by lifting his hand he stops the stream of glycerine.

Immediately after the full charge of glycerine has been added and the stirrer stopped, the glycerine feed arrangement should be removed from the nitrator in order to make sure that no more glycerine falls into the nitrator while there is no stirring. One drop of glycerine can bring about a dangerous explosive decomposition in these circumstances. An accidental explosion occurred in an emptied nitrator which was partially destroyed when a drop of glycerine fell to the bottom of the vessel onto remnants of spent acid and initiated remnants of nitroglycerine.

Equipment is also available for spraying glycerine under the surface of the nitrating acid. This arrangement does not offer any special advantages and is liable to be easily corroded in the presence of acids.

NITRATING TEMPERATURE

Experience has shown that within certain limits the lower the temperature of nitration, the higher the yield of nitroglycerine. This fact can easily be explained, because the higher the temperature of nitration, the more intensive the oxidation reactions. The nitration of glycerine may be performed on a small scale at a temperature of 40°C, but its yield is then rather low. In large scale manufacture, however, this temperature is to be considered dangerous, the more so since thermometers seldom show the temperature in the centres of decomposition, only the average temperature, so that locally the temperature can be markedly higher and sufficient to produce a spontaneous decomposition process which usually ends in an explosion. The maximum temperature allowed for nitration on plant scale is usually 30°C. On the other hand a very low nitrating temperature (e.g. about 0°C) is not recommended, as the nitration then proceeds too slowly.

A nitration temperature within the limits 30–35°C should not be considered dangerous and is often applied in some factories (e.g. Gyttorp [7]). However, should any irregularity occur which may be accompanied by an increase in temperature, obviously less time will be available to lower it than if the working temperature is lower (e.g. 20–25°C).

Stirring and cooling to keep an even temperature that does not rise above a certain limit, is an essential feature of the nitrator. During the nitration of glycerine a large amount of heat is produced; 120–170 kcal/kg glycerine are developed in the reaction of esterification plus about 200 kcal/kg glycerine due to dilution of the acid. The cooling arrangements must be able to remove, rapidly, the heat liberated. Until suitable equipment became available the nitration of large amounts of glycerine always presented a serious danger. Initially, efforts were made to modify the manufacturing process itself by dividing it into two stage (Boutmy and Faucher method [31] see p. 88). Afterwards Nobel [8] designed nitrators carrying leaden coils having a very large cooling surface and having an outer jacket. It was found, however, that the jacket is superfluous and that cooling by means of coils is entirely adequate, provided of course that the coils are fed with sufficiently cold water. Later the efficiency of the cooling arrangements was further increased by using brine or spirit at temperatures below 0°C. In effect nitrating temperatures of about 12°C can be maintained, increasing the yield by 3–4%.

The relation between the temperature of nitration and the yield of nitroglycerine is especially marked if less concentrated mixed acids are used. According to Naoúm's data, nitrating glycerine in mixed acid containing

39.0%	HNO_3
55.5%	H_2SO_4
5.5%	H_2O

at 30°C yielded 205% nitroglycerine, whilst nitration at 0°C increased the yield to 217%.

The yield differences are smaller if the acid contains less water. Thus, by using mixed acid comprising

38.7%	HNO_3
58.6%	H_2SO_4
2.7%	H_2O

in the ratio of 6.5 parts of acid to 1 part of glycerine at different nitrating temperatures the following yields were obtained:

at 30°C	216%
at 10°C	223%
at 0°C	225%

When nitration is carried out in an anhydrous mixed acid at a temperature of 30°C the yield is about 4–4.5% smaller then when nitrating at 0–10°C.

Temperatures below 12°C are not usually used, since crystallization of nitroglycerine could take place. Lower temperatures (e.g. 5–7°C) can be applied only when a mixture of glycerine with glycol or diglycerol is nitrated and if there exists no fear that the mixture of esters resulting from the reaction can freeze. In factory practice, nitration is performed mainly at temperatures of about 20–25°C or at 25–30°C. The temperature is measured by means of at least two thermometers, immersed in the vessel at different depths.

A temperature increase in the nitrator accompanied by the evolution of red-brown oxides of nitrogen indicates that dangerous decomposition and oxidation processes are occurring. Should these danger signals occur, the glycerine supply must be stopped instantly. Then, after waiting for a time, if the temperature does not fall but tends to remain high or to increase further, the contents of the nitrator should be let down into a special drowning tank.

At the beginning of each day's work the cooling coil should be checked to ensure that it is not damaged. A minute hole in the coil can bring about decomposition and explosion, due to the heat developed by the cooling water penetrating to the acid through the hole and causing the temperature to rise above the permitted limit. The condition of the coil can be checked in different ways. The best method is to remove all water from the coil, to fill the nitrator with acid and to attach the compressed air line (of 3–4 atm) to the coil. Bubbles of air appearing on the surface of acid indicate that the coil is not leakproof. Another method of checking that the equipment is undamaged consists in the following operations: an evacuated nitrator is allowed to stand over night, with the water inlet valve of the coil open, the outlet valve being shut. If there are any holes in the coil, water will be found in the nitrator after a few hours.

Damage to the leaden coil also may be brought about by excessively high water pressure. In order to avoid this, low pressures of water or an alternative cooling medium should be used. The weaker parts of the coil may be expanded by the action of water and the weakened place then attacked by corrosion. Welds are also liable to undergo corrosion and welding should therefore be carried out with great care.

In some factories a suction system is used for the water or cooling liquid in place of a pressure system. In such systems, slight damage of the coil may be less dangerous, because the cooling liquid does not escape from the coil into the nitrator or only to a very small extent, so that it is possible to complete the nitration without undue risk.

In addition to carrying out all the checks which have been discussed and adopting appropiate safety measures, an extra routine precaution to be recommended consists in changing the old leaden coil for a new one after a certain number of nitrations have been carried out.

DROWNING TANK

If decomposition begins in the nitrator with increasing temperature and evolution of brown fumes, it is necessary to make the contents of the nitrator harmless by discharging the whole into the drowning tank.

Decomposition can be caused by the following factors:

(1) insufficient purity of the glycerine, especially if sugars and fatty acids are present;

(2) defective stirring and insufficient purity of the compressed air;

(3) unadequate cooling or leaks in the cooling coil.

The nitrator should be fitted with a safety outlet of such a cross-section that the nitrator contents can be discharged into the drowning tank in a period not longer than half a minute.

The drowning tank is situated beneath the nitrator. It is constructed of concrete or of wood lined with lead or stainless steel.

Its capacity should be about 10 times greater than that of the nitrator, and it should be half filled with water. An inlet pipe feeds compressed air into the bottom of the tank and the air supply should be turned on simultaneously as the safety valve is opened to evacuate the nitrator. Another solution consists in simultaneously opening the nitrator and injecting a strong jet of cold water before the mass enters the drowning tank.

Alternatively, drowning tank may be filled with concentrated sulphuric acid. In this case, nitroglycerine is not precipitated, but remains in solution. On mixing with sulphuric acid less heat is evolved than is developed on stirring with water. As result of both these factors, decomposition ceases, whereas after passing into water, decomposition continues although the charge has been diluted.

The evacuation of nitrator should proceed with the greatest possible speed and immediately after the respective valves are opened the personnel should leave the nitration room. Good discipline and the ability to think and act quickly are essential in the employees (more especially in the nitration foreman). In order to facilitate operations at times of crisis, various automatic devices are used to ease the manipulation of the valves. When a single lever is touched or a single button pressed these devices simultaneously actuate, for example,

(1) the discharge valve emptying the nitrator into the drowning tank,

(2) the compressed air valve feeding the drowning tank and

(3) the inlet valve supplying compressed air to the danger warning whistle.

One of the simplest arrangement of this type is illustrated in Fig. 17. By means of the lever (*1*) the inflow of compressed air into the cylinder (*2*), furnished with a movable piston, is started. The movement of the piston in the direction indicated by the arrow opens the valve (*3*) which empties the contents of nitrator. When the piston is pushed through to its farthest position the compressed air passes out, via the pipe (*4*) to the drowning tank and to the whistle. The efficiency of any automatic safety device should be checked before every nitration.

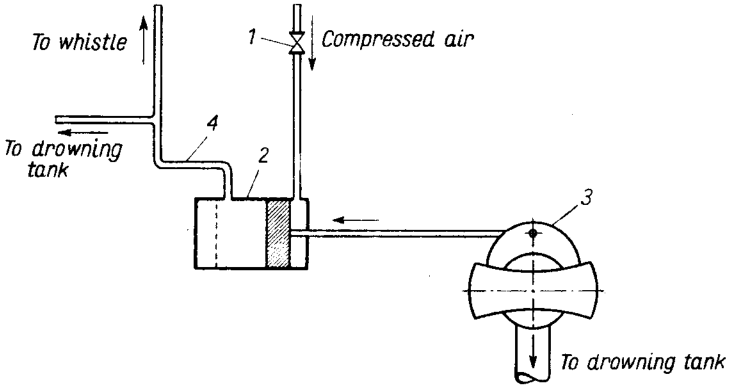

FIG. 17. Automatic quick discharge of the nitrator to the emergency drowning tank.

NITRATION TIME

The nitration rate depends, of course, on the concentration of the nitrating acid, on stirring and on the temperature. At the beginning, in the fresh anhydrous mixed acid, glycerine is nitrated at a high rate. According to Oehman [53] 80% of glycerine is nitrated within less then 1 sec. The reaction occurs mainly on the interface between the two reacting phases. As the nitric acid is consumed and water is produced the reaction rate gradually decreases. When the nitration is nearing completion (after 2–6 sec) the mixture of acids contains in addition to nitroglycerine (which is present mainly in suspension and only to a small extent in solution) dissolved glycerol dinitrates, the so called dinitroglycerines (*ca.* 4.5% according to Oehman [54]), as well as mixed esters of nitric and sulphuric acid. These substances react gradually with the nitric acid in the mixed acid to give further quantities of nitroglycerine [27]. However, this process, which is called the secondary separation of nitroglycerine, requires a long time and it cannot be included in the nitration period proper as this should be accomplished in the shortest possible time (for details concerning this process see p. 95). There exist methods (Nathan, Thomson and Rintoul, Biazzi) in which, for various reasons, the possibility of utilizing these esters is ignored, and the secondary separation process omitted (see pp. 84, 91, 107).

Above all the time of batch nitrating depends on the cooling surface, on the temperature of the cooling liquid and on the intensity of stirring. It is also related to the size of the glycerine charge. On the average the nitration of 100 kg of nitroglycerine is completed in 20 min, if the temperature of the cooling water is 10–12°C and the temperature in the nitrator is 30°C.

The original temperature of the mixture of acids also exerts its influence on the period of nitrating; the lower it is the sooner the glycerine can be introduced into the nitrator. In winter, nitration takes less time due to this factor.

In nitrators equipped with mechanical stirrers, as used in the U.S.A., 500 kg of glycerine are nitrated in 50 min.

SEPARATION OF NITROGLYCERINE FROM ACID

Originally nitroglycerine was separated from the spent acid by pouring the whole contents of the nitrator into a wooden tank containing a large amount of water. Afterwards the aqueous solution from above the nitroglycerine was decanted. This operation was troublesome and dangerous since on dilution a large quantity of heat was evolved. Further, this method was uneconomic for it was impossible to recover the spent acid. Later, the technique of removing the nitroglycerine with a ladle from above the waste acid was introduced, and finally modern methods have been applied to the separation process.

For several minutes after the nitrator has been fully charged, stirring is discontinued and then either the whole is allowed to remain in the nitrator which in this stage plays the part of separator, or it is transferred to a special separating funnel. In continuous production the mixture flows into the separator continuously.

All methods of separating nitroglycerine from acid take advantage of the difference between the specific gravities of the two liquids. Experience has shown that the purity of glycerine to be nitrated and the purity of the nitrating acid exert a big influence on the rate of separation of the two layers. It has been proved that fatty acids, which frequently occur as impurities in glycerine, delay separation. Similarly the separation rate of the two phases is decreased by the fine crystalline precipitate of sulphate (of lead or iron) which is present in the spent acid as a suspension. All colloidal components in the glycerine and in the acid also slow down the phase separation.

Normal separation of phases should be complete in 20–30 min. However, under unfavourable conditions the time required may extend to several hours or more, and in this event separation can become a dangerous operation. Several serious explosions took place (between 1904 and 1912) during the separation of nitroglycerine from spent acid. In most of these incidents the explosion was caused by the lengthy period of contact between nitroglycerine and spent acid, resulting from the too slow separation of the nitroglycerine layer.

Much experimental work designed to accelerate the separation of nitroglycerine from spent acid has been carried out. It has been established that the separation can be hastened in several ways:

(1) Using shallow separators having a large surface area in which the distance to be travelled by drops of nitroglycerine is as short as possible.

(2) Raising the temperature to 18–20°C in the final stage of nitration. This is recommended if the nitration has been carried out at a low temperature, e.g. 12–15°C, since separation of the layers proceeds too slowly at such temperatures.

(3) Adding certain substances to the emulsion of nitroglycerine in acid, which have been shown to accelerate phase separation. The first experiment in which a marked increase in the rate of separation of the phases was achieved was reported in 1904 by Naoúm [9] who added non-polar substances which do not undergo nitration, e.g. paraffin oil, vaseline, in the proportion 0.05–0.2% of glycerine by weight, towards the end of nitration. The paraffin oil remains in the nitroglycerine layer, to be removed afterwards when the nitroglycerine is washed with water. By this means the time of separation was halved in the factory at Krümmel. To the charge of 250 kg glycerine and 1600 kg mixed acid 100 ml of paraffin oil were added, thereby reducing the separation time from 30–40 min to 15–20 min.

In the Dynamite Works at Wilmington, the addition of sodium fluoride to hasten separation has been suggested by Reese [10]. Sodium fluoride has been chosen on the assumption that rapid separation is hindered due to silicic acid and silicates present in the nitrating acid. These impurities would be removed by reaction with hydrofluoric acid to form silicon fluoride. It is true that in the presence of sodium, fluoride separation is easier, though the reasons for its effect are different than those indicated by the inventor. In fact, it has been demonstrated by the investigations of Rheinische Dynamitfabrik, Opladen, 1912 [11] that with chemically pure sodium fluoride the separation of the phases is not accelerated. The commercial product however, containing silica and silicates, has a positive effect. Thus silicon fluoride, SiF_4, seems to be the factor which accelerates the separation of phases, as it is produced in the form of bubbles which flow towards the surface of the liquid simultaneously carrying up the nitroglycerine. For this reason the patent [12] based on these experiments recommends adding either a mixture of sodium fluoride with silica or with fluorosilicate. In either case silicon fluoride is formed according to the following reactions:

$$4NaF + SiO_2 + 2H_2SO_4 \longrightarrow 2Na_2SO_4 + H_2O + SiF_4 \qquad (1)$$

$$Na_6SiF_6 + H_2SO_4 \longrightarrow Na_2SO_4 + 2HF + SiF_4 \qquad (2)$$

In the second case it is possible to take advantage of the resulting hydrofluoric acid by addition of silica to produce further quantities of silicon fluoride. As reported in the patent, to a 150–200 kg charge of glycerine approaching the end of nitration, about 30 g of a mixture composed of sodium fluoride and silica are added. If the addition is made too soon its effect is lost, since the SiF_4 is carried away by the air stream and removed from the system.

Other proposals have also been published, e.g. the suggestion of Westphälisch-Anhaltische factory [13] to add 0.02–0.05% of talc. Another way of hastening the separation is found in a patent of Carbonit A.G. in Hamburg [14], wherein additions of about 1% urea, acetamide or dicyandiamide (calculated in relation to glycerine) to the mixed acid are recommended. In contact with acid these substances decompose to form gaseous products which hasten separation in the same way as silicon fluoride.

The quantitative effect of various additives on the rate of separation of nitroglycerine from spent acid has been determined by Moisak and Grigoryev [15]. They found that in the presence of 0.5% ferric sulphate or lead sulphate, the separation rate is halved. Further, they established that the separation rate is related to the composition of the spent acid. The maximum rate of separating was achieved by using acid composed as follows:

HNO_3	17%
H_2SO_4	70%
H_2O	13%

An interesting attempt was made by Lehmann [16] to use an electrochemical method to speed up the separation of nitroglycerine. His theory was that gas evolved in the course of electrolysis would help nitroglycerine to rise to the surface.

PURIFICATION OF NITROGLYCERINE

After being separated from the spent acid, nitroglycerine still contains about 10% of acid. The composition of the acid absorbed by the nitroglycerine is different from that of the acid forming the lower layer in the separating funnel, because nitric acid is absorbed by nitroglycerine more than sulphuric acid. The H_2SO_4 to HNO_3 weight ratio in the spent acid has a value of 9, whereas in the acid absorbed by nitroglycerine the ratio is approximately 1:4 (this was discussed earlier, on p. 42).

The greater part of the acid absorbed in the nitroglycerine is removed in the primary washing, which is carried out with cold water of about 15°C, usually in the same room as the nitrator. This primary washing is insufficient to remove the last traces of absorbed acid which are very difficult to eliminate. The product is therefore washed again first with hot water, then with a dilute solution of sodium carbonate (2–4%), again with hot water and finally by a cold water wash. The temperature of the hot water and sodium carbonate solution should be held at such a level, e.g. 60–70°C, that the whole contents of the washing tank can be kept at a temperature of e.g. 45–50°C. The last cold wash, referred to as stabilization, is carried out in a separate room, into which acid vapour from the nitration room should not be allowed to penetrate.

The washing of nitroglycerine would seem to be a simple and safe operation. Nevertheless numerous explosions have occurred even in the washing tanks. Explosions of this kind were the more unexpected as right from the start compressed air was used to mix the nitroglycerine with the water or carbonate solution, so that there was no risk of friction between metal parts. In 1903 in Great Britain 9 incidents of explosion in washing tanks were recorded. Analysis of the accidents indicated that a few of them may have occurred due to friction of nitroglycerine in the numerous stop-cocks situated beside the tank controlling the outflow of liquid. Several other explosions were probably caused by the fact that the compressed air supply line serving the bottom of tank was lying loose on the bottom. The introduction of air could cause the pipe to move and to strike the walls of tank exploding the nitroglycerine. For these reasons in the construction of washing tanks (washers) outlet cocks for the liquid are omitted, and the compressed air delivery pipe is rigid and attached firmly to the bottom of tank.

The design of the most widely used type of nitroglycerine washing tank is illustrated in Fig. 18. The tank of a cylindrical shape is constructed of sheet lead or of a resinous wood (e.g. pitch-pine) since lead can readily undergo corrosion. It is equipped with the device (*1*) for delivering compressed air, pipelines (*2*) for cold water supply, and pipes (*3*) and (*4*) for hot water and sodium carbonate solution respectively. It is desirable to equip the tank with a conical lid with a ventilation duct (*5*), for carrying off acid vapours evolved during the preliminary washing of the nitroglycerine, and vapours of nitroglycerine given off during hot washing. The hose pipe (*6*) ending in a funnel is used for lowering the upper layer of liquid. An accident occurred in 1894 [17] in which the rope holding the funnel was broken off and the heavy leaden funnel weighing over 10 kg fell into the warm nitroglycerine (*ca.* 50°C) and caused it to explode. Since then the funnels are made of thin tin plate, sheet copper or sheet brass. The funnel is fastened to a cable drawn over a pulley fixed in the ceiling.

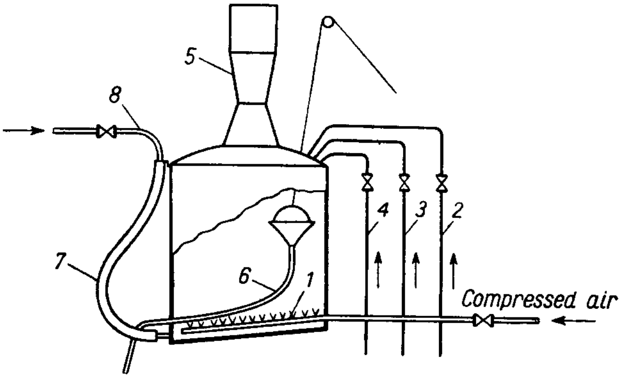

FIG. 18. Design of the tank for washing nitroglycerine (Naoúm [11]).

The lower layer, i.e. nitroglycerine, is discharged from the tank through the rubber hose (*7*) which is normally kept raised in a higher position by means of a hook fixed on the upper edge of the tank, so as to close the outlet. In order to open the nitroglycerine outflow the hose (*7*) is lowered. After washing the nitroglycerine, compressed air is applied to the hose (*7*) by means of pipe (*8*) to expel the nitroglycerine collected in the lowest part of the hose and to transfer it to the stabilization process. The tank should be equipped with a thermometer (which is not shown in the illustration) to check the temperature of the nitroglycerine. The diameter of the tank should be as large as possible and not less than its height. With these dimensions the precipitation of nitroglycerine in water proceeds rapidly and may take some 10–15 sec. It has been demonstrated experimentally that in a liquid column of 70 cm separation is accomplished after about 30 sec, while at a depth of 47 cm it requires only about 10 sec.

If hardwash-water is used, sedimentation of calcium carbonate occurs in the air supply lines. This materially increases the danger of handling the nitroglycerine since calcium carbonate is hard and its surface is uneven and friction between nitroglycerine and a surface of this kind is more dangerous than contact with the smooth surface of pure lead. For this reason hard water intended for washing should be softened before use. Water of high purity should always be used. In accordance with a report by M. Jacqué [18] at one of the dynamite plants in Mexico great difficulty was experienced in obtaining nitroglycerine capable of passing a 15-min heat test at 76°C. Systematic experiments showed that the poor stability of the nitroglycerine was caused by organic pollution of the wash water, derived from sea-weed and plankton. The difficulty was over-come by careful purification of the water supply.

In different factories various methods of nitroglycerine purification are used. A description of the British method was given by Marshall [19]. The primary washing with water at the temperature of 18°C is repeated three times to be followed by the last, fourth, washing with sodium carbonate solution. Afterwards nitroglycerine is discharged through a pipe to undergo the final washing at 30°C (the temperature inside the tank). The final washing comprises five stages;

(1) 15 min with a solution of 3.5% Na_2CO_3
(2) 30 min with a solution of 3.5% Na_2CO_3
(3) 45 min with a solution of 3.5% Na_2CO_3
(4) 15 min with softened water 3.5% Na_2CO_3
(5) 15 min with softened water 3.5% Na_2CO_3

The amount of water or solution to be used equals 2.5 parts by weight to 1 part of nitroglycerine.

Following the findings of Naoúm [11] the first washing with cold water at 15°C is succeeded by a series of washings with water wherein a larger and larger quantity of hot water is utilized. Nitroglycerine is rinsed in this way 3 or 4 times, to attain in the last washing a temperature of 40°C. Each washing lasts 5 min and consists in vigorous stirring of the nitroglycerine and water, after which the water is decanted.

Afterwards, washing with a 2–3% sodium carbonate solution heated to about 70°C takes place. After the solution is poured into the tank with the nitroglycerine the temperature inside the tank reaches about 50°C. Similarly, each washing with carbonate solution consists in stirring up the contents of the tank for 15–20 min, after which the upper solution is decanted. The decanted solution ought to give an alkaline reaction to phenolphthalein. If not, washing with sodium carbonate solution should be repeated.

After being washed with carbonate, nitroglycerine is subjected to a final washing with water: at first with hot water at 50–70°C and finally with cold water, in order to remove the sodium carbonate completely. Frequently the washing operations are shortened to 5 min except for the sodium carbonate wash, which lasts each 15 min.

The washed nitroglycerine should be neutral to litmus. If the nitroglycerine is to be used in the manufacture of mining explosives for immediate use, in certain countries the litmus paper test is considered to be a sufficient criterion of purity. If, however, the nitroglycerine is destined for the production of smokeless powders or high explosives which are to be transported to distant places, the heat test should be used to determine the purity of the nitroglycerine. German regulations require that nitroglycerine for smokeless powder manufacture should withstand the zinc iodide–starch paper test for at least 20 min at a temperature of 82°C. Nitroglycerine to be used for the production of high explosives should withstand the test with the less sensitive potassium iodide–starch paper for at least 10 min at 72°C. If a sufficiently high purity nitroglycerine cannot be obtained by means of the normal washing with sodium carbonate solution a supplementary washing with sodium carbonate solution (2–3%) containing 0.1–0.2% sodium sulphite is recommended. The addition of sodium sulphite is especially efficacious when nitroglycerine is contaminated with tetranitromethane contained in nitrating mixture prepared from spent acid from trinitrotoluene manufacture (see also p. 64). In the modern Biazzi process (p. 107) nitroglycerine is washed with 12% sodium carbonate solution without preliminary treatment with water.

Recently stabilization of nitroglycerine and nitroglycol by passing them through a layer of substances adsorbing the residual acids remaining in the nitroglycerine washed by the usual methods has been suggested (Ropuszyński [20]). Nitroglycerine purified in the usual way contained 0.0056% HNO_3 and 0.0010% H_2SO_4 and withstood the heat test at 72°C for 27 min. After passing this nitroglycerine through a layer of aluminium oxide or an anion exchanger (the commercial product Wofatit MD was used) nitroglycerine containing practically no acids and withstanding the heat test for 50 min has been obtained.

The same author (Ropuszyński [21]) claims a slight improvement in the stability of nitroglycerine achieved if it is washed with water or aqueous sodium hydrogen carbonate in a magnetic field.

For instance nitroglycerine after preliminary washing (sample 1) was stabilized by washing with water (sample 2) or by washing in a magnetic field (sample 3) at 23.0°C. The pH of samples heated for 1½ and 2½ hr at 110°C were measured:

TABLE 17

Sample	pH after 1½ hr at 110°C	pH after 2½ hr at 110°C
1. Washed	2.78	2.75
2. Stabilized at 23°C	2.97	2.70
3. Stabilized in magnetic field at 23°C	3.13	2.92

FILTERING NITROGLYCERINE

After washing, nitroglycerine is turbid, because water in the form of emulsion and an insignificant quantity of mechanical impurities are dispersed in it. Both are usually eliminated by filtering through woollen material (flannel). The fabric may be loosely covered with a layer of crystalline common salt in order to facilitate the separation of water through the salting out phenomenon. It is also possible to separate water and nitroglycerine simply by settling. Water rises to the surface to form globules which can be removed with a ladle, and the turbidity is reduced.

If the filtered nitroglycerine is still turbid owing to the presence of water in suspension, it is usually allowed to stand quietly for a day and night or longer. Throughout this time the nitroglycerine grows clearer and its content of water decreases to 0.3–0.4%, whereas immediately after filtering the water present may amount to about 0.5%.

The filtrating installation comprises leaden tanks arranged on two or three levels (Figs. 19 and 20).

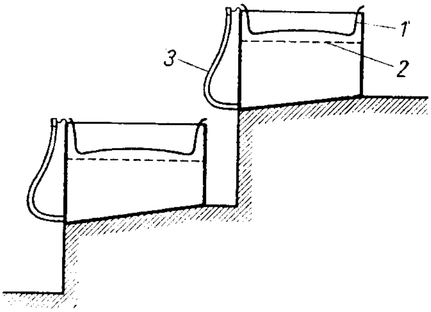

FIG. 19. Diagram of filtration of nitroglycerine through flannel: *1*—flannel, *2*—net, *3*—rubber hose.

The tank situated on the uppermost level is fed with recently washed nitroglycerine through a pipe or gutter. The lower tanks are covered with a fine brass mesh on which flannel is laid. The flow from the upper to the lower tanks proceeds via rubber

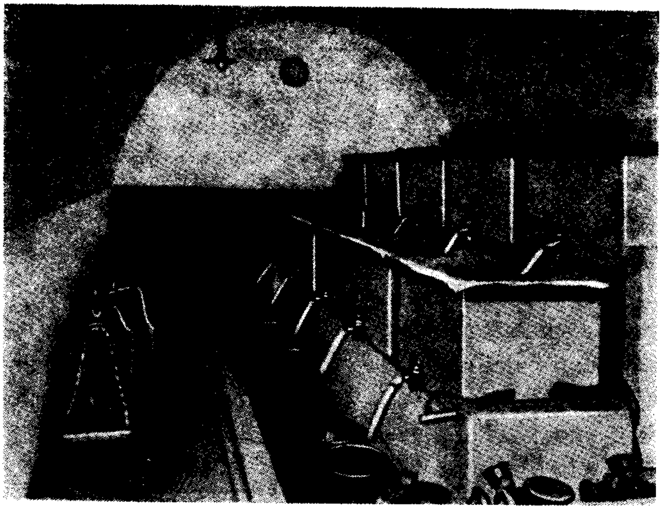

FIG. 20. General view of filtration room (Naoúm [11]).

hoses or by hooking the hose at the appropriate height. The flow is regulated mechanically by tightening a screw clip. In some factories ebonite stop cocks are used. The use of stoneware cocks is not considered to be safe enough.

An alternative is to filter the nitroglycerine through a thick layer of common salt (Fig. 21).

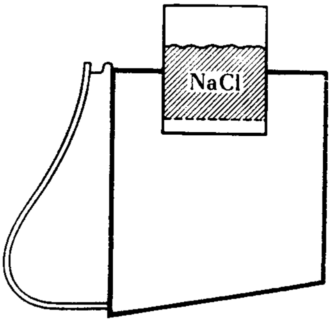

FIG. 21. Diagram of filtration of nitroglycerine through common salt.

Generally the filtration unit is situated in a separate building where the finished nitroglycerine is also stored. Here the nitroglycerine is weighed on a non-ferrous balance, before being transferred to further production.

TRANSPORT OF NITROGLYCERINE

Formerly after primary washing nitroglycerine was transported from the nitration unit to the stabilization room by means of a gutter-shaped leaden pipeline, furnished with a jacketed bottom heated in the winter with hot water. The temperature of the gutter was controlled by means of thermometers. In order to safeguard the nitroglycerine from mechanical contamination the gutter was covered with canvas or with wooden lids. Now aluminium pipelines are used, rubber hoses (sometimes made of conductive rubber to avoid production of static electricity) or even glass pipelines equipped with a jacket and heated with hot water during cold weather. To facilitate the flow of nitroglycerine the pipeline slopes downwards slightly. Explosion traps are inserted in the nitroglycerine pipe-line to prevent the spread of explosion should this occur. Various types are used:

(1) The pipeline (or gutter) includes several bends. Since liquid nitroglycerine has relatively little inclination to detonate it is highly likely that an explosion might be quenched at one of the curves.

(2) Part of the pipeline (or gutter) between buildings is replaced for a distance of about 1 m by narrow-bore hose of about 10 mm dia. Any explosion will be quenched at this point, because within pipes of this diameter nitroglycerine cannot readily detonate.

(3) The nitroglycerine conduit is equipped with a special detonation breaker. The detonation breaker (Fig. 22) is a lead tank filled with water to half or two thirds capacity. Nitroglycerine flows into the tank, collects on the bottom and runs on from below through the siphon. This arrangement interrupts the nitroglycerine stream. Detonation cannot be transferred readily through the water barrier.

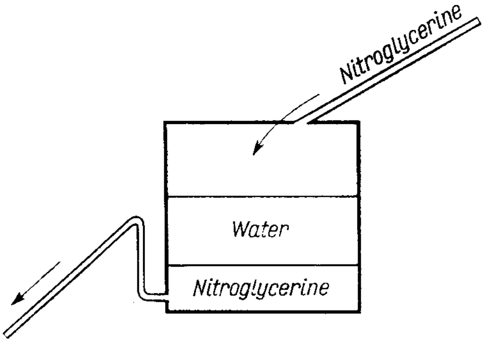

FIG. 22. Diagram of a detonation breaker.

For a time professional publications recommended carrying nitroglycerine by hand from one site to another in ebonite or brass pails. However, in practice this method of transfer was responsible for many catastrophic accidents caused for instance when the workman carrying the nitroglycerine fell, stumbled or slipped.

The transport of stabilized nitroglycerine to the rooms where it is to undergo final purification, e.g. filtration through a flannel, is now performed by means of a pipeline. In order to increase the safety of this operation, an emulsion of nitroglycerine in water or in an aqueous solution of sodium carbonate is produced by means of an injector and this emulsion is run through the pipeline.

As a safety measure, the ratio of water to nitroglycerine should be not less than 3:1, since at 1.5:1 the emulsion can detonate as shown by the investigations of Médard [22] already quoted (see p. 54).

It is important to make a stable emulsion which does not tend to form separate layers. The addition of surface active agents is recommended. According to Desseigne [23] non-ionic emulsifying agents formed by the condensation of ethylene oxide with higher alcohols, e.g. cetyl or oleyl alcohol should be used. The addition of protective colloids such as Tylose DKL (carboxymethylcellulose) makes it possible to economize considerably in the quantity of surface active agents required. For instance 0.5% of an emulsifier and 0.2% of carboxymethylcellulose may be added to the water. Tranchant [24] is of the opinion that the emulsifier mentioned above does not affect adversely the stability of the nitroglycerine if its concentration is 0.5% or less.

The emulsion of nitroglycerine is allowed to run into separating tanks in which the components are separated into two layers by an upward flow of water. Nitroglycerine is discharged from the bottom of the tank and passes to the filters.

Finally the purified, stabilized and filtered nitroglycerine is transported from the store to the departments where it is required for further manufacturing processes (to make dynamite or smokeless powder). When required for smokeless powder manufacture, nitroglycerine can be transported as an aqueous emulsion by means of pipelines as described above. Where dry nitroglycerine is required for dynamite manufacture manual transport is used. From the safety point of view, this should be mechanized as far as possible. Thus the vessels containing nitroglycerine are carried in hand trucks equipped with good leaf springs and rubber-tyred wheels, which travel paths of wood, asphalt or concrete between the buildings (Fig. 23).

FIG. 23. Nitroglycerine truck (du Pont de Nemours Co. Repauno) (Marshall [19]).

Nauckhoff [25] invented a special transport device for nitroglycerine which was introduced in the nitroglycerine factory at Gyttorp (Nitroglycerin A. B. Gyttorp). It comprises a rail over 2 m high on which a container is suspended. The rail and suspended container (*1*) are shown in Fig. 24. The container is filled by sucking nitroglycerine from the transit tank (*2*). In the mixing compartment nitroglycerine is transferred from the container (*1*) to the kneading machine (*3*) by means of compressed air.

Transport of liquid nitroglycerine from the nitroglycerine factory to another plant is not allowed in Europe. It can be transported only in mixed forms: as dynamites or semi-finished mixtures ready to be used for the manufacture of mining explosives or of double base powders. Only in U.S.A. is the transport of nitroglycerine in special trucks allowed.

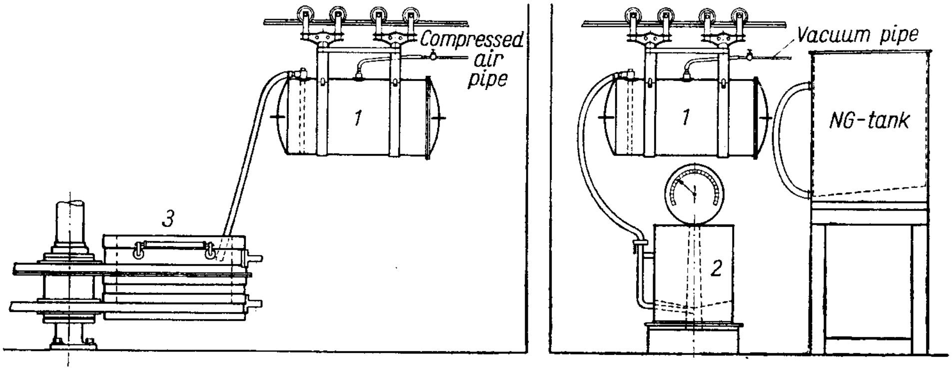

FIG. 24. Nitroglycerine transport device S. Nauckhoff system, Gyttorp 1919 (Nauckhoff and Bergström [7]).

RECOVERY OF STABILIZING WATER

Some 2% of nitroglycerine remains in the water and in the sodium carbonate solution used for washing. In the early days of the manufacture of nitroglycerine the whole of the waste wash water was allowed to flow into a river or pool, when the nitroglycerine slowly decomposed, under the influence of direct sunlight in the presence of water. Clearly, in these conditions decomposition was rather slow and in certain circumstances more and more nitroglycerine accumulated, and unfortunate accidents occurred. One explosion occurred on a river bank near to an outlet carrying waste wash water. Its cause was discussed by Naoúm [11]. In rowing a boat away, the oarsman struck the rocky bank with a metal-clad oar and initiated an explosion which killed him and destroyed the boat.

According to present practice polluted waste water flows into special trough-shaped tanks or labyrinths (Fig. 25), made of lead, stoneware or preferably of rubber-covered iron, and equipped with transverse baffle plates.

The waste water is thereby made to travel a long distance during which drops of nitroglycerine settle out on the bottom of the labyrinth. Since acid water from the first washing is mixed with carbonate solution from the final stabilization the reaction of the waste water in the labyrinth is neutral or slightly acid. Nitroglycerine flows down the sloping base of labyrinth, to be returned to the stabilization process. It is drawn off in the normal way by means of a hose-pipe, avoiding as far as possible, the use of stoneware stop-cocks.

Stabilization of the recovered nitroglycerine consists in washing and filtering by the usual methods. From the stabilization water about 1% of the total nitroglycerine output is recovered.

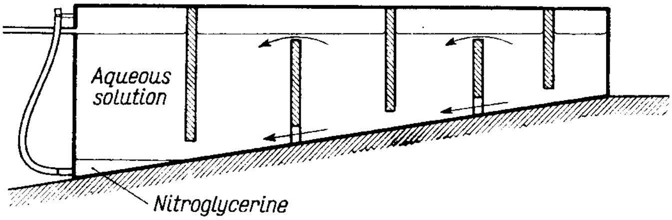

FIG. 25. Diagram of a labyrinth.

Water from which the nitroglycerine has separated flows to a tank lined with lime-stone and after being neutralized it is discharged to a river or pool. Attempts have been made to recover the appreciable quantity of ions: $NO_3^{\ominus}$, $SO_4^{2\ominus}$ and $HSO_4^{\ominus}$ still present in the water. In a patent taken out by the Dynamit A.G. in Hamburg [26] neutralization of the waste water with ammonia was suggested followed by evaporation. This yields about 8 kg of nitrates and sulphates mixed in the ratio of approx. 7:3 for every 100 kg of nitroglycerine. It was proposed to use the mixture as a chemical fertilizer.

THE SPENT ACID

After separation of the nitroglycerine, the following remain in the spent acid: nitroglycerine, dinitroglycerine, mixed esters of sulphuric and nitric acid. The two latter esters react slowly with the nitric acid contained in the waste acid to form further nitroglycerine, which floats on the surface of the acid.

There is a further method of obtaining nitroglycerine from the spent acid if the main product is separated immediately after nitrating. Nitration is commonly performed at the temperature of 25–30°C. The waste acid is cooled after nitration is complete, to the temperature of 15°C or less, and as a result a part of the nitroglycerine which was dissolved in the acid is separated.

The amount of nitroglycerine recovered from the spent acid amounts to about 2% of the total output.

The separation rate of this supplementary yield of nitroglycerine depends not only on the velocity of the additional reaction of esterification, but also on the purity of the glycerine used and the purity of the mixed acid. It should be borne in mind that the separation of nitroglycerine from the spent acid may take several days and that an acid apparently free from nitroglycerine may represent a source of danger. Lengthy contact between nitroglycerine and spent acid may be followed by decomposition. The explosions of nitroglycerine which has risen to the surface of spent acid have been known to occur, chiefly in the summer. On the basis of numerous experiments Oehman, Camera and Cotti [27] have constructed a diagram indicating the composition of spent acid which can be dangerous in contact with nitroglycerine (Fig. 26).

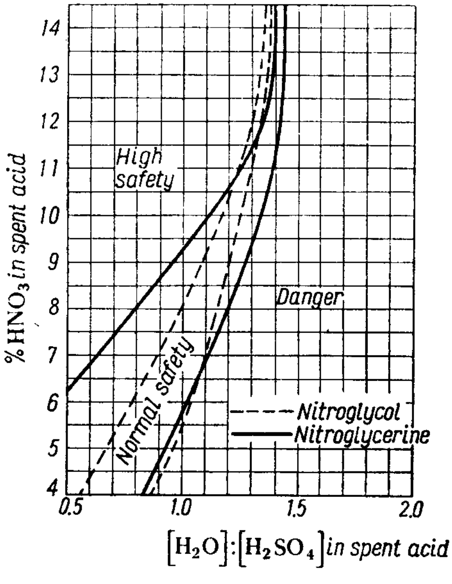

FIG. 26. Safety diagram of acidic nitroglycerine, according to Oehman *et al.* [27]. For comparison, nitroglycol is also indicated.

The supplementary separation is carried on in a special building. Several days' supply of spent acid is collected in special lead tanks (settlers) each having a capacity sufficient to hold the acid collected from a full-day's nitration. Nitroglycerine collected on the surface of the acid may be removed in various ways: by means of an aluminium spoon (the old system) or by displacing the contents of the tank from below with the waste acid (the combined process, p. 95). The handling of waste acid free from nitroglycerine is not wholly safe, since more nitroglycerine may still separate out.

Taking into account only the inorganic components of the spent acid, its composition is as follows:

HNO_3	9–14%
H_2SO_4	70–75%
H_2O	15–17%
sp. gr.	1.74–1.76

In order to make use of the spent acid it must undergo denitration, which consists in separating the nitric acid from the sulphuric acid. The spent acid should be denitrated as soon as possible after the supplementary separation of nitroglycerine.

To lessen the danger of handling the spent acid immediately after the separation of nitroglycerine, the addition of a certain amount of water was suggested by Nathan, Thomson and Rintoul [2]. On dilution with water, the solubility of the nitroglycerine in acid is increased and a loss of nitroglycerine occurs because it no longer separates. However, the method greatly enhances the safety of handling the spent acid and capital costs are reduced since no installation for the supplementary separation of nitroglycerine is required.

Originally 2% of water were added to the spent acid and this prevented the separation of nitroglycerine at temperatures from 10 to 15°C. Nevertheless in 1906 a tank filled with this dilute spent acid exploded while being transported. Further experiments showed that nitroglycerine can separate from acid diluted in that way if its temperature falls below 10°C. Addition of 5% water was therefore introduced, to prevent separation of nitroglycerine even at a temperature of 0°C. At the present time this procedure is widely used with new methods of nitration including continuous processes.

The addition of water to detain nitroglycerine in the spent acid not only increases the solubility of nitroglycerine in the acid, it also alters the equilibrium of the reaction between dinitroglycerine, nitroglycerine and acid in such a way that dinitroglycerine does not undergo further nitration and the trinitrate is not formed (Renner and Helle [28]).

Spent acid from nitroglycerine manufacture is not used to prepare nitrating mixture since it contains too much organic matter with which it is undesirable to contaminate the nitration. Decomposition of these substances during nitration could make the process difficult to control and might lead to accidents.

Generally, therefore, the spent acid remaining after manufacturing nitroglycerine and similar nitric esters undergoes denitration. The spent acid should be stored in lead tanks, and before passing on to the denitration tower, any separated nitroglycerine is skimmed from the surface by means of an aluminium ladle.

The denitrating tower (*1*) (Fig. 27) consists of a steel shell lined with special acid-resistant brick, and is packed with quartz or with Raschig rings of refractory material or of iron with a high silicon content. A distributor at the top of the tower delivers the spent acid in counter-current to superheated steam and air entering at the bottom of the tower via a jet (*2*). A temperature of 300–350°C is maintained inside the tower by means of superheated steam. The steam and air drive off nitric acid and nitric oxides (NO and NO_2) present in the spent acid or formed in the denitrating tower as the result of the oxidation of organic compounds. Denitrated sulphuric acid flows through a syphon outlet (*6*) at the bottom of the tower and is cooled in the tub (*7*) before being concentrated or used for mixing with oleum and nitric acid.

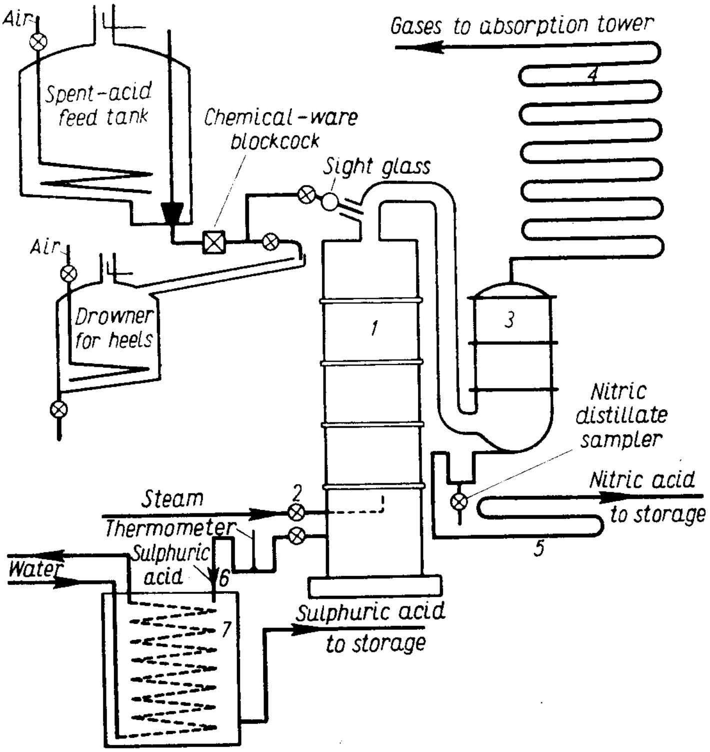

FIG. 27. Recovery (denitration) of spent acid (according to W. de C. Crater [29]).

Nitric acid and nitrogen oxides are driven off together with water vapour and pass from the tower through the top to a "Bleacher" (*3*) filled with disks or cylinders where they pass in counter-current to the condensed acid which returns from the S-bend condenser (*4*) of high-silicon iron to flow through (*5*) to storage.

When nitric acid alone is used for nitration and the product and acid are drowned in hot water or hot dilute nitric acid as in the case of cyclonite manufacture, where no organic substances remain in the acid (all being decomposed), the spent acid is readily recovered by feeding it to an absorption tower in place of part of the water normally added. The acid should be fed in at a point in the tower where the concentration of acid is approximately the same as that of the acid being added.

In a plant of this type nitric acid of about 90% and sulphuric acid of 70% are obtained. In the absorption towers nitric acid of 30–60% is produced.

According to its size a plant for denitrating spent acid may have a daily output from 5 to 25 tons of acid.

The denitration system works satisfactorily only for spent acid from the nitration of glycerine and similar alcohols. In spent acid from trinitrotoluene production the high content of dissolved nitrated hydrocarbons causes an excessive reduction of nitric acid at the top of the denitrating tower. Thus spent acid from the nitration of hydrocarbons are unsuitable for denitration and are utilized instead by mixing with oleum and concentrated nitric acid (Vol. I, p. 150).

RAW MATERIALS FOR NITROGLYCERINE MANUFACTURE

GLYCERINE

As already mentioned above, the purity of the glycerine exerts a fundamental influence on the efficiency and safety of nitroglycerine manufacture. The so-called dynamite glycerine, a very pure water-free product, distilled several times under reduced pressure is produced for manufacture of nitroglycerine.

Glycerine is obtained mainly by the hydrolysis of fats. During World War I when fats were in short supply in central Europe, glycerine was produced on plant scale by sugar fermentation. Fermentation glycerine is suitable for the manufacture of nitroglycerine although it contains certain by-products not present in glycerine derived from fats, hence the yield of nitroglycerine from fermentation glycerine is somewhat lower than that from glycerine obtained by the hydrolysis of fats. The main by-product in fermentation glycerine is trimethylene glycol (see p. 155), which forms an explosive nitric ester. When it is present the nitration temperature should be kept lower than that normally maintained during nitration of glycerine derived by hydrolysis. During the nitration of fermentation glycerine the temperature should be particularly strictly controlled. Dynamite glycerine is a transparent, highly viscous, colourless, or yellowish or even pale-brown coloured liquid. The intensity of colour is not of critical importance, but light-coloured samples are considered more suitable for nitration than darker ones. Dynamite glycerine usually has a light, distinctive smell resembling that of caramel.

According to the standards applicable in different countries, dynamite glycerine should meet the following requirements:

(1) colour — as pale as possible;

(2) odour — no unpleasant smell should develop on heating to 100°C;

(3) density at 15.6°C — not less than 1.262 g/ml;

(4) reaction neutral;

(5) glycerine content should be at least 98.5–99%, the limiting water content being 1% or in some countries 1.5%;

(6) mineral impurities should not exceed 0.05–0.15%;

(7) maximum content of non-volatile organic substances — not higher than 0.1–0.15%;

(8) it should be free from carbohydrates, proteins and other nitrogen-containing compounds, acrolein, sulphites and sulphides. Sometimes the presence of white arsenic as well as calcium, magnesium or ammonium salts is admissible, but in trace quantity only. Sulphates and chlorides are permitted only in traces e.g. not more than 0.01% calculated as NaCl;

(9) no oils or fats, i.e. glycerides of fatty acids, may be present. In the U.S.A.

standards the admissible amount of fats is equivalent to 0.1% of Na_2O, used as NaOH for hydrolysis. Further no fatty acids should be present.

The most reliable method of determining the quality of glycerine is the laboratory nitrating test. This should be carried out under conditions that correspond as closely as possible to those prevailing in the plant. During the laboratory nitration, temperature, the rate of separation of the nitroglycerine and the acid layers, the contact surface of phases and so on should be recorded.

After separating and washing the products as in large-scale operations the yield is determined. According to the temperature applied this should amount to:

nitrating temperature	yield
30°C	225–226%
15°C	228–229%

For experimental nitration either the Schlegel–Novak apparatus [30] simulating a large scale nitrator or Hofwimmer's nitration burette [31] are usually used. Normal laboratory apparatus with a mechanical stirrer can also be used.

ACIDS

Acids for nitrating glycerine must be as pure as possible. Nitric acid (sp. gr. 1.50) should not contain more than 1% N_2O_4.

Sulphuric acid (sp. gr 1.84) and oleum (20–25%) should be virtually free from lead sulphate which is liable to be present in old installations constructed of lead, and also from sulphates of iron, as these substances hinder the separation of nitroglycerine and acid. Since such acid is not always available storage of sulphuric acid and oleum in special cast iron tanks is recommended in order to allow impurities to settle. Acid is drawn from the upper part of the tank so that the slime composed of iron and lead sulphates remains on the bottom. Similarly, the mixed acid is stored in tanks so designed that the precipitate can collect on the bottom.

BATCH METHODS OF NITROGLYCERINE MANUFACTURE

OLD PROCESSES

The oldest recorded method of manufacturing nitroglycerine was a most primitive process that consisted of dropping small amounts of glycerine, e.g. 350 g, into a cast iron pot containing a mixture of nitric and sulphuric acid. The pot was cooled by standing in a larger, stoneware vessel containing water and ice, and hand stirring was performed with an iron rod. When the nitration was completed (or if danger of decomposition arose) the contents of the cast-iron pot were turned out into the water and ice. Water was then removed by decantation and the blasting oil was washed. In that way a 200% yield of nitroglycerine was obtained.

The design of apparatus to facilitate rapid and efficient removal of the heat produced during nitration was not known at that time. Solution of these difficulties was therefore sought in modification of the manufacturing process itself, as suggested by Boutmy and Faucher [32]. They divided the nitrating process into two stages. At each stage a certain amount of heat is developed, which is less, of course, than the total heat of nitration.

The stages suggested by Boutmy and Faucher are as follows:

(1) Dissolving glycerine in sulphuric acid to form glyceryl-sulphuric acid.

(2) Adding nitric acid to the solution of glycerine in sulphuric acid.

The greater part of the heat is produced during the relatively safe process (1). The amount of heat developed during nitration proper (2) is therefore relatively small and the temperature can be controlled easily even if primitive methods of cooling are used.

For several years (until 1882) the Boutmy–Faucher method was used in France and Great Britain. In completely primitive apparatus, about 680 kg nitroglycerine were made at a time. The disadvantage of this method was that the nitroglycerine obtained by nitrating according to reaction (2) separated only very slowly from the acid. In the standard method the contents of the nitrator were allowed to stand overnight to permit separation of the nitroglycerine. This lengthy contact between the nitroglycerine and the acid involved the danger of decomposition. Indeed, in factories where this method of nitroglycerine manufacture was practised frequent explosions occurred during the separation stage. Finally this method had to be abandoned and at the present time it is of historical importance only.

NOBEL PROCESS

Nobel invented a radically new design of nitrator for the manufacture of nitroglycerine. Originally it was made of sheet lead and equipped with a cooling coil supplied with water, (Fig. 15, p. 65) and later a water-cooled jacket made of wood was added (Fig. 28). In later versions of the Nobel nitrator the cooling jacket was omitted in favour of a four-fold cooling coil with which it was easier to control the nitration temperature.

Before starting the nitration the cooling coil and the compressed air inflow should be checked to ensure that they are not damaged, and it is also necessary to ensure that the lower discharge stoneware cock is well lubricated with vaseline and that its discharge outlet is situated above the drowning tank. The inlet valve admitting the cooling water to the coil and to the jacket is then opened fully, and through the pipe (*1*) mixed acid is introduced to fill the nitrator to $\frac{1}{2}$–$\frac{2}{3}$ its volume. Afterwards compressed air is introduced by means of three pipes (*2*), (*3*) and (*4*) and then the glycerine pipeline closed by a tap (*5*) and the lever (*6*) is opened. The lever (*6*) is fitted with a spring which closes the cock instantly when the nitration foreman ceases to press the lever.

Glycerine is run into the nitrator through a funnel in the cover. The part of pipe containing (*5*) and (*6*) is joined by means of a hose to the stiff pipe for feeding glycerine.

During nitration the temperature inside the nitrator is measured by thermometers (*7*) and (*8*) and is controlled by the operator who reduces the flow of glycerine if the temperature rises too high. Acid vapours together with the air used for mixing

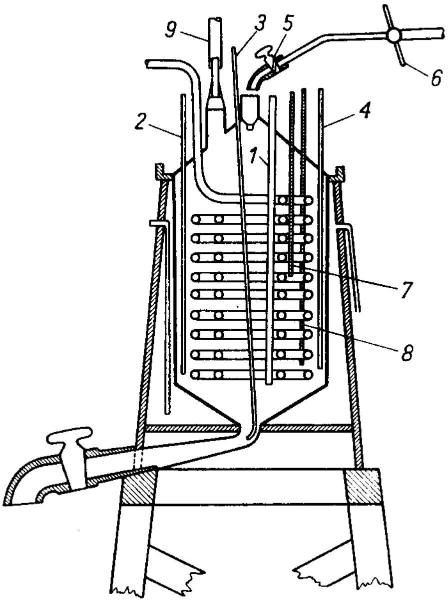

FIG. 28. Nobel nitrator, old pattern.

is removed through the ventilator duct (*9*). The conical cover of the nitrator is equipped with several sight windows through which it is possible to observe the interior of the nitrator.

After a measured amount of nitroglycerine has been introduced the exit of the glycerine supply pipe is pushed as far as possible away from the funnel, and under the lower discharge tap a leaden gutter is attached to permit the contents of the nitrator to flow into a separator. Several minutes after the glycerine feed has been stopped the cooling and then the compressed air supply are interrupted, after which the lower cock is opened immediately to allow the nitroglycerine and acid emulsion to stream via the gutter to the separator (Fig. 29).

The separator is a rectangle-shaped tank with a conical bottom and is made of sheet lead. Its cover, also of lead plate reinforced with lead-coated iron rods, is equipped with a number of windows through which it is possible to observe the liquid surface in the separator. The exhaust duct with a sight glass, and a thermometer are also fitted in the cover. Sometimes a compressed air line is led through the cover to be opened in case the separator contents have to be discharged to the drowning tank. In the lowest part of the separator there is a window (*1*) and three outlet valves: two at the side for acid (*2*) and nitroglycerine (*3*) respectively and one at the bottom leading to the drowning tank (*4*). While the separator is being filled and during the separation process the tap (*4*) is connected with the drowning tank. At the side of the separator, slightly higher than the separation line between the nitroglycerine and acid phases, a cock (*5*) is fitted for discharging the nitroglycerine into the primary washing tank (*6*). The level at which the cock (*5*) is fitted is

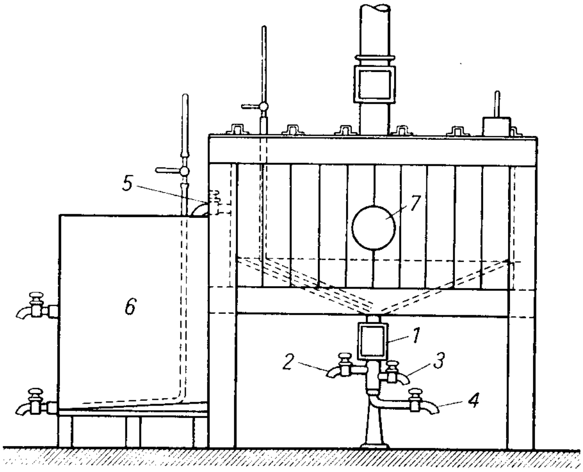

FIG. 29. Nobel separator (Naoúm (11]).

determined accurately by calculation of the charge and of the nitroglycerine yield from one nitrator.

When through the sight glass (*7*) a distinctly clear separation line is visible between the phases, the main yield of nitroglycerine is removed by means of the cock (*5*). Then acid is discharged through the tap (*2*) to leaden settling tanks situated in another room. The separation surface of the two phases is observed through the window (*1*) so that the tap (*2*) can be closed at the right time and the cock (*3*) opened. The amount of nitroglycerine discharged via the tap (*3*) is added to the main yield of nitroglycerine in the washing tank (*6*).

After-separators wherein the waste acid is stored, are open tanks of lead. Nitroglycerine that collects on the surface is removed every few hours with an aluminium ladle, and is to be poured into the preliminary drowning tank situated in the same room.

After the primary washing nitroglycerine is transferred to the final washing by the usual methods. The solutions and water remaining after washing are transferred to the labyrinth. The flow-sheet is shown in Fig. 30 and a complete view of the plant is given in Fig. 31.

NATHAN, THOMSON AND RINTOUL PROCESS

As compared with the Nobel process for nitroglycerine manufacture certain innovations were introduced in this method, namely:

(1) new design of the nitrator;

(2) use of the nitrator as a separator;

(3) omission of nitroglycerine discharge cocks connecting the separator to the washer;

(4) abandoning the additional recovery of nitroglycerine from the spent acid and hence the elimination of settling tanks.

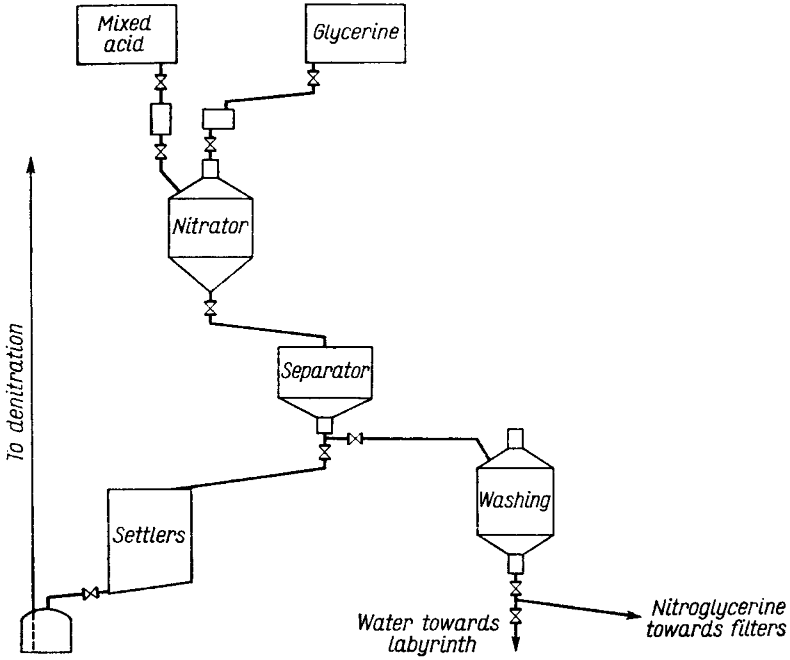

FIG. 30. Flow-sheet of Nobel system of manufacture of nitroglycerine.

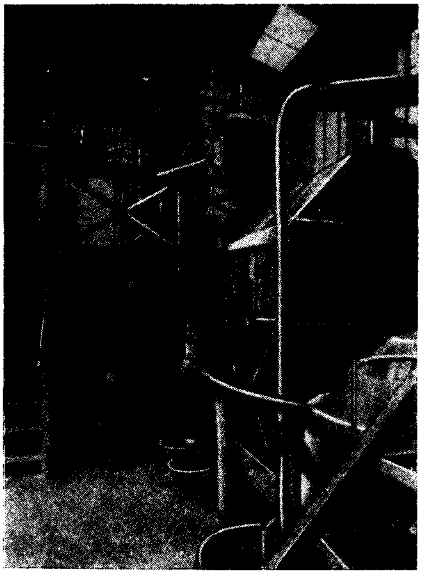

FIG. 31. General view of nitrator, separator and pre-wash tank, Nobel system (Naoúm [11]).

The nitrator-separator used in the Nathan, Thomson and Rintoul process is a cylindrical vessel with a conical cover carrying a small chimney (Fig. 32).

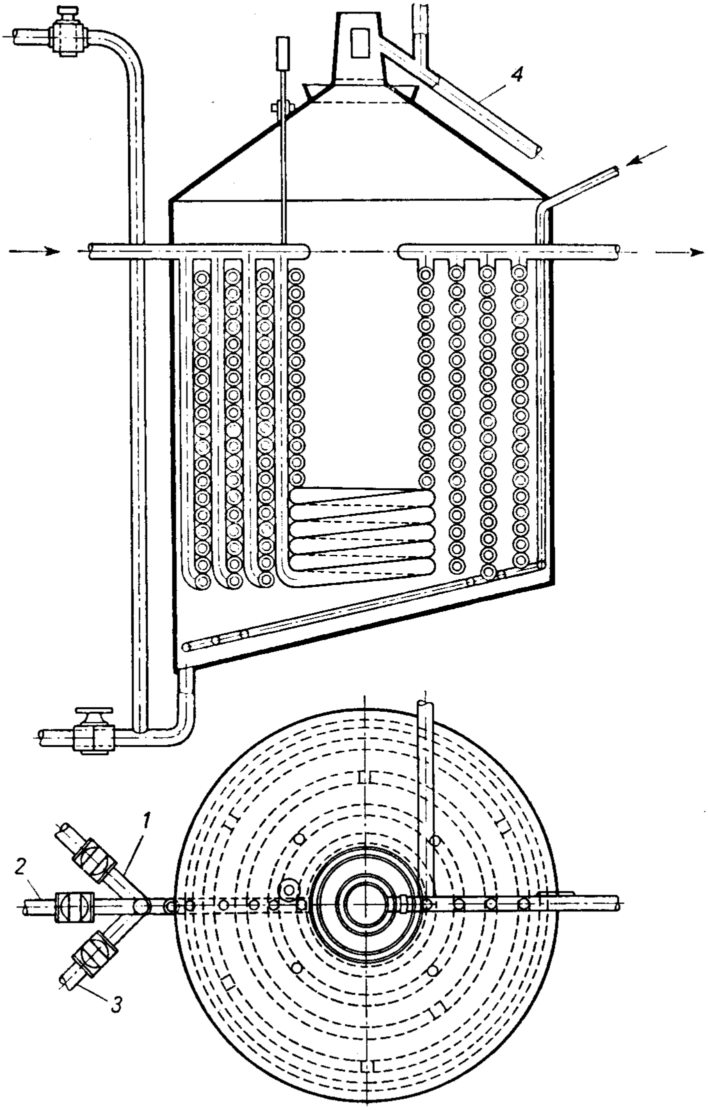

FIG. 32. Nitrator–separator of Nathan, Thomson, Rintoul [2].

The cover, the chimney and the cylindrical part of the nitrator are fitted with sight glasses so that it is possible to watch the nitrator contents. The bottom of the vessel slopes downwards at one side. Inside the nitrator there is a four-fold cooling coil, a compressed air pipe connected to the bottom, and two thermometers (one of the two visible in the drawing). The lowest part of the nitrator is connected with a duct that branches into three pipes (*1*, *2*, *3*). Pipe (*1*) is used for removing the spent acid to denitration, after the separation of nitroglycerine is complete. Pipe (*2*) allows the nitrator contents to be discharged into the drowning tank. Pipe (*3*) has two branches leading to the acid tanks situated above the nitration house. One of these tanks holds nitrating mixture and the other spent acid. Spent acid is used to displace the nitroglycerine layer through the overflow (4) in the upper part of the nitrator. In order to avoid any leakage of nitroglycerine from the nitrator to pipe (*3*), for instance during stirring, the three-way discharge pipe is kinked at a point about 30 cm below the lowest part of the nitrator. Nitroglycerine is discharged from the nitrator through the overflow (*4*). Acid vapours are drawn off through the chimney by means of an exhauster fan.

In the nitration house two nitrators are situated with the primary washing tank between them (Fig. 33).

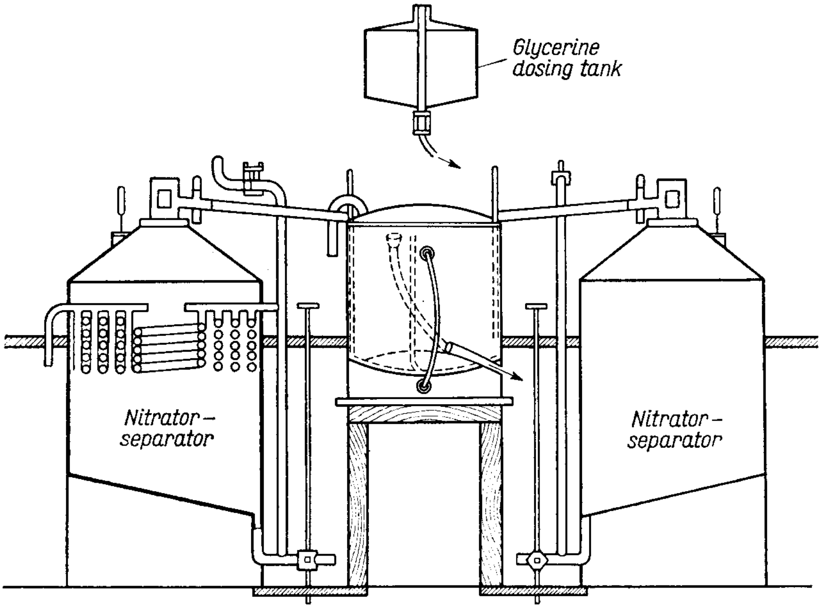

FIG. 33. A unit composed of two nitrator–separators and pre-wash tank.

The course of nitration is as follows: the nitrator is fed with the mixed acid Then the cooling water and compressed air lines are opened and glycerine is forced through the nitrator chimney in the form of a spray by means of compressed air. When the whole of the glycerine has been introduced into the nitrator its contents are stirred for a certain time and then the cooling water inlet is closed and stirring is stopped. The suspension is allowed to stand in the nitrator until the nitroglycerine has separated, the progress of separation being watched through the inspection window. Water is then added to prevent further separation of nitroglycerine.

When the separation is complete spent acid is introduced upwards into the nitrator through the pipe (*3*) to displace the nitroglycerine, the latter passing through the overflow (*4*) into a washer filled with cold water stirred by means of compressed air. There are some plants where the separation of nitroglycerine and acid is repeated after a lapse of at least 2 hr after the end of nitration, water then being added as described below. When the nitroglycerine has been removed from the nitrator part of the spent acid (about $\frac{1}{5}$ of the nitrator's capacity) is discharged to a pressure-egg situated beneath the nitrator, the water inlet to the cooling coil is opened again and stirring with compressed air is renewed in order to cool the spent acid to 15°C or less, 5% of water being added through the nitrator chimney. The temperature of the acid is increased approximately by 3°C for 1% water. The acid is cooled to about 15°C and transferred via the pipe (*1*) to the tank below the nitrator, when it goes to the denitration process. Sometimes a certain amount of nitroglycerine is separated from the dilute acid on cooling. This should be discharged to the washer by displacement with spent acid as already described.

While one of the nitrators is in use as a separator, nitration is carried out in the other one and vice versa thus maintaining uninterrupted operation.

The nitroglycerine, washed twice with cold water, is then transferred to the final purification stage in another building and the wash water is transferred to the labyrinth in the usual way.

According to British reports from World War I [33], during nitroglycerine manufacture the nitrogen content of the nitric acid (including that recovered by denitration) was consumed as follows:

95.6%	chemically combined in nitroglycerine
4.0%	lost during nitration
0.4%	lost during denitration

COMBINED PROCESS

The method of Nathan, Thomson, and Rintoul was used only in a few factories and generally on the Continent a combined process incorporating the advantages of the Nobel process with those of the Nathan, Thomson and Rintoul process was used.

In this arrangement the nitrator–separator of the Nathan system was combined with settlers of improved design so as to achieve a more precise separation of the nitroglycerine and spent acid. This settler is reminiscent of the Nathan nitrator (Figs. 34 and 35).

It comprises a cylindrical vat with a conical cover with which a glazed or glass

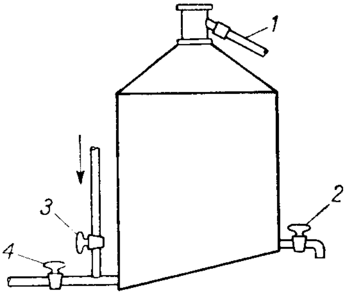

FIG. 34. Spent acid after separating tank (settler) in the combined method.

FIG. 35. General view of a battery of secondary separation tanks (Naoúm [11]).

chimney with a small duct (*1*) is connected, made of a down-bent pipe. Spent acid from the nitrator–separator is run into the settler through a pipe in its cover. The bottom is sloping and to its lowest part a pipe is connected through which spent acid can be led to the settler from a high-level tank by means of the cock (*3*). Another branch of this pipe permits the contents of settler to be discharged if the valve (*4*) is opened. The capacity of each settler is large enough to contain the full day's output of one nitrator. A flow-sheet is given on Fig. 36.

After nitration is completed, the contents of the nitrator are allowed to stand

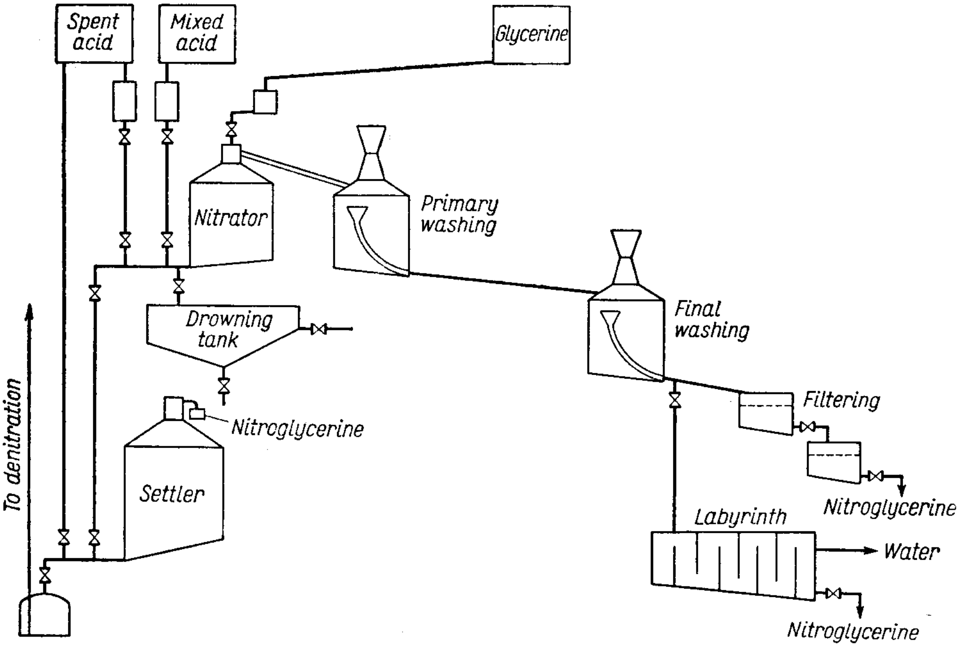

FIG. 36. Flow-sheet of the combined method of nitroglycerine manufacture.

quietly while the other nitrator comes into operation. When the layers of nitroglycerine and acid have separated, spent acid is introduced into the bottom of the nitrator–separator from the upper waste acid tank to displace the nitroglycerine which is transferred for primary washing. The spent acid free from nitroglycerine, after passing through a transit tank, flows to the settlers. At intervals of a few hours nitroglycerine collecting on the surface of acid is displaced by means of spent acid flowing down from the upper tank and into the settler from below. The overflowing nitroglycerine passes through a gutter to an aluminium vessel. By repeating this operation every few hours lengthy contact between the nitroglycerine and the acid, which involves the risk of nitroglycerine decomposition, is avoided. Separation of nitroglycerine is almost 100% and of course the safety of the operation is considerably increased.

In one of German plants in which this method was used the following materials balance based on the average of a years' production, was achieved:

From 100 parts by weight of glycerine, 228.7 parts by weight of nitroglycerine were obtained.

Consumption of glycerine:

94.1% converted to nitroglycerine passed directly to filtration,
3.0% converted to nitroglycerine recovered from the spent acid,
0.8% converted to nitroglycerine recovered from the wash waters.
Total yield was 97.7%.

2.1% of glycerine was lost.

Consumption of nitric acid:

For 100 parts by weight of glycerine, altogether 261 parts by weight of nitric acid were used, whereof:

74.0% were combined to form nitroglycerine,
17.8% were recovered in the denitration process,
8.2% represent losses (of which the washing water accounted to 7.3%, and the denitration process 0.9%).

Consumption of sulphuric acid:

For 100 parts by weight of glycerine, 314.5 parts by weight of H_2SO_4 were used, whereof:

99% were recovered in the denitration process, 1% was lost.

CONTINUOUS METHODS OF NITROGLYCERINE MANUFACTURE

The manufacture of nitroglycerine is one of the most dangerous operations in the whole explosives industry, due to the high sensitiveness of nitroglycerine to impact and friction and its ability to burn to detonation. The decomposition of nitroglycerine can readily be induced by autocatalytic chemical decomposition in contact with mineral acids.

All this makes the manufacture of nitroglycerine particularly dangerous and all that has been said previously with regard to the danger of TNT manufacture and the advisability of producing it by continuous methods applies with much greater emphasis to nitroglycerine.

Continuous nitration of glycerine was suggested as early as 1866 by Nobel [8] who mixed the two reactants by pouring them through a perforated funnel, and by Rudberg [34]. The latter system was in limited operation for a short time. The nitrator is shown diagrammatically in Fig. 37. It comprised a lead trough (*1*) with a step shaped bottom, to which cooling was applied, in the form of a stream of cold water, to maintain a temperature below 30°C. Two streams: one of glycerine from a container (*2*) and the other of mixed acid from (*3*) were introduced into the nitrator. Reaction occurred as they flowed down into a tub (*4*) filled with water. Nitroglycerine was collected through an overflow.

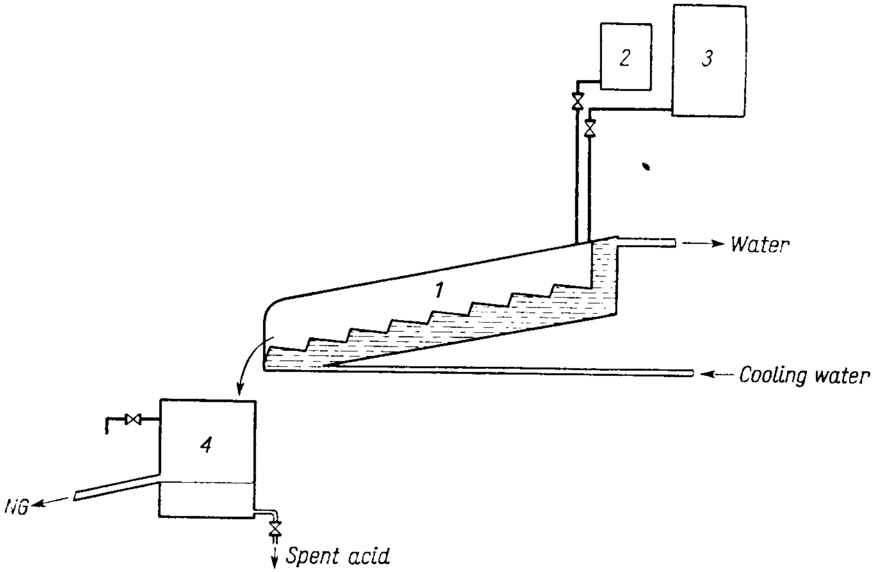

FIG. 37. Continuous nitration of nitroglycerine according to Rudberg: *1*—nitrator, *2*—glycerine, *3*—mixed acid, *4*—separator.

Two patents for the continuous nitration of glycerine by Kurtz appeared in 1878–1879 [35] and other methods comprising a continuous manufacturing scheme where glycerine and nitrating acid were mixed in a spraying nozzle were patented by Maxim in 1891 [36] and Evers in 1902 [37]. These ideas were incorporated into the modern plants (p. 114).

However, largely because of doubts about the safety of the innovations proposed, they have not found acceptance and it was not until 1927 when the Schmid process was devised and 1935, when the Biazzi process was developed that these continuous production processes were recognized as efficient and safe.

SCHMID PROCESS

The continuous method of nitroglycerine manufacture invented by A. Schmid [38] involves not only continuous nitration, but also continuous separation and washing of the product. A novel idea introduced by Schmid was the nitrator made of acid-resistant steel with mechanical stirring (Fig. 38).

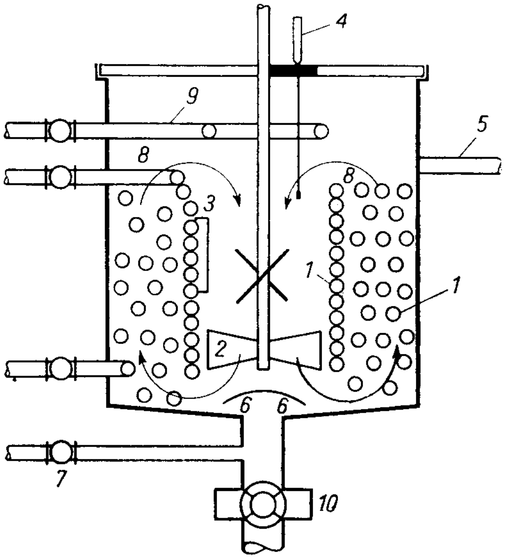

FIG. 38. Nitrator for continuous nitroglycerine manufacture according to Schmid (original pattern).

The nitrator is constructed of acid-resistant steel and equipped with refrigerating coils (*1*) (a baffle formed by the coil separates the interior of the nitrator from the cooled section). Their cooling surface is four times larger than in the usual nitrators, thus cooling is efficient in spite of the high flow rate of the liquid. The propellers of the mechanical stirrer (*2*) revolving at a speed of 200–300 revolutions per minute, extend to within 0.5–1.0 cm of the coils. Above the propellers steel plates (*3*) parallel to the axis of the nitrator are fixed to promote a better circulation of liquid. It is also possible to attach above the main propellers (*2*) another pair of smaller ones acting in the opposite direction. In the cover a sight glass and a thermometer (*4*) are installed. Due to the high flow velocity of the liquid during nitration the thermometer must be protected by a metal sheath.

Before nitration starts, the nitrator is filled with spent acid up to the level of the overflow (*5*). The water inlet to the cooling coils is opened, the stirrer is set in motion, and through pipes (*6*) and (*7*) fresh mixed acid is introduced to be carried off with the stream of liquid and blended with the spent acid. Mixing takes place without any notable thermal effect. Part of the liquid is recirculated via the pipe (*8*) and part is run through the overflow (*5*) to a separator. Glycerine enters through the pipe (*9*) in one or several streams. Should decomposition of the nitroglycerine occur the contents of nitrator are discharged through a valve (*10*) into a drowning tank.

For efficient operation, a steady supply of glycerine and acid at a pre-determined, constant ratio is necessary. The raw materials are delivered by means of pumps driven by a common motor and regulated in such way that a constant relation is established governing the quantity of liquid pumped. The pumps are placed in an auxiliary room above the nitration house. Further tanks for glycerine and mixed acid are located in the same room.

Due to the high velocity of stirring and to the large cooling surface the output of this nitrator is about 10 times larger than that of conventional nitrators of the same capacity.

An improvement to the Schmid nitrator has been introduced by Nauckhoff [25]. He replaced the cooling coils by a tubular cooler (Fig. 39).

In the separator for continuous separation of nitroglycerine and acid originally used in the Schmid process, certain faults were detected, which were later eliminated in a new design of 1928 (Fig. 40).

The separator, made of acid-resistant sheet-steel, resembles an inclined cylinder and its method of operation is as follows. The emulsion from the nitrator enters through the conduit (*1*). To facilitate the separation of acid and nitroglycerine baffles (*4*) of corrugated steel sheets and a cooling jacket (*5*) are installed. The spent acid is collected in the lower region to form the layer (*2*) while nitroglycerine collects in the upper part of the separator as the layer (*3*). Nitroglycerine is removed continually through the outflow (*6*) while the spent acid is discharged from below over the siphon (*7*), which is a situated at the same level as pipe (*6*).

A general view of a nitrator and separator is given in Fig. 41.

Washing nitroglycerine. According to the Schmid process the continuous washing of nitroglycerine is carried out in towers made of cylindrical glass segments carrying perforated plates shelves of stainless steel between the segments (Fig. 42). All is strengthened on the outside by means of steel rods. Washing towers can also be constructed of stainless steel. An air outlet is connected to the cover of the tower.

Nitroglycerine leaving the separator enters an injector fed with water or with a solution of sodium carbonate or of ammonia, to form an emulsion which flows into the tower from below. Compressed air is also introduced to facilitate mixing and the shelves are also intended to ensure thorough mixing of the emulsion. The latter rises to flow through a siphon pipe into a separator. The separator is built of wood impregnated with paraffin, or of sheet aluminium. It is fitted out with several baffle plates and its construction resembles that of a labyrinth (see Fig. 22). Here the emulsion forms separate layers. Water flows out through the upper siphon pipe, and nitroglycerine through the lower one.

For washing, two towers are usually used: one in which the nitroglycerine is washed with water, the other for washing with sodium carbonate solution or with dilute aqueous ammonia.

In a small plant equipped with a nitrator of 25 l. capacity yielding about 100 kg of nitroglycerine per hour, towers of the following dimensions are used: for water washing the diameter is 0.2 m, and the height 2 m; for alkaline washing the diameter is 0.3 m and the height 2.5 m.

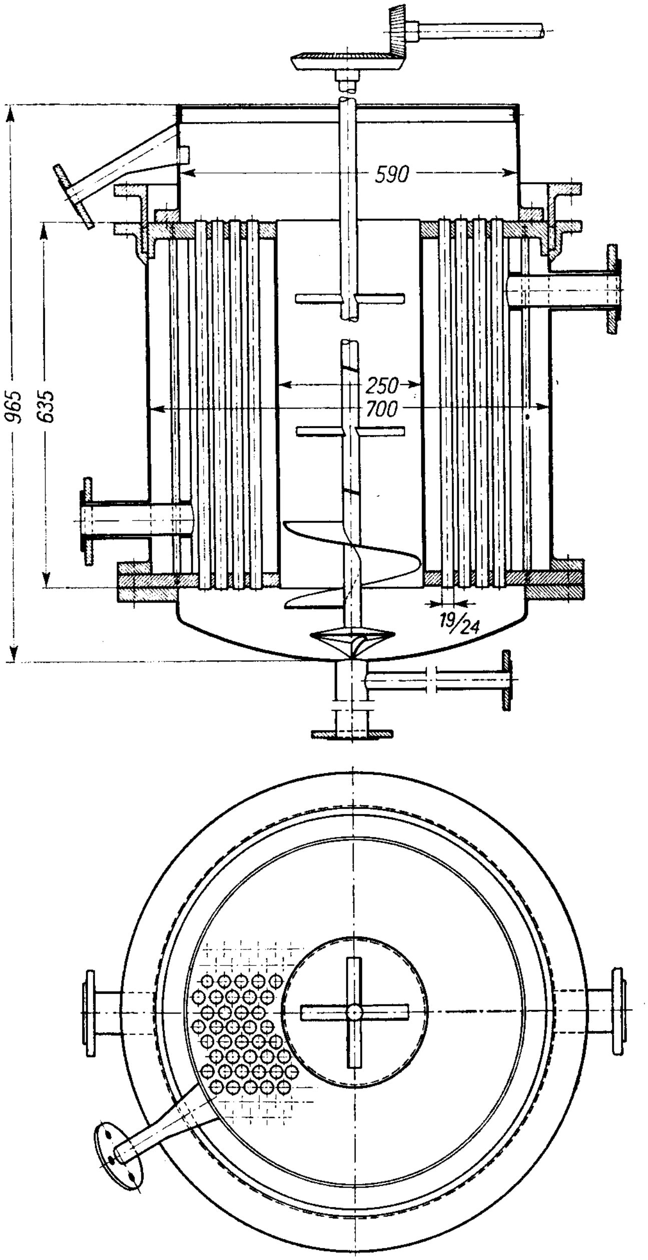

FIG. 39. Nitrator for continuous manufacture of nitroglycerine according to Schmid, improved pattern with tubular cooler by Nauckhoff (Nauckhoff and Bergström [7]).

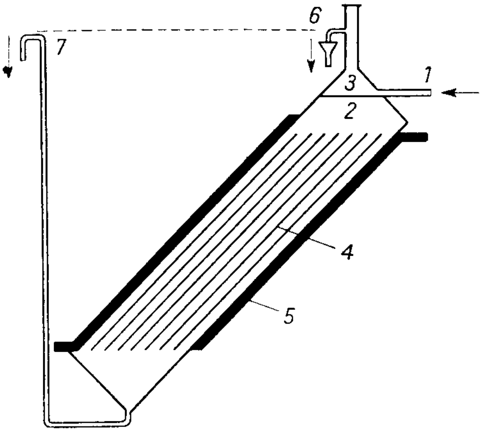

FIG. 40. Continuous separator according to Schmid.

FIG. 41. Schmid nitrator (centre) and separator (left) in Nitroglycerine Aktiebolaget, Gyttorp, Sweden.

A flow-sheet for nitroglycerine manufacture by the continuous Schmid method is shown in Fig. 43.

The whole apparatus is usually located in one room so as to facilitate supervision of the operation. During continuous manufacture the amount of nitroglycerine present in the apparatus is several times smaller (4–5 times) than that in common methods of batch nitrating. The purified product is removed from the column 30–45 min after nitration begins, whereas in existing batch processes nitroglycerine washing does not take place earlier than 2 hr after the start of nitration. The manufacture of nitroglycerine by the continuous method is therefore safer and its safety is further increased, since long pipelines for carrying acid contaminated with nitroglycerine are eliminated, and nitroglycerine passes through the valves in an emulsified form only so that handling of such cocks is less hazardous.

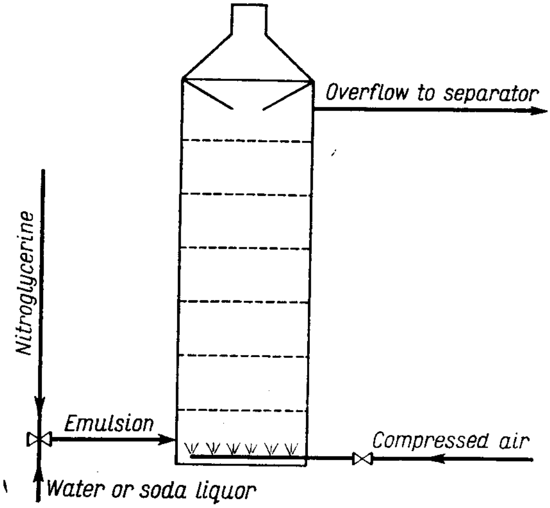

FIG. 42. Continuous washing of nitroglycerine according to Schmid.

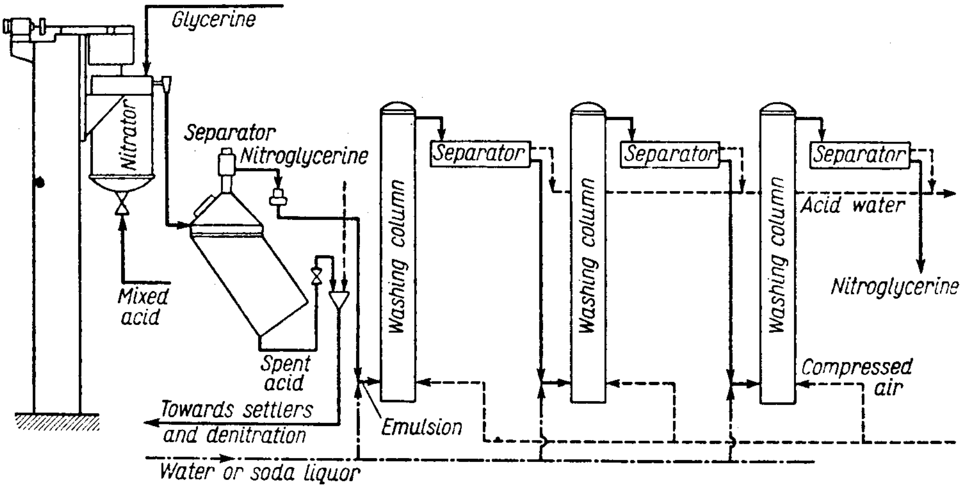

FIG. 43. Flow-sheet of continuous manufacture of nitroglycerine according to Schmid.

Some data published by Stettbacher [39] concerning the Schmid plant at Gyttorp' Sweden, which had a production capacity of 600 kg nitroglycerine per hour are listed below:

capacity of nitrator	75 l.
cooling surface	15 m^2
temperature of the cooling liquid	+10°C
nitrating temperature	+18°C
composition of mixed acid	50% HNO_3+50% H_2SO_4
glycerine to acid ratio	1:5
yield	231.5%

SCHMID-MEISSNER PROCESS

The process invented by Schmid and improved and developed by Meissner [40] has since been adopted in many factories. A distinctive feature of the improved method consists in the extensive use of metering devices and rotameters.

A diagram of the plant is illustrated in Fig. 44. It operates as follows. Nitrating acid filtered through a ceramic filter (*1*) is transferred by compressed air from tanks (*2*) and (*3*) over a rotameter into the nitrator (*14*). Glycerine heated in the heater (*9*) is transported by means of the pump (*10*) through a bronze mesh filter (*11*) to the metering tank (*12*) from which it is discharged by a pressure controlled on the board (*16*). In order to permit the use of a rotameter for metering the glycerine a temperature of 40°C is maintained in the glycerine feed tank, so that no variation in viscosity occurs which would otherwise prevent the use of a rotameter. From the compressed air tank (*13*) an air pressure of about 1.5 atm is applied to both the glycerine and the mixed acid contained in measuring tanks. Thus the glycerine and acid are delivered under the same pressure and any changes in the pressure applied to the raw materials are the same for both liquids.

Nitroglycerine is discharged from the separator (*17*) through an overflow (*17a*) and passing through injectors (*22c*) (*23c*), (*24c*) it enters in turn the washing columns (*22*), (*23*) and (*24*).

In the earlier design when the plant was started up, the first nitroglycerine produced may be polluted by slime from the nitrator and separator. It is therefore transferred to a "hand" washer (*17b*) to be washed as in batch production.

In more modern designs there is no slime in the nitrator and separator as the whole installation is constructed of high-grade acid-resistant steel. The washing tank is maintained, however, in order to wash the residue of nitroglycerine remaining in the separator when the installation is shut down.

To the separator, an overflow for spent acid (*18a*) is fitted, by means of which the height of the boundary layer between the two liquid phases can be regulated. Spent acid flows down to a pressure-egg (*19*), from which it is discharged by means of compressed air to a tank (*18*) (only a part of the pipe is shown) and then to setling tanks as in the combined process, (p. 95).

Columns for nitroglycerine washing are built of glass rings of 200–300 mm diameter, resting on acid-resistant steel plates. Into the first column (*22*) an emulsion of nitroglycerine with cold water produced in the injector (*22c*) is introduced from below. The temperature inside the column is shown by a remote thermometer (*22b*). In the second column (*23*) the washing is carried out in an identical manner except that a warm 3% sodium carbonate solution is used here, while in the third column (*24*) warm water is used to remove sodium carbonate from the nitroglycerine.

The primary separation of nitroglycerine from water or sodium carbonate solution is performed in separators (*22a*), (*23a*) and (*24a*). The lower parts of these columns and separators are equipped with cocks by means of which the residue of nitroglycerine remaining after a shut down is removed together with an aqueous

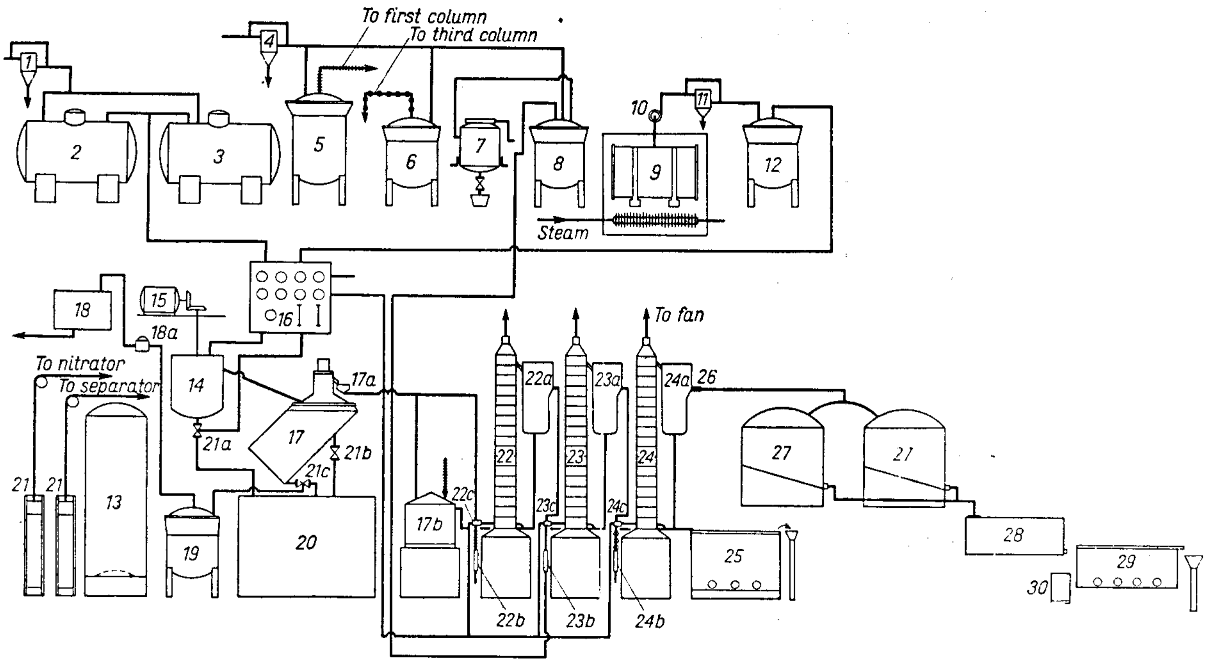

FIG. 44. Flow-sheet of continuous production of nitroglycerine according to Schmid–Meissner: *1*—ceramic filter, *2,3*—measuring tanks for nitrating mixture, *4,11*—bronze mesh filters, *5*—cold water tank, *6*—warm water tank, *7*—sodium carbonate container, *8*—sodium carbonate storage tank, *9*—glycerine warming container, *10*—glycerine pump, *12*—glycerine measuring tank, *13*—compressed air, *14*—nitrator, *15*—motor driving the stirrer in the nitrator, *16*—control panel connected with acid rotameter, reduction valve and distance-thermometer in the pre-washing vat *17b*, *17*— separator, *17a*—nitroglycerine over-flow, *17b*—pre-washing vat, *18*—spent acid tank, *18a*—nitroglycerine over-flow, *19*—pressure egg, *20*—emergency drowning tank, *21*—electric release of safety valves, *21a, b, c*—valves to the drowning tank: (*a*) from the nitrator, (*b, c*) from the separator, *22, 23, 24*—washing columns, *22a, 23a, 24a*—separators, of nitroglycerine from wash-water, *22b, 23b, 24b*—rotameters, *22c, 23c, 24*—injectors emulsifying nitroglycerine with water or sodium carbonate solution, *25*—labyrinth, *26*—injectors for stabilized nitroglycerine, *27*—tanks separators, *28*—nitroglycerine filter, *29*—labyrinth, *30*—nitroglycerine can.

solution or water to a labyrinth (*25*). Nitroglycerine collects here to be sent to a washer (*17b*).

Through the injector (*26*) and by means of rubber pipes nitroglycerine stabilized with an extermely dilute solution of sodium carbonate is transferred to the separating tanks (*27*) wherein the final separation of the emulsion into layers is accomplished. Nitroglycerine is passed through a filter (*28*), whilst the aqueous layer flows down into the labyrinth (*29*). The product removed from the labyrinth is stabilized in the washing tank (*17b*).

RACZYŃSKI PROCESS

The distinctive feature of the process invented by Raczyński [41] is exact metering of mixed acid and glycerine by means of automatic mechanical devices.

The nitrating acid is metered by means of tipping vessel fixed on a horizontal shaft (Fig. 45a).

Acid flows into the vessel (*1*) from a pipe ending inside a container constructed of acid-resistant steel or lead, in which the tipping vessel is located. The stream of acid fills the vessel, and as a determined weight is reached it tips over and another empty vessel swings into place under the acid inlet pipe. This fills in turn and tips over to pour off its contents and so the cycle continues. A volume-meter connected to the equipment indicates the volume of liquid measured out. Acid from this device passes into the nitrator.

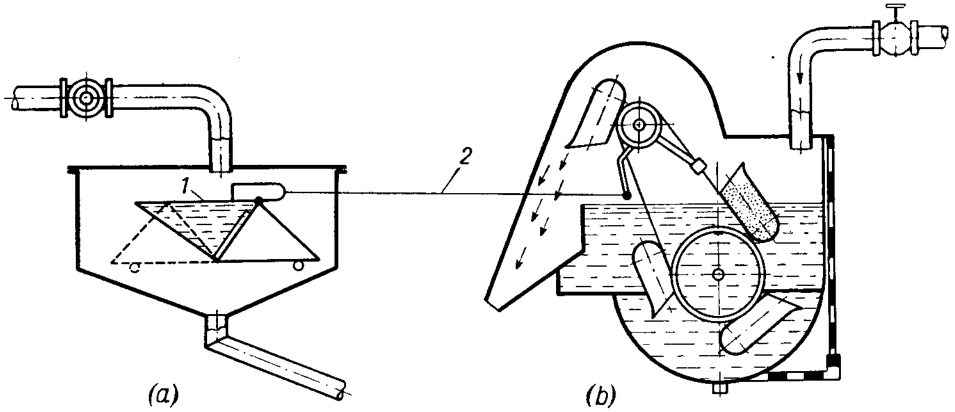

FIG. 45. Apparature for continuous dosage of acid (*a*) and glycerine (*b*) according to Raczyński [41].

Glycerine is metered by means of a bucket conveyer (Fig. 45b) driven by hydraulic turbine.

The arrangements for introducing measured quantities of acid and glycerine are connected by a lever (*2*) in such a way that the influx of acid and nitroglycerine into the nitrator proceeds at a pre-determined ratio. Movement of the tipping vessel exerts a pull on the lever and this takes the brakes off the bucket conveyer. At once the conveyer starts to move and continues to do so until the acid metering vessel returns the lever to its former position and stops the conveyer again.

A diagram of a plant for nitroglycerine manufacture by the continuous Raczyński process, including the separating and washing units, is outlined in Fig. 46.

For nitration a nitrator (*1*) equipped with cooling coils and a mechanical stirrer comprising a cylindrical rotor equipped internally with turbine paddles is used. At a sufficiently high rate of rotation, the liquid flows rapidly through the rotor in one direction thus ensuring correct circulation between the coils.

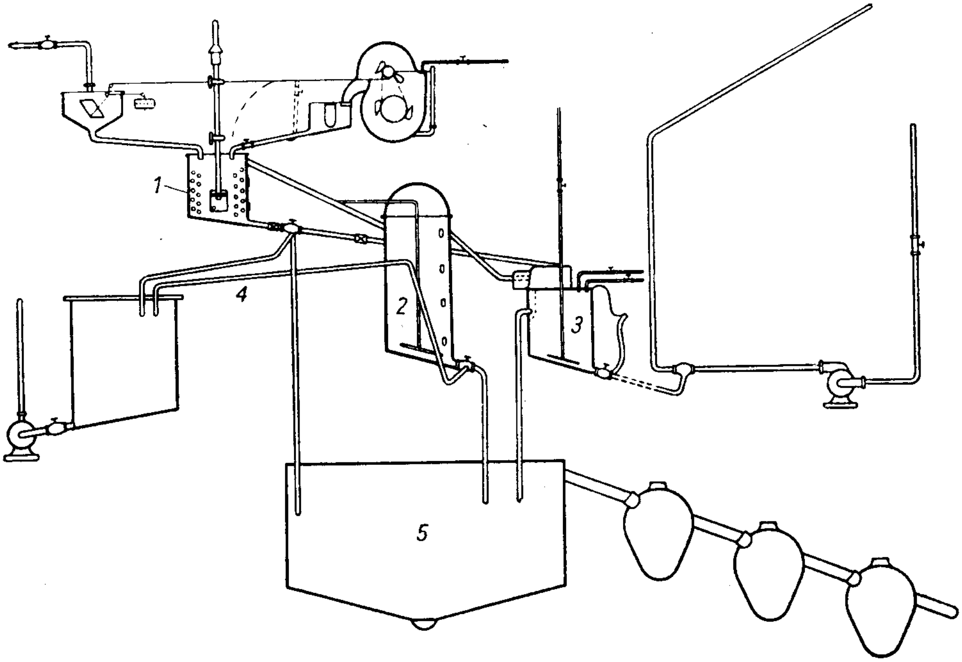

FIG. 46. Flow-sheet of continuous method of manufacture of nitroglycerine according to Raczyński [41].

The emulsion of nitroglycerine and acid flows to a cylindrical separator (*2*) from which the upper nitroglycerine layer flows over the high level pipeline to a primary washing tank (*3*). The spent acid is removed from below by a hydraulic system (*4*). Should any danger of decomposition arise it is possible to empty the contents of the nitrator or separator into the drowning tank (*5*). As the separator is emptied the compressed air inlet valve should be opened simultaneously to mix the nitroglycerine with the acid again.

BIAZZI PROCESS

An original version of the continuous process worked out by Biazzi (Vevey, Switzerland since 1935) [42] includes a new type of acid-resistant steel nitrator (Fig. 47) and the application of "tangential" separators, the liquid content of which is constantly in motion.

One of the first plants nitrating glycerine by the Biazzi process was in operation at Schlebusch in Germany [43]. For a plant with a rated output of 800–1000 kg nitroglycerine per hour a nitrator of 250 l. capacity was used.

The flow sheet of a more modern Biazzi automatic plant is given in Fig. 48. According to the original description [44] glycerine and glycol are pumped to an intermediate tank (*13*).

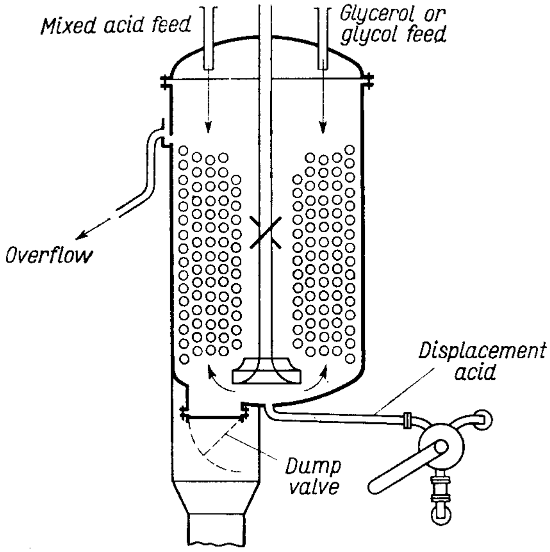

FIG. 47. Continuous nitrator for Biazzi nitroglycerine manufacture (according to Kuhn, W. J. Taylor, Groggins [4]).

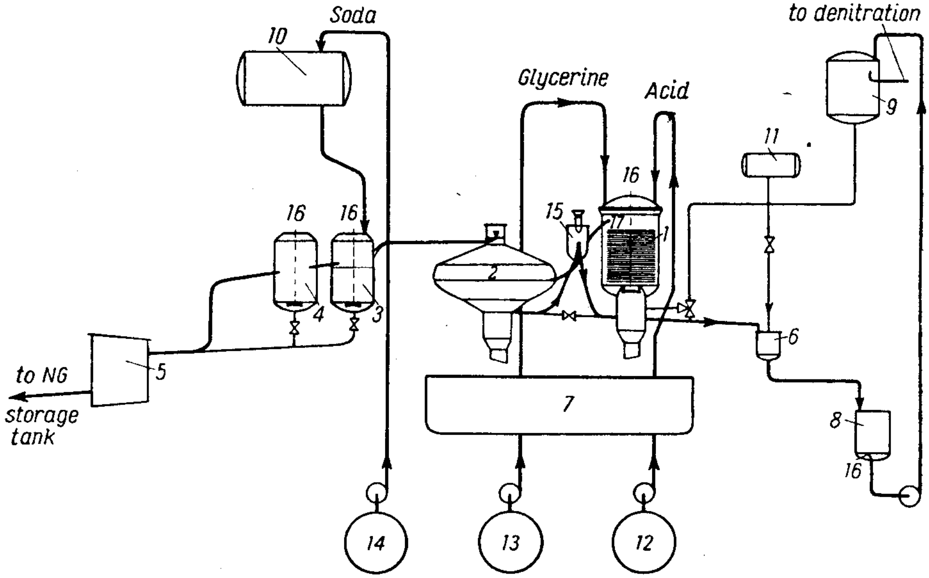

FIG. 48. Flow-sheet for nitroglycerine manufacture according to Biazzi (Stettbacher [45]).

A metering pump introduces the required quantity of glycerine to the nitrator.

The mixed acid (*12*), brought to the nitration house by means of a centrifugal pump, is fed into the nitrator via a metering pump. The flow of the two reacting liquids is maintained in the correct proportion by means of speed controller.

A high speed stirrer (*ca.* 600 r.p.m.) [45] emulsifies the content of the nitrator (*1*).

The temperature in the nitrator is kept within 10–15°C by cooling coils fed with cold water, brine (−5°C) or freon [45, 46]. The temperature is kept constant by means of a thermostatically controlled valve,

The suspension of nitroglycerine in acid flows from the nitrator to acid-resistant steel separator (*2*). The separator inlet enters the vessel tangentially about 0.6 m below the nitrator outlet. The separator itself is a shallow cylindrical vessel having a large diameter which is nearly twice as big as that of the nitrator. Its upper part is conical, topped with a cylindrical chimney.

A stream of emulsion enters the separator to meet the emulsion already present there. Above the emulsion there is a nitroglycerine layer, and below it an acid layer. Owing to the tangential direction of flow, the emulsion circulates slowly with respect to the two stationary layers already separated. Since the diameter of the separator is large this rotary movement is extremely slow (peripheral rate of 2–3 cm/sec) and therefore favourable for the agglomeration of small drops of both liquid phases. According to the data contained in Biazzi's patent, by this system separation is accomplished in a time not longer than 10 min.

The temperature inside the separator is determined by means of thermometers situated at two levels: the upper one in the separated nitroglycerine and the lower one in the acid layer. The separator is equipped with a sight glasses through which the boundary line of the liquid phases can be observed.

The spent acid leaves the separator from below to flow via a siphon, the height of which can be automatically controlled, to a diluter (*6*) where 1–2% water is added and then to a spent acid mixer (*8*). Dilute spent acid is pumped to tank (*9*), and is used for displacement of nitroglycerine from the nitrator and separator after nitration has finished. Most of the dilute acid is sent to denitration.

Acid nitroglycerine flows into a battery of stainless steel continuous washing tanks (*3*) and (*4*) provided with stirrers (580 r.p.m.). The first tank (*3*) is fed with 12% sodium carbonate solution. This is one of the characteristic features of the Biazzi process and represents a radical change in approach to the stabilization of nitroglycerine since for the first time the acid nitroglycerine is treated directly with sodium carbonate solution without previous water washing. The heat of neutralization in tank (*3*) is removed by means of a water cooling jacket.

This direct neutralization has the advantage of eliminating the appreciable loss of the nitroglycerine which occurs with acidic wash water systems. No further washing of nitroglycerine is necessary after direct treatment with sodium carbonate solution. Tank (*3*) is supplied with sodium carbonate solution through an automatic outlet valve coupled with a pH-meter. To neutralize 100 kg of nitroglycerine *ca.* 7 kg anhydrous sodium carbonate is required (i.e. 52 l. of 12% solution). Each washing tank contains *ca.* 160 kg of emulsion.

A sample of the washed nitroglycerine is subjected to a heat-test. After removing sodium carbonate to max. 0.04%, nitroglycerine should give a positive test for 20 min at 80°C.

After stabilizing in the washing tanks the emulsion flows to another separator where the nitroglycerine is removed and sent for storage prior to incorporation. There is no final separator in the most recent Biazzi plants [44, 46]. The stabilized nitroglycerine is emulsified with warm water in (*5*) and flows to a low level storage tank.

The flow-sheet for the remote control of the nitroglycerine storage, transport and weighing installation is given in Fig. 49.

Stabilized nitroglycerine in the form of an aqueous emulsion flows into storage tank (*1*). If every batch of nitroglycerine is subjected to heat-test two storage tanks should be provided.

Water separated from the emulsion flows over to tank (*2*). The small quantity of nitroglycerine collected at the bottom can be sent back to (*1*) through the water pump (*3*) or drained through valve (*4*). If the nitroglycerine level is too high or too low a signal is given in the control room, that automatically sets in motion a number of injectors (*5*). They transport nitroglycerine from (*1*) to the weighing house and settling tank (*6*) until the level in the tank becomes satisfactory. The separated water flows to tank (*7*) and nitroglycerine collected at the bottom can be sent back through the water pump (*8*) or drained through valve (*9*). Nitroglycerine, free from water, passes through a common salt filter (*10*). Here the last traces of water are removed and the nitroglycerine is weighed in tank (*11*) which is mounted on scale (*12*).

Automatic filling of the weighing tank (*11*) is effected by pneumatic remote control through valve (*12*) and micrometric valve (*13*). The valves close automatically when the desired weight is reached.

Nitroglycerine flows out to the mixing room. The quantity of nitroglycerine in the weighing house is *ca.* 150 kg. As a rule no workmen come into contact with nitroglycerine in either the storage or the weighing house.

The great advantage of the Schmid–Meissner and the Biazzi processes is the small amount of separated explosive present in the plant at any given time—up to 10% (and 4% respectively) of the output per hour—the remainder of the nitroglycerine in the system is in a safe emulsified form.

The largest nitroglycerine plant in the world has been in operation since 1956 by I.C.I. of Australia and New Zealand Ltd. at Deer Park, Victoria [47]. The Biazzi system is used there. The normal output from this unit is 4400 lbs per hour of nitroglycerine, and it can be raised to 6600 lb [46].

One of most up-to-date Biazzi plants which came into operation in 1956 is the plant run by the Nobel Division of I.C.I. at Ardeer, Great Britain [48]. It has a production capacity of about 2500 lbs/hr (1130 kg/hr). The installation com-

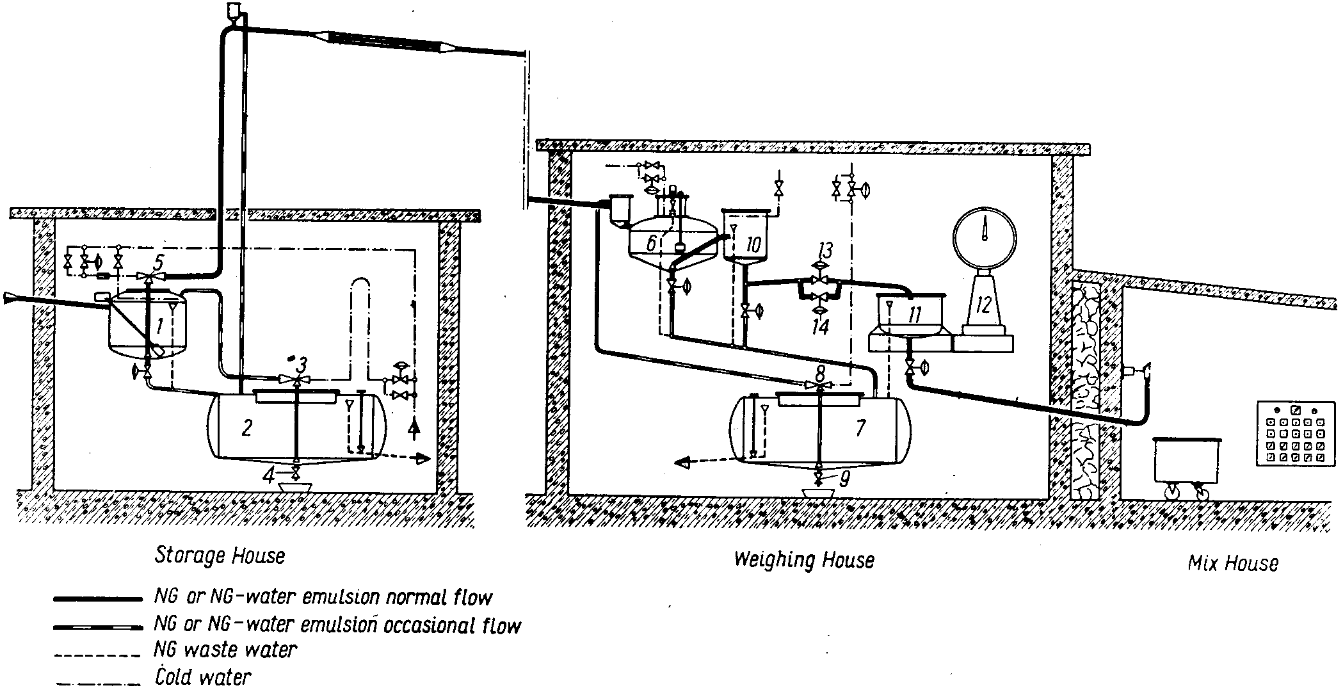

FIG. 49. Flow-sheet for a remote controlled nitroglycerine storage, transport and weighing installation according to Biazzi.

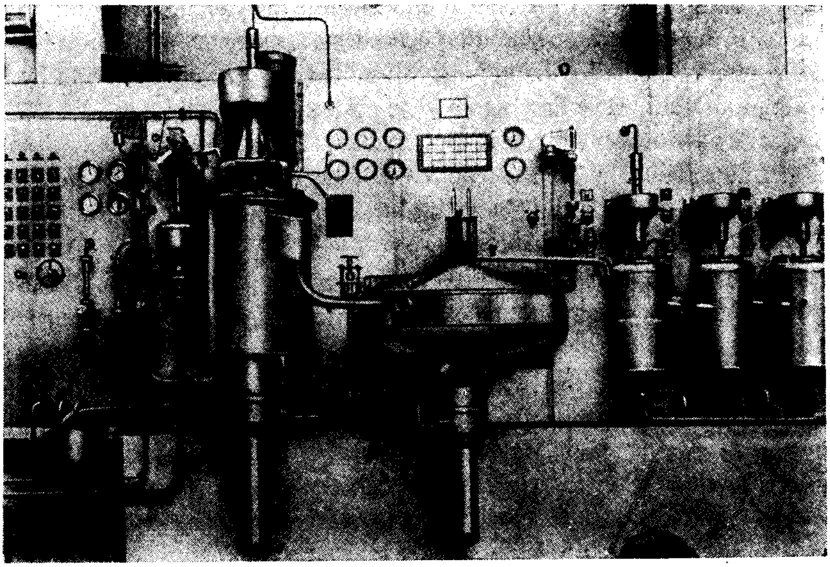

FIG. 50. Nitroglycerine manufacture — a general view of the nitrator, separator and washing equipment in a remote controlled Biazzi continuous plant (Ardeer Factory, Nobel Division, Imperial Chemical Industries Ltd., Great Britain, photograph of Vista of Glasgow, Glasgow, C 3).

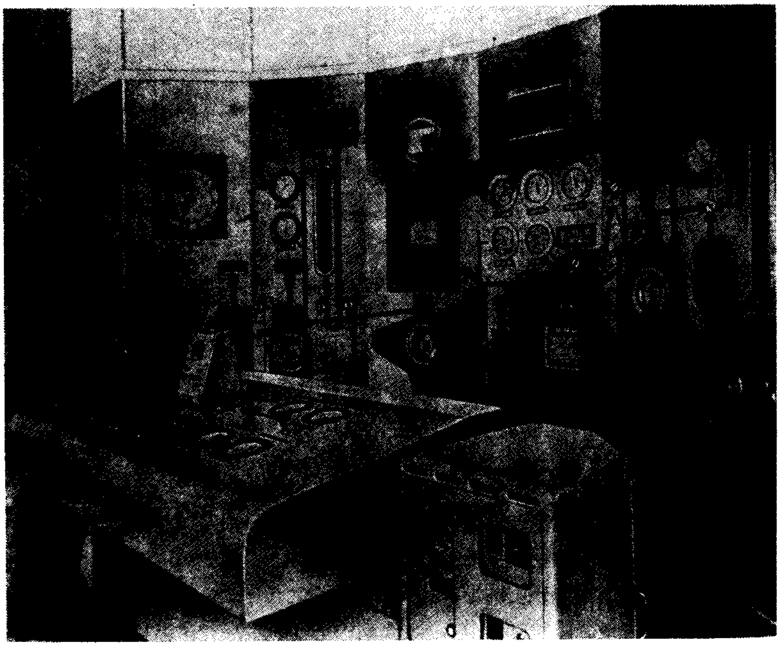

FIG. 51. Nitroglycerine manufacture — the remote control room of a Biazzi continuous plant (Ardeer Factory, Nobel Division, Imperial Chemical Industries Ltd., Great Britain, photograph of Vista of Glasgow, Glasgow, C 3).

VI. Automatic discharge of the contents of nitrator and separator into a drowning tank occurs, if the temperature in either exceeds the upper of safety limit.

VII. The contents of the drowning tank are subjected to forcible stirring by means of a strong jet of cold water flowing into the tank automatically.

The electrical control system is powered by means of 24-V batteries which are charged automatically from a rectified a.c. supply. All the control devices are located beyond the safety wall. The separator is monitored by a closed circuit television system.

Klassen and Humphrys [49] quote data comparing the main features of the Biazzi process as compared with batch nitration. The most recent data [50] are given in Table 18.

The Biazzi process has been applied to the nitration of other substances, to produce not only esters similar to nitroglycerine, but also for the preparation of such substances as PETN, cyclonite and TNT.

TABLE 18

	Nitrators producing 1200 kg nitroglycerine/hr	
	Biazzi	batch
Nitrator capacity, l.	125	305
Total cooling surface, m^2	10	23
Unit cooling surface, m^2/l.	0.08	0.0075
Time in nitrator, min	10	50
Heat transfer, kcal/m^2°C hr	800	365
Brine inlet temp., °C	−5	−25 to −20
Nitroglycerine in nitrator (at 4.7:1 acid ratio), kg	80	1590
	Raw materials and labour per 100 kg dry nitroglycerine	
Glycerine (and ethylene glycol 50:50), kg	42.2	42.2
Sulphuric acid (100%), kg	101	99
Nitric acid (100%), kg	104	99
Sodium carbonate, kg	6.0	1.7
Operating, labour-man-hours	0.04	0.18
Maintenance, labour-man-hours	0.01	0.08

N. A. B. INJECTOR NITRATION PROCESS (NILSSEN AND BRUNNBERG OR N. A. B. PROCESS)

This new method of manufacturing nitroglycerine developed by Nilssen and Brunnberg in 1950 at Nitroglycerin Aktiebolaget Gyttorp, Sweden [51] consists essentially in nitrating glycerine in an injector and separating nitroglycerine in a centrifuge. The flow of nitrating acid through an injector sucks in the correct amount of glycerine mixed with air. Nitroglycerine forms an emulsion with the spent acid.

After cooling, the emulsion flows into a centrifuge. Here nitroglycerine is separated from the spent acid and transferred to the washing house.

The main features of the N.A.B. process applied industrially since 1956 are as follows:

(1) **Mixed acid.** The nitrating acid is a conventional mixed acid, and spent acid is added in such a quantity that the HNO_3 content is 26.5–27.5% HNO_3 and the water content 9.5–10.0%. This water content is below the limit which may cause incomplete nitration. The ratio spent acid : mixed acid is 1.6–1.75.

(2) **Ratio acid : glycerine.** The flow of glycerine into the nitration injector is controlled by the flow of acid and this gives a high degree of safety for a reduction in the acid flow to less than the normal operating level results in a greater reduction of the glycerine flow.

The inlet pressure of the acid into the injector is 3.5 kg/cm^2 (50 p.s.i.) above atmospheric pressure.

(3) **Temperature.** A most important parameter characterizing nitration by injection is its high temperature, which lies within the limits 45–50°C. Small variations in temperature during normal operation are the result of small variations in the flow ratio of the reactants or in the initial temperature of the nitrating acid. This high temperature can be maintained for a short while owing to the particular conditions of the nitration, in which the heat of reaction is absorbed by a large mass of nitrating acid. Thus the temperature of the system is not dependent on the immediate removal of the heat of reaction as in other processes.

The glycerine or glycerine–glycol mixture (50:50) is pre-heated to 45–50°C before entering the injector.

The temperature of the mixed acid is 0°C.

The temperature increase during nitration, i.e. the difference between the nitrating temperature and the temperature of the incoming mixed acid, is a very good index of the ratio of glycerine to mixed acid. The exact value of the temperature rise depends on the HNO_3 content in the incoming mixed acid and on the spent acid, and the HNO_3 content of the latter depends (for a given concentration of mixed acid) on the ratio of glycerine to mixed acid.

In practice it has been found that an additional temperature rise of about 3°C corresponds to about a 1% decrease in the HNO_3 content of the spent acid and that a 1% higher HNO_3 content in the mixed acid gives a 1.7°C temperature rise for the HNO_3 content in the spent acid remaining constant. With the help of the diagram (Fig. 52) it can be seen what temperature increase will be obtained for a given mixed acid composition and for a given HNO_3 content in the spent acid.

If the temperature rises 4°C above the normal temperature, a warning signal is given and the flow of glycerine is reduced by the nitration operator. Should the amount of glycerine remain uncorrected despite the warning signal, and the temperature continues to rise, the electromagnet is de-energized at +54°C and the nitration process is stopped.

The nitroglycerine–acid emulsion enters a cooling system immediately after

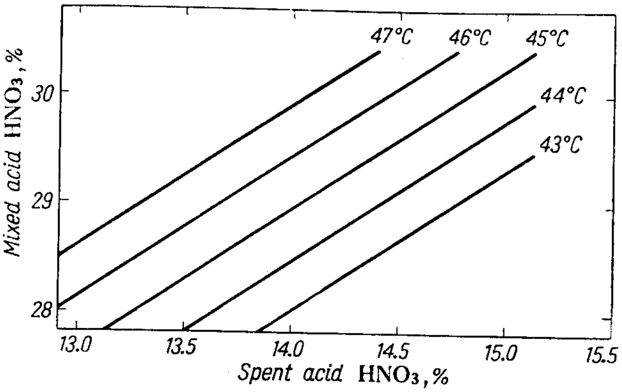

FIG. 52. Temperature diagram for injection nitration.

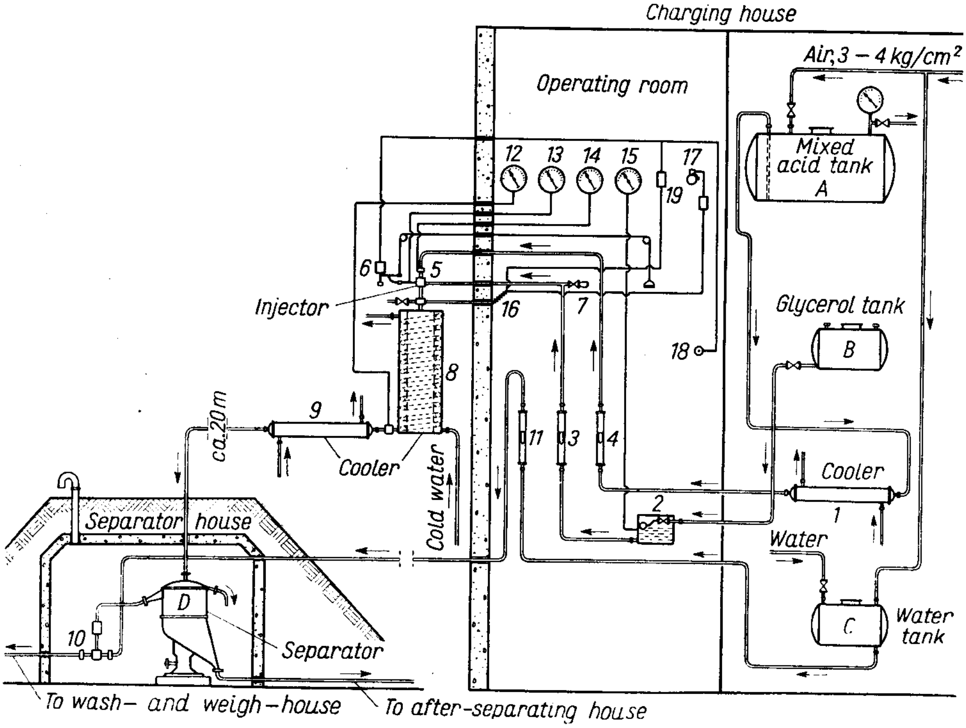

FIG. 53. Flow-sheet of injector nitration of glycerine and centrifugal separation of nitroglycerine at Gyttorp (Nitroglycerin Aktiebolaget Gyttorp, Sweden): *1* and *9*—tubular coolers (−12°C), *2*—glycerine suction tank with a constant level, *3*—glycerine rotameter, *4*—acid rotameter, *5*—injector-nitrator, *6*—electromagnet, *7*—needle valve for the air inlet to the injector, *8*—cold water cooler, *10*—injector to supply nitroglycerine-water emulsion, *11*—rotameter supplying water to *10*,*12*,*14*,*15*—thermometers, *13*—vacuum-meter, *16*—glass thermometer, *17*—alarm bell, *18*—current switch, *19*—relay to electromagnet *6*.

leaving the injector and the temperature of 45–50°C is maintained for only about half a second. During the next 80–90 sec the mixture is cooled to 15°C. In the following 30 sec the nitroglycerine is separated from the spent acid.

Cooling is achieved in two stages: the mixture is cooled to 25°C by ordinary water at 15°C and then it is cooled to +15°C by a cooling brine composed of a 30% solution of sodium nitrate at —12°C.

The flow sheet for injector-nitration and centrifugal separation is given in Fig.53 and the general view of the injector–nitrator in Figs. 54 and 55.

(4) **Separator** (Fig. 56). Another characteristic feature of the N.A.B. system is the continuous centrifugal separation of nitroglycerine from the spent acid. The centrifuge operates at 3200 r.p.m. For a unit with a capacity of 2500 l./hr the quantity of nitroglycerine in the separator bowl during operation is 3.5 kg. The separated acid nitroglycerine is emulsified immediately by the wash-jet to form a non-explosive mixture and is removed continuously from the separator house to the nitroglycerine wash-and-weigh house.

The spent acid from the separator contains a small amount of emulsified nitroglycerine. The portion which is to be used to prepare fresh mixed acid need not separated further, since when nitrating acid is added the emulsified oil redissolves and returns to the cycle.

The remainder of the spent acid is allowed to separate in the usual way and normally yields a maximum of 0.1% emulsified nitroglycerine. Instead of after-separation, water can of course be added to prevent separation.

(5) **Nitration.** To start the nitration, current from the switch (*18*) (Fig. 53) is applied to the electromagnet (*6*), which closes the air inlet to the injector. Mixed

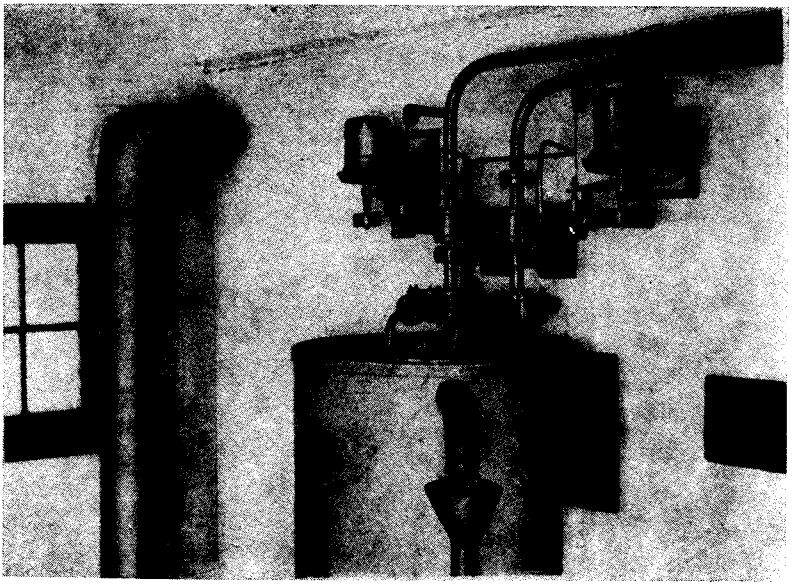

FIG. 54. Injector nitration apparatus at Gyttorp, general view (Nitroglycerine A. B. Gyttorp).

acid is admitted by opening the valve under the acid rotameter (*4*). The injector now comes into operation. The manometer (*13*) must show full vacuum. The needle valve (*7*) is then opened and the vacuum adjusted to *ca.* 300 mm Hg. The glycerine–glycol mixture is sucked in through the rotameter (*3*) to the injector from (*2*).

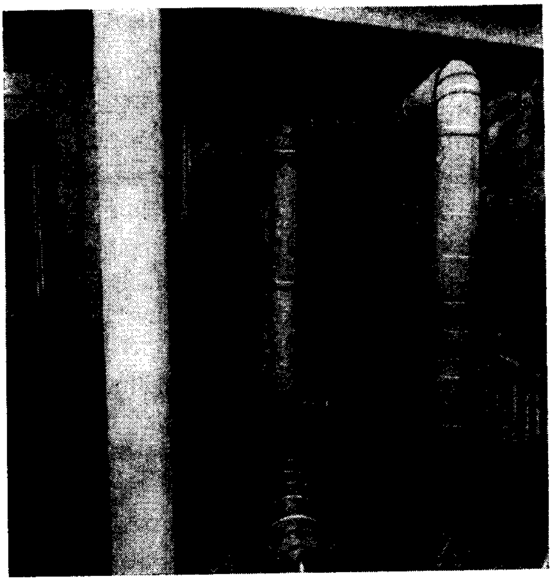

Fig. 55. Injector nitration apparatus at Gyttorp, side view (Nitroglycerine A. B. Gyttorp).

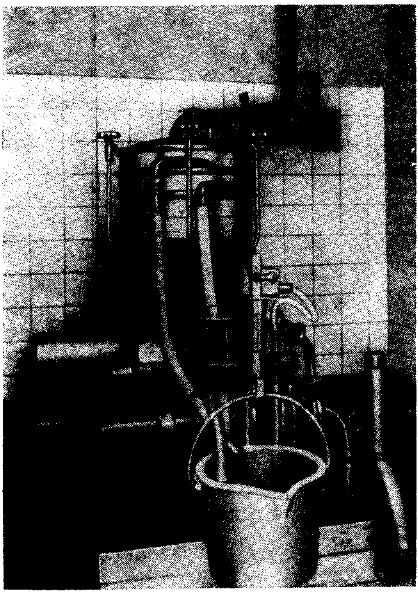

Fig. 56. Centrifugal separator of nitroglycerine at Gyttorp (Nitroglycerine A. B. Gyttorp).

The exact setting of the acid and glycerine rotameters is adjusted by means of the corresponding valves and the nitrating temperature is checked. It should be 40–45°C higher than the temperature of the incoming mixed acid.

Through the inspection glass nitroglycerine can be seen leaving the separator within about 2 min after nitration has begun.

To stop the process the circuit through the electromagnet (*6*) is broken at (*18*), so that air rushes into the injector and the glycerine in the pipe and in rotameter (*3*) runs back to (*2*). Mixed acid should be allowed to flow for 1 min in order to flush the pipes and cooling system. The separator is stopped about 10 min later and empties automatically.

The contents of the separator are collected in a special small separation vessel. The emulsified explosive oil is separated and delivered direct to the wash jet (*10*). After rinsing with separated spent acid, the separator is ready to be restarted.

A general view and a diagram of the operating room is given in Fig. 57 and 58 respectively.

Continuous washing of nitroglycerine is carried out in three wash columns: (*3*), (*6*) and (*9*), (Fig. 59).

Nitroglycerine Aktiebolaget Gyttorp quote the following figures which refer to the plant which has been in operation since 1956:

production: 500–650 kg nitroglycerine/hr
acid consumption: 2600–3400 kg/hr
glycerine consumption: 216–281 kg/hr
the yield of nitroglycerine–nitroglycol mixture is 231–232.5 kg of explosive oil, i.e. 93.9–94.5% of theoretical

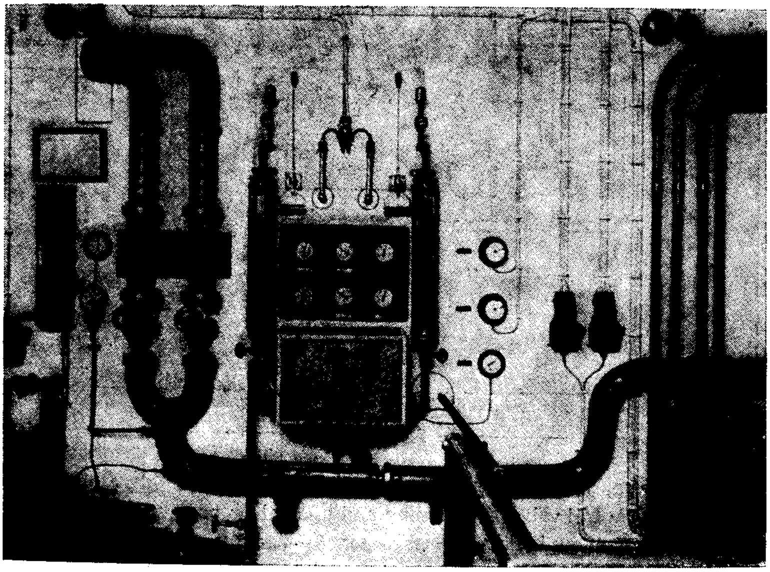

FIG. 57. Operating room, general view (Nitroglycerine A. B. Gyttorp).

brine (30% $NaNO_3$) consumption (Fig. 53):
cooler (*1*): *ca.* 75 l./min
cooler (*9*): *ca.* 100 l./min
water consumption cooler (*8*): 80–100 l./min
compressed air at 4 kg/cm^2 consumption: 1 m^3/min

SEMI-CONTINUOUS PROCESSES

The invention of continuous methods of nitration of glycerine stimulated the improvement of the old batch processes by transformation into semi-continuous ones. One such methods was designed by Jarek [52] and is in use in Poland (Fig. 60).

The batch nitrator (*1*) is connected with a separator (*2*) and the drowning tank (*3*). The displacing acid tank (*4*) can produce a flow of nitroglycerine from the separator through the pipe (*6*) to the wash columns (*7*), (*9*) and (*11*). These columns

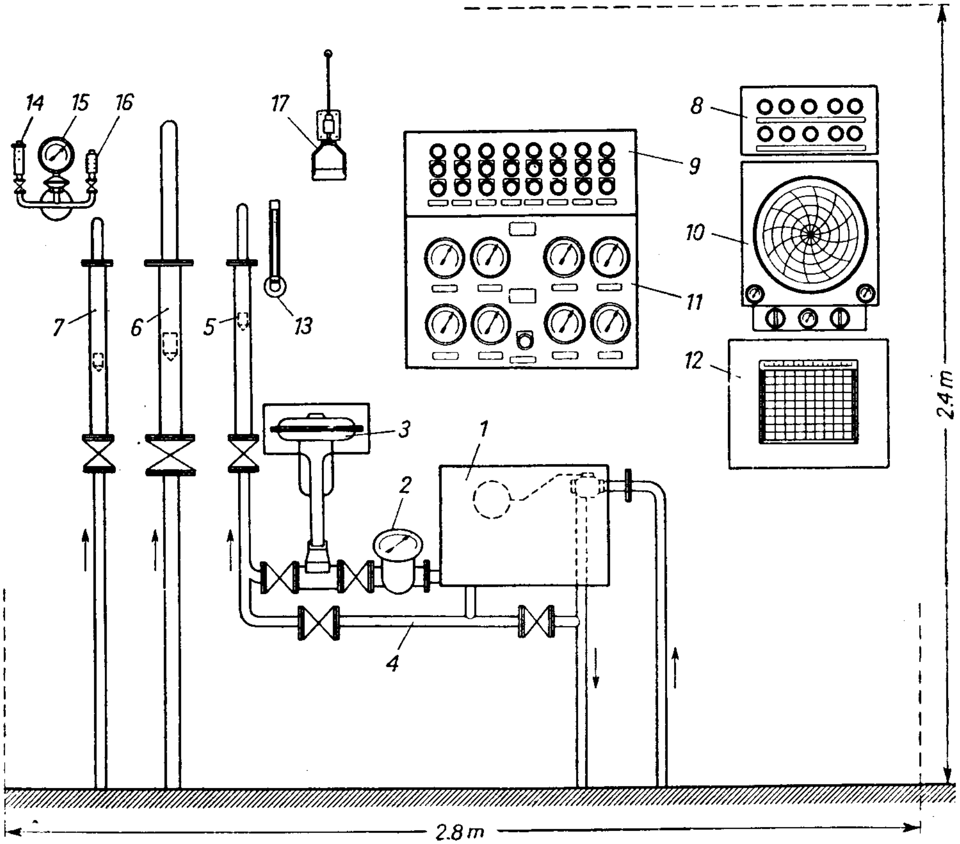

FIG. 58. Operating room, diagram (Nitroglycerine A. B. Gyttorp): *1*—glycerol vessel, *2*—glycerol meter, *3*—temperature control valve, *4*—draining and manual by pass, *5*—flow indicator glycerine, *6*—flow indicator acid, *7*—flow indicator wash water, *8*—signal lamps, *9*—switch board, *10*—temperature recorder controller, *11*—instrument board, *12*—temperature recorder, *13*—nitration thermometer, *14*—vacuum valve, *15*—vacuum gauge, *16*—air filter, *17*—emergency nitrating stopper.

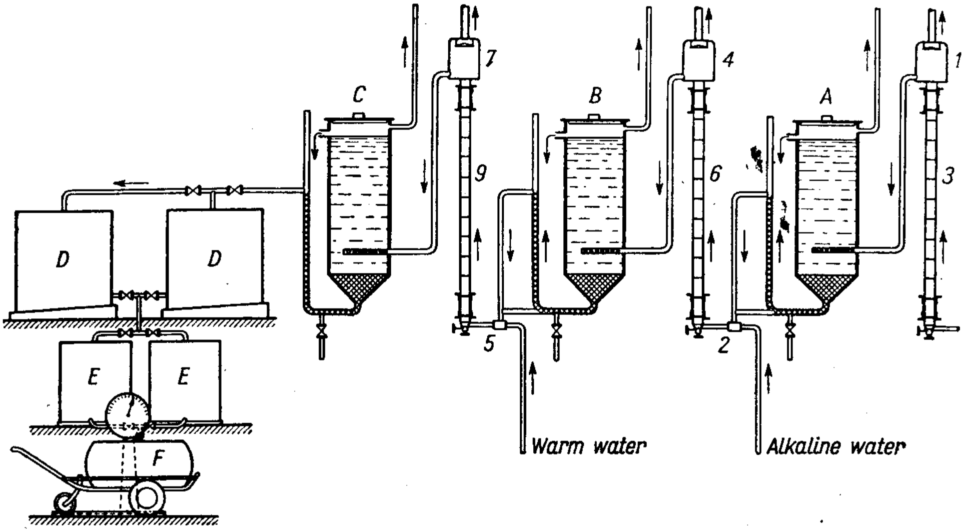

FIG. 59. Flow-sheet of washing nitroglycerine at Gyttorp: *A*—separator of acid wash-water, *B*—separator of alkaline wash-water, *C*—separator of warm wash-water, *D*—storage tanks, with wash-equipment, *E*—storage tanks with refrigerating coils, *F*—nitroglycerine waggon on a balance, *1*, *4*, *7*—air separators, *2*, *5*—injectors, *3*, *6*, *9*—wash-columns.

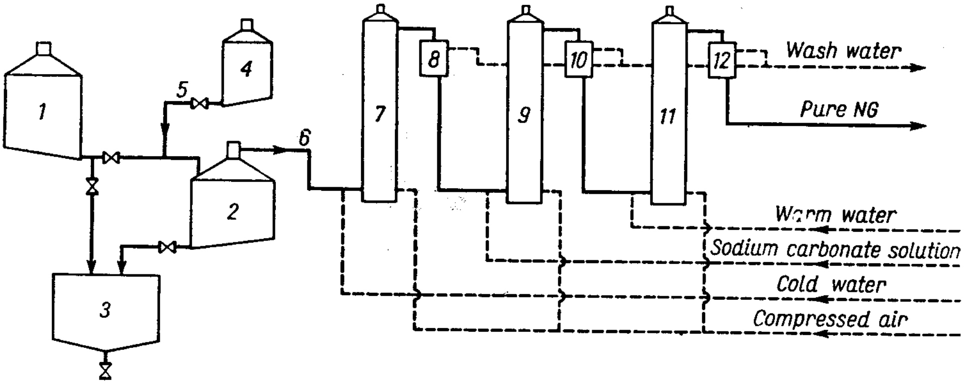

FIG. 60. Semi-continuous method of manufacture of nitroglycerine according to Jarek [52].

are connected with the separators (*8*), (*10*) and (*12*) respectively. The columns (*7*), (*9*) and (*11*) are fed with cold water, aqueous sodium carbonate solution and warm water respectively. The contents of the columns are agitated by means of compressed air fed to the bottom of the columns. Washed nitroglycerine flows from the bottom of the separators (*8*) and (*10*) to the columns (*9*) and (*11*) respectively. Nitroglycerine leaving the separator (*12*) is ready for use.

The method uses a batch nitrator but the separator (*2*) and the wash-columns run continuously.

GENERAL SAFETY RULES

The earliest plants for nitroglycerine manufacture were installed in buildings of very light construction made of planks and surrounded by a high mound of earth (Fig. 61).

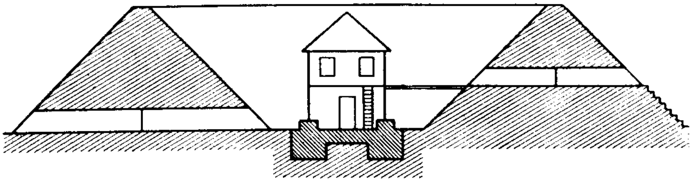

FIG. 61. Light building for manufacture of nitroglycerine with direct access to the lower and upper storeys.

Explosion of nitroglycerine is always violent and produces a large number of fragments partially retained by the safety mound. However, buildings of such light construction were unable to withstand the blast produced by an explosion in the neighbourhood. Another disadvantage was that in the event of explosion, not all the splinters were caught by the protective ramparts, and those that were projected beyond could initiate explosion in neighbouring parts of the plant.

Later, during World War I and since then, massive underground buildings made of concrete have become customary. Formerly this type of construction was used only for storage buildings. The underground buildings are semicylindrical in design and are completely buried except for the end intended for entrance and exit (Figs. 62 and 63).

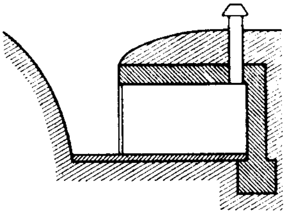

FIG. 62. Heavy underground building for manufacture of nitroglycerine.

If an explosion occurs the building is destroyed. However, owing to its robust construction no fragments are projected. Further the danger that the detonation might be transmitted from one building to another is reduced to a minimum. Towards the end of World War I 360 kg of nitroglycerine exploded in a German factory in the Rhineland but owing to its massive underground construction effects of the explosion were limited to the building concerned. Being situated in hollows, the buildings are fairly well earth-protected and danger of explosion by lightning is reduced to the minimum. Some disadvantage arises from the limited space which precludes certain changes or repairs, and from the high cost of the exhaust system.

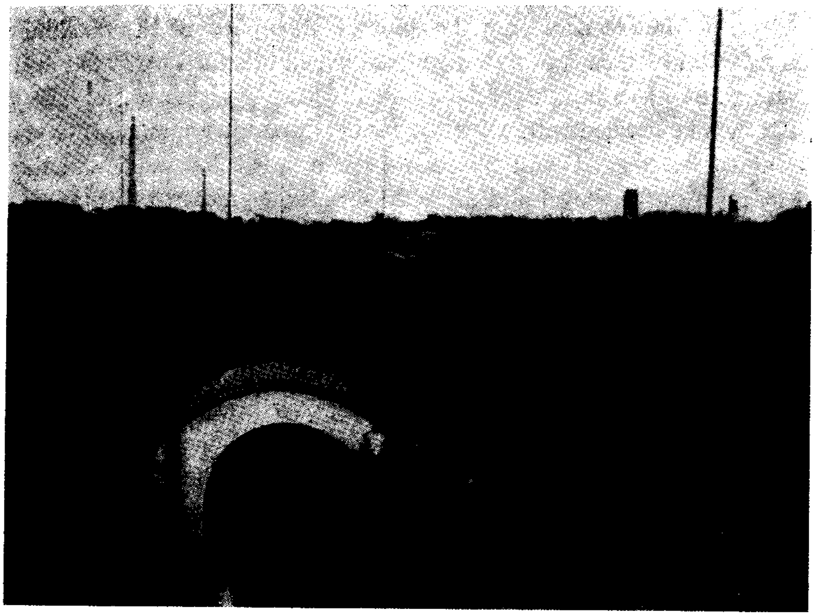

FIG. 63. General view of a heavy underground building.

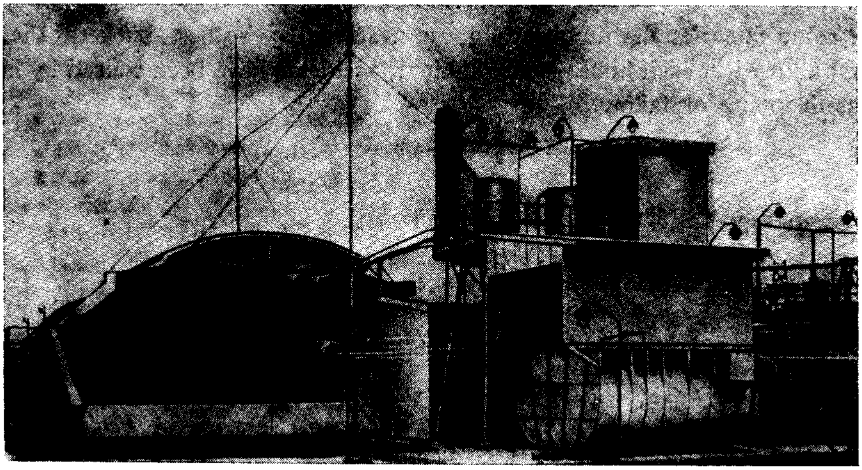

FIG. 64. Nitration Biazzi system building surrounded by earth mound with service tanks in centre and right foreground. The nitration building is protected by lightning arrestors [47]. (I.C.I. of Australia and New Zealand Ltd. at Deer Park, Victoria).

There is now a tendency to revert from underground buildings to less expensive lightly constructed surface ones, as for example the buildings for the modern Biazzi plant shown in Fig. 64.

The floor inside each building should be lined with sheet-lead, turned up at the edges close to the walls and door in order to form a border about 10 cm high, intended to contain any nitroglycerine that may be spilt.

Nitroglycerine that escapes onto the floor or onto parts of the machinery, etc. should be removed by means of a sponge from which it is then extracted and rinsed under a stream of water into a special vessel for nitroglycerine waste. The spillage area should then be washed with water, by means of another sponge. If acid escapes the area should be covered with siliceous earth or with fine sand, and the whole removed by means of a shovel and drowned in a large amount of water. A copper or aluminium shovel is necessary in case nitroglycerine is present in the acid.

All leaden apparatus should be cleaned and washed inside at least once a week to remove "lead slime". In all departments scrupulous cleanliness should be observed.

An old safety precaution required all work to stop in the nitroglycerine and dynamite factory during a thunderstorm passing over head. In the nitrating house no fresh charge could be started. All the men were to leave the building except those in charge of nitration and separation. Nowadays since the design of lightning-conductors has considerably improved, this regulation is not so necessary.

Every building must have a notice board at the entrance showing the maximum number of workman that may be in it at one time. Usually this number should not exceed two.

The maximum quantity of explosives in the building should also be limited and indicated.

In some factories the number of loose articles (e.g. bottles, buckets, thermometers) allowed in each house is also limited; accidents have been caused by heavy objects dropping or falling.

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CHAPTER IV

OTHER GLYCERINE ESTERS

THE most important drawbacks in the use of nitroglycerine are the danger of manufacturing and handling the material and its comparatively high freezing point. The danger of production has been partially overcome by improvements in manufacturing process and by strict observation of safety rules elaborated on the basis of many years' experience.

Much scientific effort has been devoted to the problem of how to lower the freezing point of nitroglycerine. This is very important from the practical point of view. If the nitroglycerine present in dynamite or in smokeless powder in the form of a gel is frozen, it separates in the form of an oil on melting. This seldom happens in the case of nitroglycerine powder, owing to its relatively low content of nitroglycerine, but the phenomenon is very frequent with dynamites. Handling dynamite from which oily nitroglycerine has partially separated is very dangerous because of the high sensitiveness of the oil to mechanical stimuli.

The problem of lowering the freezing point of nitroglycerine has been solved in many ways. Most of these methods are now of historical interest only, since they involved the use of substances which either weakened the explosive power of the nitroglycerine significantly or increased the price of product appreciably.

The first experiments on lowering the freezing point of nitroglycerine were undertaken by Rudberg [1] who blended nitroglycerine with nitrobenzene. Nobel [2] suggested admixing methyl and ethyl nitrate, nitrobenzene and glyceryl acetates. Methyl or ethyl nitrates certainly achieved the desired aim but owing to their high volatility, their use was of no practical value. Addition of the other substances mentioned reduced the explosive effect of the product.

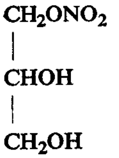
The first effective work was carried out by Wohl [3], who proposed polymerizing the glycerine prior to nitration. At first the method was not widely used owing to various technical difficulties but eventually it found an application many years later (see p. 138). A Polish chemist, Antoni Mikołajczak (A. Mikolajczak) [4] is credited with being the inventor of the so-called low-freezing dynamites. In 1904 he obtained a patent for the production of glycerol dinitrate (so-called dinitroglycerine) and suggested adding this to nitroglycerine with a view to lowering the freezing point. Dinitroglycerine is a cheap substance and for several years Mikołajczak's invention was widely used. It also opened the way for further investigations. In later patents of various authors the substances proposed for lowering the freezing point of nitroglycerine are glycerine derivatives, each molecule of which contains two nitrate groups, the third hydroxy group being esterified by another acid or being converted to an ether. Substances of this type include the so-called dinitrochlorohydrin, formyldinitroglycerine, acetyldinitroglycerine and tetranitrodiglycerine. Compounds containing one nitrate group, such as the so-called mononitroglycerine, nitrodichlorohydrin and nitroglyceride have found limited application.

The first theoretical basis for calculating the decrease of freezing point according to van't Hoff law as applied to nitric esters was given by Nauckhoff [5].

As progress was made in application of synthetic methods in the chemical industry, ethylene glycol obtained from ethylene became available and large scale manufacture of glycol dinitrate for blending with nitroglycerine in low-freezing dynamites began. Diethylene glycol also became a commercial product and yielded dinitrate used as an ingredient of smokeless ("double base") powders.

GLYCEROL MONONITRATE

Glycerol mononitrate (or "mononitroglycerine") exists in two isomeric forms, α and β:



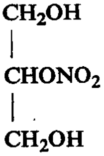
$$\begin{array}{c} CH_2ONO_2 \\ | \\ CHOH \\ | \\ CH_2OH \end{array}$$

α

m.p. 58–59°C

b.p. 155–160°C (15 mm Hg)

sp. gr. 1.53



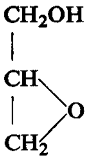
$$\begin{array}{c} CH_2OH \\ | \\ CHONO_2 \\ | \\ CH_2OH \end{array}$$

β

m.p. 54°C

b.p. 155–160°C (15 mm Hg)

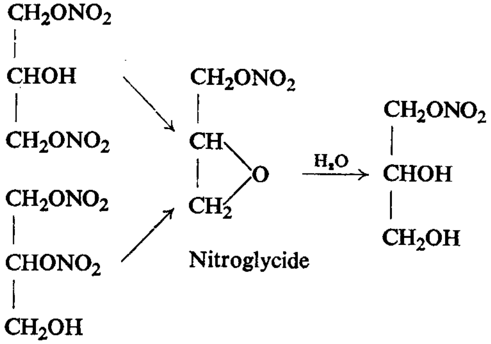
The pure α-isomer was first obtained by Hanriot [6] by nitrating glycide:



The properties of mononitroglycerine were investigated by Will *et al.* [7] and Naoúm [8].

Mononitroglycerine, mainly as the α-isomer, is a by-product accompanying dinitroglycerine produced by Mikołajczak's method [4]. Naoúm's method of separating of mononitroglycerines consists in making use of their appreciable solubility in water and relatively low solubility in ether, in which they differ from dinitroglycerines which are barely soluble in water but dissolve fairly well in ether. Thus, in order to isolate mononitroglycerines an aqueous solution of crude dinitroglycerine is prepared, and the dinitrates are extracted with ether. Mononitrates remain in the aqueous solution, from which water is removed by evaporating under reduced pressure to leave the mononitrates.

Pure α-mononitrate can be obtained by converting dinitroglycerine into "nitroglycide" which in the presence of hot water is hydrolysed to form the mononitrate. Afterwards water is removed under reduced pressure:



Both the free hydroxyl groups readily undergo esterification. By chemical reaction with benzoyl chloride, dibenzoates are obtained, namely:

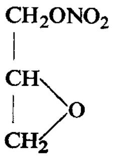
α-nitrate forms a dibenzoate of m.p. 68–69°C
β-nitrate forms a dibenzoate of m.p. 52°C

A characteristic addition product is formed by the α-nitrate with calcium nitrate (m.p. 117°C). Its composition is: $[C_3H_5(OH_2)(ONO_2)]_4 \cdot Ca(NO_3)_2$. The product is purified by crystallization in alcohol. β-Nitrate does not form such a compound.

Glyceryl mononitrates are stable substances which do not undergo decomposition when heated to a moderate temperature. In a sealed tube they decompose explosively at a temperature of about 170°C.

Mononitroglycerines are weak explosives. In consequence of a distinctively negative oxygen balance, only 434 kcal/kg are evolved on explosive decomposition (water in the form of vapour). Their sensitiveness to impact is extremely low. Indeed they are virtually insensitive. Their liability to detonate depends on their physical state. According to Naoúm the lead block expansion produced by liquid mononitroglycerine is 75 cm³ only and products of incomplete decomposition, e.g. acrolein, are evolved. The crystalline product, on the other hand, detonates readily to produce an expansion amounting to 245 cm³.

GLYCIDOL NITRATE

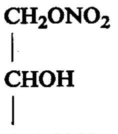


Glycidol nitrate ("nitroglycide") decomposes if boiled under normal pressure at a temperature of 174–175°C. Under a pressure of 20 mm Hg boiling takes place at 94°C. The specific gravity is 1.332 at 20°C.

As is stated above, glycidol nitrate is produced by hydrolysis of both isomeric glycerol dinitrates (Naoúm, 1907) [8]. According to Naoúm hydrolysis of the dinitrates is carried out by means of a 30% solution of KOH at room temperature. After a time the oily glycidol nitrate is precipitated with a yield of 95%. The oil is separated, washed with water and dried in desiccator. Nitroglycide dissolves slightly in cold water (5 g in 100 ml of water at 20°C). When boiled in water it yields α-glyceryl nitrate. Nitroglycide readily dissolves collodion cotton. Its explosive properties are well established. The heat of explosion is 824 kcal/kg. It detonates readily on impact (2 kg from 10–20 cm), and it explodes on heating to a temperature of 195 to 200°C. In a lead block with water tamping it produces an expansion of 430 cm^3.

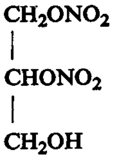
GLYCEROL DINITRATE ("DINITROGLYCERINE")

Two isomeric glycerol dinitrates (dinitroglycerines) are known.



$$\begin{array}{l} CH_2ONO_2 \\ | \\ CHOH \\ | \\ CH_2ONO_2 \end{array}$$

α (or K)



$$\begin{array}{l} CH_2ONO_2 \\ | \\ CHONO_2 \\ | \\ CH_2OH \end{array}$$

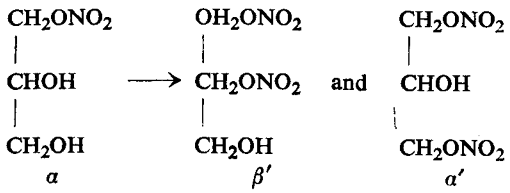
β (or F)

According to Will *et al.* [7] and Naoúm [8] the commercial product containing both isomers has a specific gravity of 1.47 at 15°C. On cooling it freezes at a temperature of —40°C. Under a pressure of 15 mm Hg it distils at 146°C almost without decomposition. It dissolves in water up to 8.6% at 20°C [25]. The product readily dissolves in most of organic solvents. It is insoluble in carbon tetrachloride and petrol. Being hygroscopic it picks up 10% of water at room temperature. It readily dissolves collodion cotton. Dinitroglycerine is nearly twice as volatile as nitroglycerine. Its physiological activity resembles that of nitroglycerine. The viscosity of dinitroglycerine is approximately twice as high as that of nitroglycerine due to intermolecular hydrogen bonds between the hydroxyl groups.

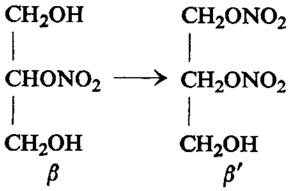
The isomers of dinitroglycerine have been separated by Will, Haanen and Stöhrer [7], utilizing the capacity of the α-isomer to form a crystalline hydrate. Thus by cooling dinitroglycerine with a 3.2% water content, crystallization of the hydrate occurs, whilst the β-isomer hydrate remains in solution. The α-isomer hydrate, melting at 26°C, has the formula: $[C_3H_5(OH)(ONO_2)_2]_3 . H_2O$. It dissolves readily in water and benzene. At a temperature of 40°C both hydrates lose their combined water.

According to Will *et al.* the chemical structure of the isomers can be demonstrated as follows. By introducing one more nitro group to the α-mononitrate, two isomeric dinitrates — a symmetric α′ and an asymmetric β′ — are formed.

By nitrating the β-mononitrate, on the other hand, only one product, i.e. the asymmetric dinitrate β′, can result.



$$\begin{array}{c} CH_2ONO_2 \\ | \\ CHOH \\ | \\ CH_2OH \\ \alpha \end{array} \longrightarrow \begin{array}{c} OH_2ONO_2 \\ | \\ CH_2ONO_2 \\ | \\ CH_2OH \\ \beta' \end{array} \text{ and } \begin{array}{c} CH_2ONO_2 \\ | \\ CHOH \\ | \\ CH_2ONO_2 \\ \alpha' \end{array}$$



$$\begin{array}{c} CH_2OH \\ | \\ CHONO_2 \\ | \\ CH_2OH \\ \beta \end{array} \longrightarrow \begin{array}{c} CH_2ONO_2 \\ | \\ CH_2ONO_2 \\ | \\ CH_2OH \\ \beta' \end{array}$$

As mentioned above, dinitroglycerine is hydrolysed in the cold in the presence of a concentrated potassium hydroxide solution to form nitroglycide.

Dinitroglycerine is more resistant to heating than nitroglycerine: it begins to show signs of decomposition after 14 days' heating at a temperature of 75°C. On heating to 150°C it evolves brown fumes of oxides of nitrogen, on heating above 170°C it undergoes explosive decomposition, the latter being the more violent the larger the amount of the substance heated.

EXPLOSIVE PROPERTIES

According to Naoúm [8] the explosive decomposition of dinitroglycerine can be expressed by the equation:

$$C_3H_5(OH)(ONO_2)_2 \longrightarrow 2CO_2 + CO + 2H_2O + N_2 + H_2 + 1201 \text{ kcal/kg}$$

The large thermal effect entitles this substance to be regarded as a very powerful explosive. Its sensitiveness to shock is barely less than that of nitroglycerine, as it explodes under the impact of a 2 kg weight dropped from a height of 7–10 cm.

The crystalline α-dinitrate hydrate explodes under the impact of a weight dropped from a height of 90–100 cm; for explosion of the liquid β-isomer a drop of only 30–40 cm is required.

In the lead block with water tamping, dinitroglycerine gives an expansion of 500 cm^3. Under these conditions nitroglycerine causes an expansion of 600 cm^3. A 92% blasting gelatine made from dinitroglycerine produces an expansion of 440 cm^3, whereas the same gelatine made of pure nitroglycerine produces an expansion of 585 cm^3. Considering these experiments and the heat of detonation, the explosive strength of dinitroglycerine seems to amount about 80% of that of nitroglycerine.

To bring about complete detonation, as with liquid nitroglycerine, a rather powerful initiator is necessary. Thus the expansion in the lead block test, using a No. 1 detonator amounts to 290 cm^3, whereas that produced by a No. 8 detonator is 500 cm^3 (with water tamping).

The detonation rate of 92% dinitroglycerine blasting gelatine is 3300 m/sec, according to Blochmann [9] the corresponding value for nitroglycerine being 7000 m/sec.

For a 75% Kieselguhr dynamite made from dinitroglycerine the rate of detonation is 4300 m/sec (with nitroglycerine it is 6800 m/sec).

According to Blochmann transmission of detonation from a 100 g charge of blasting gelatine made from dinitroglycerine is 5 cm, whereas for nitroglycerine gelatine it is 25 cm.

MANUFACTURE OF DINITROGLYCERINE

The sole commercially important method of manufacturing dinitroglycerine is that developed by Mikołajczak [4]. Glycerine is dissolved at a temperature of 15–20°C in 3–4 parts of nitric acid as free as possible from oxides of nitrogen. In order to achieve complete nitration the solution is allowed to stand for 2–6 hr. Then it is diluted with water in the proportion of 1 part of water and ice to 1 part of acid, and finally neutralized with calcium carbonate thus forming a concentrated calcium nitrate solution (1.51 g/ml). Being insoluble in this solution, which is of high density, dinitroglycerine rises to the surface to form an oily layer. This oil is separated and washed by means of a concentrated sodium chloride solution containing sodium carbonate or ammonia. Sodium chloride is added to lower the solubility of the dinitroglycerine, so that washing can be carried out even at 40–50°C with negligeable loss of the product. (8 parts of dinitroglycerine dissolve in 100 parts of water at 20°C whereas only about 2 parts dissolve in 100 parts of a 30% solution of sodium chloride). Finally the dinitroglycerine is rinsed with a solution of sodium chloride. In order to minimize the loss of dinitroglycerine, the same solution of sodium chloride is used several times.

If nitrous and nitric oxides are present in the nitric acid, products of oxidation may contaminate the main product. Such dinitroglycerine should be washed with special care. The product is dried by passing a stream of warm air through it.

The calcium nitrate solution is treated with a calculated quantity of ammonium sulphate to precipitate calcium sulphate and ammonium nitrate is recovered from the resulting solution by evaporation, for use in the manufacture of explosives.

The raw materials consumption in the production of 100 kg of dinitroglycerine is as follows:

glycerine	71.4	kg
nitric acid	250	kg
ice	75	g
calcium carbonate	125	kg
ammonium sulphate	165	kg
ammonia	1.5	kg

The following by-products are obtained:

ammonium nitrate	200	kg
calcium sulphate	165	kg

The consumption of raw materials is such that the price of dinitroglycerine is higher than that of nitroglycerine.

The Mikołajczak process is usually safer than nitroglycerine manufacture. It is necessary, however, to maintain a low nitrating temperature and to use acid free from oxides of nitrogen which favour oxidation reactions. Local overheating should be carefully avoided, because dilute acid is specially prone to produce oxidation processes.

According to du Pont Company [10], ammonia can be used for the neutralization of the dilute solution of dinitroglycerine in nitric acid, thus producing a solution of ammonium nitrate which is recoverable.

Pütz [11] obtained a patent for the preparation of dinitroglycerine relatively free from the trinitrate by dissolving 1 part of glycerine in 3.3 parts of nitric acid (sp. gr. 1.5) below 15°C. The solution was diluted with 1 part of water and neutralized with calcium carbonate. The product was separated as an oil and a small quantity was extracted with ether from the aqueous solution.

Dinitroglycerine was also obtained from nitroglycerine by denitrating it with sulphuric acid [12, 25]. The denitration occurs simply by dissolving nitroglycerine in conc. sulphuric acid without cooling. The solution is dissolved in water and the dinitroglycerine extracted with ether.

Commercial dinitroglycerine contains a certain amount of glycerol mononitrate and trinitrate. In dynamites dinitroglycerine is blended with nitroglycerine, hence in a number of patents it has been proposed to nitrate glycerine in conditions which enable a low freezing mixture of nitroglycerine and dinitroglycerine to be obtained in one operation. In principle a higher yield is obtained when more acid is used for the nitration. For the nitration of 100 parts by weight of glycerine, Naoúm [8] obtained the following results which are tabulated below (Table 19).

TABLE 19

THE RESULTS OF NITRATING 100 PARTS BY WEIGHT OF GLYCERINE (AFTER NAOÚM)

Amount of 95% HNO_3 used to nitrate, in parts by weight	Yield of esters, parts by weight			Percentage ratio	
	total	nitro-glycerine	dinitro-glycerine	nitro-glycerine	dinitro-glycerine
250	77.3	6.8	70.5	9	91
350	127.5	20.5	107.0	16	84
450	175.6	44.8	130.8	26	74
500	191.0	51.0	140	27	73

A few papers [7, 25] and patents [13] suggest the preparation of dinitroglycerine by nitrating with a dilute mixed acid (e.g. containing 9% water), followed by dilution of the whole with water to separate dinitroglycerine. This method, however, is uneconomic.

Other patents [4, 11] recommend manufacturing blends of dinitroglycerine and nitroglycerine in any ratio by nitrating glycerine with mixed acid containing less sulphuric acid than usual, for example, a mixture containing

HNO_3	60%
H_2SO_4	30%
H_2O	10%

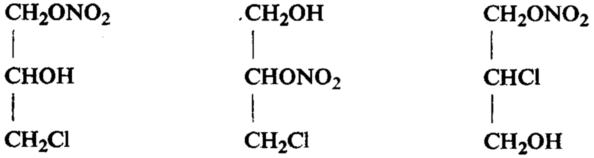
yields an oily product, the dinitrate to trinitrate ratio of which is *ca.* 70:30. The separation of the oil is followed by dilution of the spent acid with water to precipitate a further quantity of oil containing a higher proportion of dinitroglycerine, e.g. *ca.* 90:10.

MIXED GLYCERINE ESTERS

CHLOROHYDRIN NITRATES

Mononitrochlorohydrin

Mononitrochlorohydrin is a chlorohydrin mononitrate, existing in the three isomeric forms shown below:

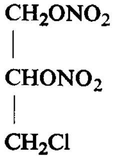


$$\begin{array}{c}CH_2ONO_2\\ |\\ CHOH\\ |\\ CH_2Cl\end{array}\qquad\begin{array}{c}CH_2OH\\ |\\ CHONO_2\\ |\\ CH_2Cl\end{array}\qquad\begin{array}{c}CH_2ONO_2\\ |\\ CHCl\\ |\\ CH_2OH\end{array}$$

All are obtained by nitrating chlorohydrin with not overmuch concentrated nitric acid, e.g. with a threefold excess of 80% acid. They can also accompany dinitrochlorohydrin as impurities. Owing to the presence of a hydroxy group they are moderately soluble in water. In the warm they dissolve collodion cotton. Mononitrochlorohydrin has weak, but distinct explosive properties; it can be made to detonate by a strong initiator though it is not exploded by impact.

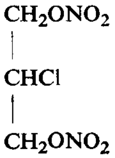
Dinitrochlorohydrin

The most important of the chlorohydrin nitrates are the chlorohydrin dinitrates ("dinitrochlorohydrins"), existing in two isomeric forms:



$$\begin{array}{c}CH_2ONO_2\\ |\\ CHONO_2\\ |\\ CH_2Cl\end{array}$$

α-dinitrochlorohydrin
(m.p. +5°C)



$$\begin{array}{c}CH_2ONO_2\\ |\\ CHCl\\ |\\ CH_2ONO_2\end{array}$$

β-dinitrochlorohydrin
(m.p. +16.2°C)

Dinitrochlorohydrin was first obtained by Henry [14] and Volney (15] who was the first to call attention to its explosive properties. It was used in blends with nitroglycerine for the manufacture of non-freezing dynamites [16, 17] as early as in 1904 and since then it has been rapidly adopted for this purpose in some countries, owing to its relative cheapness and simplicity of manufacture. The commercial product is a mixture of both isomers, the α-isomer predominating. Cooling to a temperature of —20°C usually fails to convert the substance into a solid since it is liable to supercooling. The specific gravity is 1.541 at 15°C. At 190°C commercial dinitrochlorohydrin boils and rapid decomposition occurs, whereas "boiling" under reduced pressure at 10 mm Hg occurs at 117.5°C with little decomposition. Dinitrochlorohydrin is more volatile than nitroglycerine. Naoúm reported that the loss of weight from a vessel of 50 mm diameter after standing for a day at 75°C was 3.1%, for dinitrochlorohydrin and 0.35% for nitroglycerine. It is non hygroscopic and dissolves in water only to small extent (about 2.3 g in 1 l. of water at 15°C). It dissolves with ease in most organic solvents, except carbon disulphide and petrol. Dinitrochlorohydrin mixes with nitroglycerine at any proportion, such mixtures having a very low freezing point. A blend of 75% nitroglycerine with 25% dinitrochlorohydrin can be considered practically non-freezing.

Collodion cotton is soluble with difficulty in pure dinitrochlorohydrin. Dissolution takes place more rapidly in the warm, but on cooling the dinitrochlorohydrin separates again from the sol. In blends of dinitrochlorohydrin with nitroglycerine nitrocellulose dissolves with great ease. Dinitrochlorohydrin is less viscous than nitroglycerine. According to Naoúm [8] its relative viscosity is 155, taking the viscosity of water as 100, as compared with 278 for the relative viscosity of nitroglycerine.

The chemical stability of dinitrochlorohydrin is higher than that of nitroglycerine. It withstands the Abel heat test at 72°C for 30 min. On heating at a temperature of 75°C, the first signs of decomposition and the development of acid fumes do not appear before 10–12 days. A small quantity of chlorohydrin dinitrate heated in a test tube undergoes decomposition with the evolution of oxides of nitrogen at temperature above 170°C. Complete decomposition takes place (without explosion at 180°C. Larger quantities of the substance decompose with a weak explosion, if heated rapidly to a temperature of about 190°C.

The explosive properties of dinitrochlorohydrin are as follows. The heat of explosion determined by Naoúm [8] in a calorimeter bomb (water in the liquid state, hydrogen chloride as hydrochloric acid) is 1140 kcal/kg. This value corresponds to a heat of explosion of 1000 kcal/kg when water and hydrogen chloride are assumed to be in the gaseous state in agreement with the equation given by Naoúm:

$$C_3H_5Cl(ONO_2)_2 \longrightarrow CO_2 + 2CO + 2H_2O + HCl + N_2 + 1000 \text{ kcal/kg}$$

Decomposition in accordance with the following equation is also possible:

$$C_3H_5Cl(ONO_2)_2 \longrightarrow 2CO_2 + CO + H_2O + H_2 + HCl + N_2 + 1050 \text{ kcal/kg}$$

Dinitrochlorohydrin can be ignited with difficulty to burn calmly without explosion. Chlorohydrin dinitrate placed in a can and thrown into a fire burns quietly, whereas in these circumstances nitroglycerine explodes. Dinitrochlorohydrin is less sensitive to shock than nitroglycerine or dinitroglycerine. According to Kast [18] in a drop test with a weight of 2 kg dinitroglycerine explodes on impact from a height of 10–20 cm (for nitroglycerine a height of 4 cm is sufficient to initiate explosion). The explosion of dinitrochlorohydrin caused by impact is appreciably weaker than that of nitroglycerine. Owing to its low sensitiveness to impact and the small risk of explosion on burning [19] in Germany chlorohydrin dinitrate was regarded as an explosive safe for transport by rail in containers of 25–200 kg.

Dinitrochlorohydrin produces the following expansion in the lead block (Naoúm) [8]:

with a No. 8 detonator and water tamping	475 cm^3
with a No. 1 detonator and water tamping	380 cm^3
blasting gelatine (made with 42% of dinitrochlorohydrin)	440 cm^3

The rate of detonation of dinitrochlorohydrin is lower than that of nitroglycerine, but no exact data have been reported.

The explosive strength of dinitrochlorohydrin is assumed to be about 80% that of nitroglycerine. As a component of mining explosives chlorohydrin dinitrate has the disadvantage of producing hydrogen chloride on explosion. It does not seem to be any more of practical use.

The raw material from which dinitrochlorohydrin is produced is chlorohydrin, made by treating glycerine with hydrochloric acid at a temperature of 100–120°C under pressure [20]. The substitution product is a mixture of α- and β-isomers. (The boiling point of α-chlorohydrin is 130°C at 18 mm Hg; that of β-chlorohydrin is 146°C at 18 mm Hg).

Chlorohydrin for the manufacture of dinitrochlorohydrin must be as pure as possible and should contain the minimum amount of water, HCl and polymerization products of glycerine, since the presence of these substances favours the formation of an emulsion during nitration and washing. Usually chlorohydrin was made in the explosives factory. After a single distillation the substance was transferred to the nitrating unit generally in admixture with glycerine.

Dinitrochlorohydrin is formed by nitrating monochlorohydrin with mixed acid in a manner analogous to the nitration of glycerine. Less heat is evolved than during the nitration of glycerine, and the operation can therefore be carried out more rapidly. Chlorohydrin is also less viscous than glycerine so that separation of the nitrated product is accomplished in a shorter time than in the corresponding process in nitroglycerine manufacture.

When 450 parts by weight of mixed acid composed of

40%	HNO_3
60%	H_2SO_4

are used to treat 100 parts of chlorohydrin at a temperature of 10–15°C, 161.5 parts of dinitrochlorohydrin (both isomers) are obtained, i.e. an 89% theoretical yield.

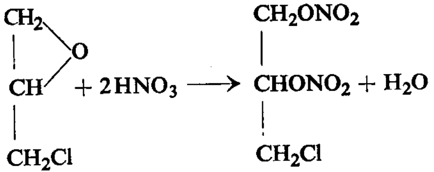
The composition of the spent acid is:

HNO_3	16.6%
H_2SO_4	75.0%
H_2O	7.4%

The solubility of dinitrochlorohydrin in the spent acid is negligible.

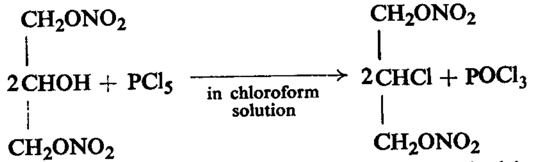
In practice, usually a mixture of chlorohydrin with 10–20% of glycerine is nitrated, to yield 165–175 parts of chlorohydrin dinitrates with nitroglycerine.

The pure isomers are obtained by the following chemical reactions:



Epichlorohydrin α-dinitrochlorohydrin

[14]



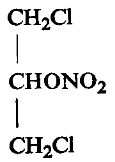
$$\begin{array}{c} CH_2ONO_2 \\ | \\ 2CHOH \\ | \\ CH_2ONO_2 \end{array} + PCl_5 \xrightarrow[\text{solution}]{\text{in chloroform}} \begin{array}{c} CH_2ONO_2 \\ | \\ 2CHCl \\ | \\ CH_2ONO_2 \end{array} + POCl_3$$

α-glycerol dinitrate β-dinitrochlorohydrin

[8]

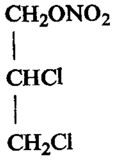
DICHLOROHYDRIN NITRATES

Two isomers of dichlorohydrin nitrate exist, also called "nitrodichlorohydrins" [14]:



$$\begin{array}{c} CH_2Cl \\ | \\ CHONO_2 \\ | \\ CH_2Cl \end{array}$$

b.p. 174°C

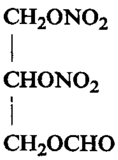


$$\begin{array}{c} CH_2ONO_2 \\ | \\ CHCl \\ | \\ CH_2Cl \end{array}$$

b.p. 182–183°C

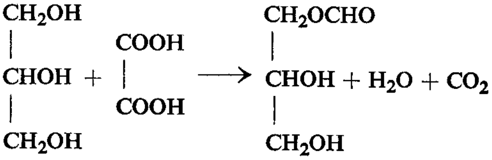
A mixture of these isomers has been suggested for addition to nitroglycerine for the production of low-freezing dynamites [21]. However, it possesses many properties undesirable for a component of explosives. It is more volatile than dinitrochlorohydrin, it is a poor solvent of collodion cotton and its explosive strength is insignificant. The heat of explosion developed by nitrodichlorohydrin is approximately 350 kcal/kg and the lead block expansion is 75 cm^3 including the effect produced by the initiator. For these reasons nitrodichlorohydrin has not found practical application. Nitrating dichlorohydrin by means of a water-free mixed acid is carried out with ease to produce a 94.5% yield (127.5 parts of nitrodichlorohydrin are obtained from 100 parts of dichlorohydrin).

FORMYLGLYCEROL DINITRATE



$$\begin{array}{l} CH_2ONO_2 \\ | \\ CHONO_2 \\ | \\ CH_2OCHO \end{array}$$

α-Formylglycerol dinitrate ("dinitroformylglycerine") is a strong explosive, its explosion producing about 1000 kcal/kg of heat. It is obtained as follows: 2 moles of glycerine are heated with 1 mole of anhydrous oxalic acid to a temperature of 140–150°C during a period of 20 hr to form monoformylglycerol:



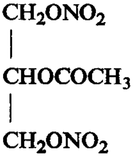
$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + \begin{array}{l} COOH \\ | \\ COOH \end{array} \longrightarrow \begin{array}{l} CH_2OCHO \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + H_2O + CO_2$$

A proportion of the glycerine remains unchanged and the resulting product is a solution of formylglycerol in glycerine. This is nitrated by means of a mixed nitric and sulphuric acid to yield a mixture containing 70% of nitroglycerine and 30% of dinitroformylglycerol.

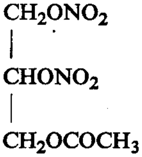
The explosion of this mixture which was proposed by Vender [22] as an additive to nitroglycerine in the manufacture low-freezing dynamites produces approximately 90% of the explosive power of nitroglycerine.

ACETYLGLYCEROL DINITRATE

Acetylglycerol dinitrate ("dinitroacetin", "nitroacetin") exists in two isomeric forms:



$$\begin{array}{l} CH_2ONO_2 \\ | \\ CHOCOCH_3 \\ | \\ CH_2ONO_2 \end{array}$$



$$\begin{array}{l} CH_2ONO_2 \\ | \\ CHONO_2 \\ | \\ CH_2OCOCH_3 \end{array}$$

This is another explosive suggested by Vender [22] for lowering the freezing point of nitroglycerine.

The commercial product composed of both isomers does not freeze at —20°C. Its boiling point is 147°C under 15 mm Hg. The specific gravity is about 1.42 at 15°C. Commercial nitroacetin is more volatile than nitroglycerine but less so than dinitrochlorohydrin. It is insoluble in water. Lower and even higher nitrated cellulose is dissolved in it with ease. The substance is a little less stable than nitroglycerine, because it undergoes a distinct decomposition accompanied by the evolution of oxides of nitrogen after being kept for 24 hr at a temperature of 75°C. Heated in a test tube it starts to decompose at 160°C. At 170–180°C decomposition proceeds violently. According to Naoúm [8] explosive decomposition is accompanied by the production of about 660 kcal/kg of heat.

Acetylglycerol dinitrate is almost insensitive to shock. Initiated with a No. 8 detonator it gives a lead block expansion of about 200 cm^3. A 92% blasting gelatine made from dinitroacetin produces an expansion of about 145 cm^3.

In comparison with dinitrochlorohydrin, dinitroacetin is more expensive but has the advantage that it does not evolve gases detrimental to health. In spite of this, the substance found only limited and transient application.

For blasting purposes mixtures in the proportion of 80 parts of nitroglycerine to 20 parts of dinitroacetin were usually used. This composition has an explosive strength of about 90% that of nitroglycerine. The manufacture of dinitroacetin, reported by Vender [22], consists in nitrating monoacetyl glycerol (monoacetin) by means of anhydrous mixed acid at a temperature below 25°C in the same kind of apparatus as that used for nitrating glycerine, the product being washed in the usual way. The yield is 159 parts by weight of dinitroacetin from 100 parts of monoacetin, i.e. 95% of theoretical.

POLYGLYCEROL ESTERS

As mentioned earlier the idea of nitrating glycerine polymerized by dehydration was suggested by Wohl [3]. He obtained a low-freezing blasting oil. However, this idea has not found an immediate practical application. One problem was the difficulty of feeding a nitrator with polyglycerine either dispersed as droplets or in the form of a thin stream owing to its very high viscosity. An even greater drawback was the tendency of polyglycerol nitrate to form emulsions not easy to separate and purify due to the presence of impurities.

Wohl proposed to polymerize glycerine by heating it with a small amount of sulphuric acid at a temperature between 130 and 160°C. Further investigations were reported by Will [23] who discovered that polymerization accompanied by the formation of water is most successful when glycerine plus a small quantity of sodium carbonate or sulphite (about 0.5%) is heated to a temperature approaching its boiling point. i.e. 290°C. The main product is diglycerol ether, more strictly 2,2′,3,3′-tetrahydroxydipropyl ether [*sym*-bis(2,3-dihydroxypropyl) ether], or the so called "diglycerine":

$$2C_3H_5(OH)_3 \longrightarrow CH_2OH—CHOH—CH_2—O—CH_2—CHOH—CH_2OH + H_2O$$

Triglycerine and polyglycerine are produced in inappreciable quatities (4–6%). The residual 30–40% is unchanged glycerine. The mixture can be nitrated directly and none of the difficulties accompanying the nitration of polyglycerol reported by Wohl occur. Diglycerine, the chief component of the mixture, starts to boil under a reduced pressure of 8 mm Hg at a temperature of 245–250°C. Its specific gravity is 1.33 and its viscosity is about 11 times greater than that of glycerine.

DIGLYCEROL TETRANITRATE

By nitrating "diglycerine" diglycerol tetranitrate, also called "tetranitrodiglycerine" or simply "nitrodiglycerine", is obtained:

$$CH_2ONO_2—CHONO_2—CH_2—O—CH_2—CHONO_2—CH_2ONO_2$$

Nitrodiglycerine is a liquid more viscous than nitroglycerine, which does not freeze even if subjected to the strongest cooling. It does not dissolve in water and is non-hygroscopic. Like nitroglycerine, it dissolves in the majority of organic solvents. Collodion cotton is only partially dissolved by it. The chemical stability of dinitroglycerine is not less than that of nitroglycerine.

The explosive properties of nitrodiglycerine are as follows. According to the work of Naoúm [8] and Will [7] nitrodiglycerine is capable of undergoing an explosive decomposition in accordance with the following equation:

$$C_6H_{10}N_4O_{13} \longrightarrow 2CO_2 + 4CO + 5H_2O + 2N_2 + 1330 \text{ kcal/kg}$$

Thus the substance is one of the strongest explosives known, and a composition made from 75% of nitroglycerine and 25% of nitrodiglycerine gives practically the same thermal effect as that caused by pure nitroglycerine.

In comparison with nitroglycerine, nitrodiglycerine has the advantage of being less sensitive to shock; it explodes on the impact of a 2 kg weight falling from a height of 8–10 cm.

The nitration of diglycerine to nitrodiglycerine is usually performed in the same way as the nitration of glycerine, certain differences being occasioned by the different properties of the substances. For the nitration of diglycerine slightly less mixed acid is needed than in the case of nitroglycerine. This is clear from the stoichiometric proportions and also follows from the fact that diglycerine is more prone to oxidation than glycerine and more sensitive to the action of an excess of nitrating acid. Owing to its high viscosity, diglycerine is heated up to 50–60°C before being introduced into the nitrator.

The separation of nitrodiglycerine is slower than that of nitroglycerine, mainly due to the high viscosity of nitrodiglycerine and to its tendency to form emulsions. The more impure the diglycerine, the easier is the formation of emulsions. After the separation of nitrodiglycerine, washing with a solution of common salt follows, the presence of which prevents emulsification. Moisture retained by the washed product is appreciably more difficult to remove than from nitroglycerine.

100 parts of diglycerine yield 168 parts of nitrodiglycerine, i.e. 81% of the theoretical yield. In practice the most commonly used method is the nitration of a mixture of 60–70% glycerine with diglycerine, from which a virtually non-freezing mixture of nitric esters is obtained [24].

Nitrodiglycerine is superior to dinitrochlorohydrin in low-freezing dynamites since it does not evolve hydrogen chloride among the explosion products. Also in favour of nitrodiglycerine is the fact that it does not dissolve in water. A further advantage is the ease of preparation of mixtures of diglycerine and glycerine. On the other hand, however, the removal of impurities from such mixtures presents difficulty, and their presence leads to difficulties in manufacturing the nitric ester. The high viscosity of diglycerine and of the resulting nitration product is also a disadvantage in the manufacturing process.

For these reasons, nitrodiglycerine has not been adopted in practice in some countries e.g. in Germany, where dinitrochlorohydrin was for many years the most widely used raw material until it was replaced recently by nitroglycol. Nitrodiglycerine came into a broad use only in Great Britain in the years between 1920 and World War II.

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23. W. Will, *Z. ges. Schiess- u. Sprenstoffw.* **1**, 231 (1906); *VI Intern. Congress of Appl. Chemistry, Rome 1906*, Vol. 2, p. 549.
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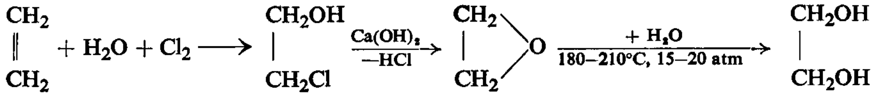
CHAPTER V

GLYCOL ESTERS

ETHYLENE GLYCOL ESTERS

THE first reference to the application of ethylene glycol dinitrate ("nitroglycol"), as a component of explosive mixtures was published by Claessen [1] as early as 1904 and Propach [2] in 1905. Subsequently in the years 1909–1914 [3] the original experiments were carried out aimed at decreasing the freezing temperature of nitroglycerine by adding nitroglycol. At that time the manufacture of glycol was based on the hydrolysis of dibromoethane. The method was very expensive and did not produce an economic yield, so glycol was not then manufactured on a commercial scale.

As a result of the acute shortage of glycerine that occurred in Germany during World War I a method was developed for manufacturing ethylene glycol by the hydrolysis of dichloroethane. However, this reaction produces a number of glycols of different chain length composed of various numbers of ethylene oxide units. Hence the method was superseded by another, which is still in use, consisting in the following chemical reactions:



(1)

In the presence of hypochlorous acid ethylene reacts to form ethylene chlorohydrin which, by means of calcium hydroxide in aqueous solution, is converted into ethylene oxide. The ethylene oxide is then hydrolysed with water to form glycol. In addition to ethylene glycol ("glycol") a certain amount of diethylene glycol ("diglycol") and triethylene glycol ("triglycol") are formed. On the average the percentage composition of the product is as follows:

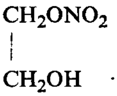
glycol	87–89%
diglycol	9–11%
triglycol	2–3%

All these components are capable of being nitrated.

Glycol, diglycol and triglycol are at present used for manufacturing their nitric esters all over the world. Glycol dinitrate, or nitroglycol, is the most important additive to nitroglycerine in the preparation of low-freezing dynamites. The marked volatility of this substance precludes its use for the production of smokeless powder.

Diglycol (2,2′-dihydroxydiethyl oxide) is also used as a substitute for glycerine. Diglycol dinitrate, or dinitrodiglycol, is less volatile than nitroglycol and most of it is utilised for the production of smokeless powder.

ETHYLENE GLYCOL MONONITRATE

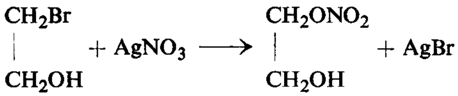


$$\begin{array}{c}CH_2ONO_2\\|\\CH_2OH\end{array}$$

Glycol mononitrate (mononitroglycol) is a by-product accompanying the nitration of glycol in the manufacture of nitroglycol (glycol dinitrate). Mononitroglycol is a liquid with a boiling point of 91–92°C under a vacuum pressure of 10 mm Hg. Its specific gravity at 20°C is 1.35, its viscosity being slightly higher than that of nitroglycol. Mononitroglycol is soluble in water and in most organic solvents. It readily dissolves collodion cotton. It is powerful enough explosive, its heat of explosion is 855.6 kcal/kg (water as vapour) and in the lead block test it produces an expansion of 375 cm^3 [4].

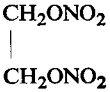
Mononitroglycol may be obtained in a manner analogous to the Mikołajczak process. Glycol is dissolved in 3 parts of nitric acid (density 1.51 g/cm^3) at a temperature of 0°C, the solution is poured onto ice and neutralized with a sodium carbonate solution. An oil consisting of glycol mononitrate (75%) and dinitrate (25%) separates [4]. From this oil mononitroglycol is extracted with water and purified by distillation under reduced pressure. The mononitrate can be further purified by re-dissolving in water and re-distillation. The yield of mononitrate is about 52% of theoretical. Mononitroglycol can be obtained from ethylene oxide and dinitrogen tetroxide. Nitrito-nitrate is formed and then the O-nitroso group is hydrolysed with sodium carbonate solution [39].

The simpliest laboratory method of preparing mononitroglycol consists in reacting ethylene bromohydrin with silver nitrate [5] in acetonitrile solution [6]:



$$\begin{array}{l}CH_2Br\\|\\CH_2OH\end{array} + AgNO_3 \longrightarrow \begin{array}{l}CH_2ONO_2\\|\\CH_2OH\end{array} + AgBr \qquad (2)$$

ETHYLENE GLYCOL DINITRATE ("NITROGLYCOL")



$$\begin{array}{c}CH_2ONO_2\\|\\CH_2ONO_2\end{array}$$

Physical properties

Ethylene glycol dinitrate (EGDN, GDN, or nitroglycol respectively) is a transparent liquid characterized by the following physical parameters: freezing point —22.3 or —22.8°C; boiling point 197.5, 105.5 (19 mm Hg) or 70°C (2 mm Hg);

density 1.5176 (at 0), 1.496 (at 15) or 1.489 g/ml (at 20°C). The latent heat of fusion of the frozen product is 30 kcal/kg. Nitroglycol, like nitroglycerine, is fairly soluble in the majority of organic solvents except carbon tetrachloride and petrol in which it dissolves to a smaller extent. Water mixes with it slightly more readily than with nitroglycerine. The solubility of nitroglycol in 100 ml of water varies with temperature (Naoúm [4]):

at 15°C	0.62 g
20°C	0.68 g
50°C	0.92 g

Other authors [40] quote the following value:

at 0°C	0.57 g

Nitroglycol dissolves collodion cotton with the greatest ease even in the cold, in this respect performing better than nitroglycerine. Nitroglycol is practically non-hygroscopic, and is significantly more volatile than nitroglycerine.

Different authors have published divergent values for the volatility of nitroglycol. Thus Moreschi [7] reported a vapour pressure of 0.3 mm Hg at 20°C. According to Rinkenbach [8] at a temperature of 22°C the vapour pressure is 0.0565 mm Hg. The data quoted are cited both by Naoúm and Meyer [9] and by Crater [10]. The most accurate values are those published by Marshall [11] for the temperature range 0–100°C:

temperature, °C	0	20	40	60	80	100
pressure, mm Hg	0.0044	0.038	0.26	1.3	5.9	22.0

According to the work of Brandner [12] the vapour pressure of nitroglycol at different temperatures is as follows:

temperature, °C	20	30	40	50
pressure, mm Hg	0.048	0.125	0.299	0.648

The vapour pressure of solutions of nitroglycol in nitroglycerine has been reported on p. 44 (Table 13).

In a publication of Rinkenbach [13] the volatility of nitroglycol was reported to be 2.2 mg/cm^2/hr. This value is 20 times greater than that for nitroglycerine. Since it possesses a sufficiently high vapour pressure at 100°C nitroglycol can be slowly steam distilled.

The viscosity of nitroglycol is appreciably lower than that of nitroglycerine (Moreschi [7]). At 15°C it amounts to 0.08056 P while at 40°C it is 0.02831 P. Rinkenbach [8] has reported a viscosity of 0.0363 P at 23.6°C the corresponding viscosity of nitroglycerine being 0.288 (and that of water 0.01 P), while in more recent data by the same author [13] a value of 4.2 cP (0.042 P) at 20°C is reported. The refractive index (*n*) is:

temperature, °C	0	15	25	35
n	1.4546	1.4491	1.4454	1.4417

Values for the physical constants of ethylene glycol dinitrate found by de Kreuk [14], and Boileau and Thomas [15] are given in Tables 2 and 3 respectively (p. 3). Dipole moments are given in Table 4 (p. 4).

Chemical stability

Like nitroglycerine, on heating with aqueous solutions of sodium or potassium hydroxides, nitroglycol is hydrolysed. In contact with an alcoholic solution of potassium hydroxide, it reacts vigorously to yield potassium nitrite and potassium glycolate.

Again like nitroglycerine, it is hydrolysed to some extent by hot water, the degree of hydrolysis (0.008% of the substance at 60°C during 5 days) being rather more marked than that of nitroglycerine. This is most probably due to the higher solubility of nitroglycol.

Like nitroglycerine, nitroglycol decomposes on prolonged contact with concentrated acids. Nevertheless numerous experiments have shown nitroglycol to be more stable than nitroglycerine. Thus when maintained at a temperature of 75°C the first symptoms of decomposition do not occur until after 11 days' heating. In spite of this nitroglycol usually fails to pass a heat test at 72°C. This is due to its high volatility and hydrolysis of the product that condenses on the potassium iodide–starch paper. Heating to a temperature of 195–200°C provokes an explosion less violent than that of nitroglycerine.

The activation energy E of the thermal decomposition of nitroglycol has been estimated:

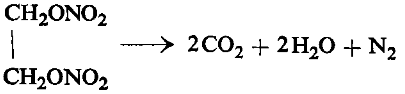
by Apin, Khariton and Todes [16] as 35.0 kcal/mole

by Andreyev *et al.* [17] as 35.7 kcal/mole

(for the coefficient B the authors found values of $\log_{10} B = 14$ and 14.3 respectively).

Explosive properties

Nitroglycol is a powerful high explosive, which detonates with complete decomposition:



$$\begin{array}{l} CH_2ONO_2 \\ | \\ CH_2ONO_2 \end{array} \longrightarrow 2CO_2 + 2H_2O + N_2 \tag{3}$$

Owing to thorough utilization of the carbon, hydrogen and oxygen the thermal effect of explosion is larger than in the case of nitroglycerine. An explosion of 1 kg nitroglycol is accompanied by the evolution of 1580 kcal (water vapour) or 1705 kcal (condensed water), i.e. 7% more than that produced by nitroglycerine. The heat of formation $-\Delta H_f$ of nitroglycol is 67.7 kcal/mole.

Nitroglycol is less sensitive to impact than nitroglycerine. It explodes under a 2-kg weight falling from a height of 20–25 cm.

According to Andreyev's [17] experiments when contacted with a flame nitroglycol behaves in a slightly different way from nitroglycerine: it burns quietly at atmospheric pressure. In glass tubes 4 mm dia. within a pressure range of 300–770 mm Hg at 14–15°C, its burning rate increases linearly with the pressure, in accordance with the equation

$$U = A + Bp$$

Burning ceases as soon as the pressure drops below 230 mm Hg.

The same linear relation between the rate of burning and the pressure holds for values up to 10 kg/cm^2, after which a further increase in pressure causes a faster increase in the rate of burning, until detonation occurs.

Analysis of the combustion products of nitroglycol obtained at atmospheric pressure (Altukhova and Andreyev [18] indicates a high content of NO (nearly all the nitrogen being present in that form), and of CO_2, CO and CH_4.

The combustion of large amounts of the substance can lead to explosion. Liquid nitroglycol is more readily initiated by means of a detonator than liquid nitroglycerine, and explosive combinations containing nitroglycol behave similarly.

Nitroglycol, like nitroglycerine, can detonate with high or low velocity. The following figures indicate the rate of detonation:

TABLE 20

DATA CHARACTERIZING THE DETONATION RATE OF NITROGLYCOL

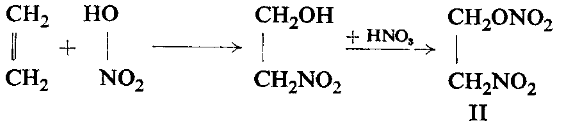
State of aggregation	Method of loading	Initiation	Rate m/sec	Author
liquid	in an iron pipe, 32–38 mm dia.	No. 8 detonator	7830	Naoúm and Berthmann [19]
liquid	in an iron pipe 32–38 or 35–43 in. dia.	80 g picric acid	8200–8300	Naoúm and Berthmann [19]
liquid	in a crucible	No. 8 detonator	1000–3000	Stettbacher [20]
solid (−70°C)	in a crucible	No. 8 detonator	over 8000	Stettbacher [20]

In a lead block with water tamping nitroglycol causes an expansion of 650 cm^3, i.e. 110% of that produced by nitroglycerine.

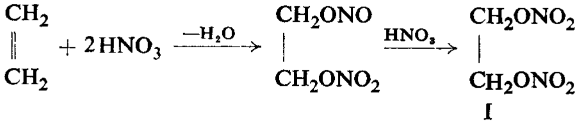
The biological properties of nitroglycol resemble those of nitroglycerine, but the effect caused by breathing the vapour of nitroglycol is usually stronger, on account of its higher volatility and hence its higher concentration in air, though less persistent for the same reason of higher volatility [21].

Manufacture of nitroglycol

The first papers discussing methods of preparing glycol dinitrate from glycol and its properties were published by Champion [22] and Henry [5]. At that time they were only of theoretical interest in the absence of economic methods of preparing ethylene glycol. According to a report by Kekulé [23] published as early as 1869, by passing ethylene through a mixture of nitric and sulphuric acids an oily substance was obtained which was hydrolysed in the presence of water vapour to form nitric acid, oxides of nitrogen, glycolic acid and oxalic acid. By reduction with sodium amalgam, a certain amount of glycol and ammonia were obtained. It was not until 1920 that Wieland and Sakellarios [24] made it clear that the components of Kekulé's oil were: nitroglycol (glycol dinitrate) (I) and nitric ester of β-nitroethyl alcohol, i.e. β-nitroethyl nitrate (II). They suggested that the reaction of nitrating ethylene proceeds as defined by equations (4) and (5).



$$\begin{array}{l} CH_2 \\ \| \\ CH_2 \end{array} + \begin{array}{l} HO \\ | \\ NO_2 \end{array} \longrightarrow \begin{array}{l} CH_2OH \\ | \\ CH_2NO_2 \end{array} \xrightarrow{+HNO_3} \begin{array}{l} CH_2ONO_2 \\ | \\ CH_2NO_2 \\ \quad II \end{array} \qquad (4)$$

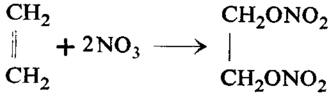


$$\begin{array}{l} CH_2 \\ \| \\ CH_2 \end{array} + 2HNO_3 \xrightarrow{-H_2O} \begin{array}{l} CH_2ONO \\ | \\ CH_2ONO_2 \end{array} \xrightarrow{HNO_3} \begin{array}{l} CH_2ONO_2 \\ | \\ CH_2ONO_2 \\ \quad I \end{array} \qquad (5)$$

Fifty to sixty per cent of ethylene reacts in accordance with eqn. (4), and 40–50% in accordance with eqn. (5). Numerous attempts to use an oil comprising a mixture of (I) and (II) in the manufacture of explosives have been unsuccessful, because β-nitroethyl alcohol nitrate is insufficiently stable. Experiments have been made to partially hydrolyse the oil with hot water at 80–90°C. Under these conditions nitroethyl nitrate undergoes decomposition, whereas nitroglycol remains unchanged (Oehme [25]). However, the method was not adopted in practice because the yield of nitroglycol is relatively low, i.e. about 40% by weight of the oily product.

Finally in 1920 Oehme proposed a method for the nitration of ethylene oxide, whereby an oil composed mainly of nitroglycol is produced. Unfortunately, the quality of the product is appreciably impaired by other products which are formed simultaneously, hence the method was not accepted by the industry.

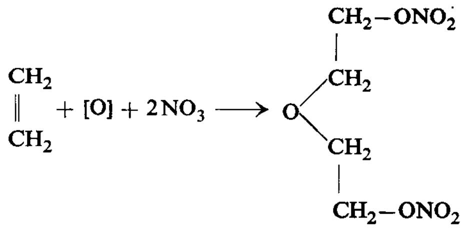
A later method proposed by Oehman [26] produces glycol nitrate and diethylene glycol from ethylene by electrolysis. A platinum wire mesh submerged in an acetone solution of calcium nitrate acts as anode, ethylene being blown through the solution continuously. The cathode space behind the aluminium cathode is filled with a solution of calcium nitrate in nitric acid. At the anode the nitrate ion forms a free radical NO_3 which combines partially with ethylene to produce nitroglycol (6);



$$\begin{array}{l} CH_2 \\ \| \\ CH_2 \end{array} + 2NO_3 \longrightarrow \begin{array}{l} CH_2ONO_2 \\ | \\ CH_2ONO_2 \end{array} \qquad (6)$$

According to Oehman a proportion of the free nitrate radicals reacts with one another according to reaction (7) probably accompanied by the evolution of oxygen that combines with NO_3 radicals to form diethylene glycol dinitrate, as outlined in eqn. (8):

$$2NO_3 \longrightarrow N_2O_5 + [O] \xrightarrow{+H_2O} 2HNO_3 \longrightarrow 2NO_3 \qquad (7)$$



(8)

The anode liquor is neutralized by means of calcium hydroxide, and acetone is removed by distillation. The residue consists of calcium nitrate and glycol dinitrate. These are separated by filtering and the product is washed with water in the usual way. For a certain time this method was used industrially.

In the present time nitroglycol is produced in exactly the same way as nitroglycerine.

Particularly extensive investigation into the kinetics of ethylene glycol nitration have been carried out by Oehman *et al.* [40, 41], Roth, Stow and Kouba [27]. The mixed acid ranged in composition from 11.5 to 20% of water, 18–40% of HNO_3 and 45–68.5% of H_2SO_4. The ratio of mixed acid to ethylene glycol weight ranged from 12 to 24.

Roth *et al.* found that with mixed acids containing less than 15% water, conversion of glycol to ethylene glycol dinitrate was quantitative. Increase in the temperature of the nitrator content can serve as a criterion of the progress of the reaction.

The heat evolution of the reaction is strongly influenced by the amount of water in the mixed acid (Fig. 65). The bottom curve (mixed acid with 20% H_2O) has practically no slope. In these experiments no glycol dinitrate was obtained. The initial increase of temperature here is probably due to the heat of solution of glycol in mixed acid followed by slow nitration.

The heat of nitration ΔH_n from the equation: $\text{Glycol} + 2HNO_3 \text{ (liq.)} \longrightarrow$ $\longrightarrow \text{GDN} + 2H_2O \text{ (liq.)} + \Delta H_n$ was found to be 8.5 kcal/per mole of glycol.

The reaction carried out in larger equipment duplicated the data found on a small scale.

The reaction is virtually finished after 1–$1\frac{1}{2}$ sec.

The manufacture of nitroglycol on an industrial scale consists in the nitration of glycol in the same type of plant as those used for the production of nitroglycerine.

German standards [28] require that glycol used for nitrating should correspond to the following conditions: the limits of boiling temperature to be 196–200°C, density 1.1130–1.1135 g/cm^3 (20°/4°), acidity below 0.1, and saponification value below 1.0 (Na_2O).

In consequence of the slightly different properties of the raw materials and the products, there exist some divergencies in the course of nitrating glycol as compared with glycerine nitration. No pre-heating of the glycol is necessary before nitration, since the viscosity of glycol is appreciably lower than that of glycerine. The heat produced during the nitration of glycol is a little less than with glycerine, and the slightly higher nitration rate makes the process quicker. Furthermore, it is possible to use more intensive cooling without any danger of freezing the product. The optimal temperature of nitrating is 10–15°C, higher temperature reduces the yield.

In view of the higher solubility of nitroglycol in water as little water as possible should be used for washing. Both for the above reason and because of the higher volatility of nitroglycol, the use of very warm wash water should be avoided. In order to minimize the loss caused by the volatility of nitroglycol gentle stirring with water and neutralizing solutions by means of compressed air must be carried out with care. This does not exert any adverse effect on the purity of product, because the viscosity of nitroglycol is lower than that of nitroglycerine and vigorous stirring is not necessary.

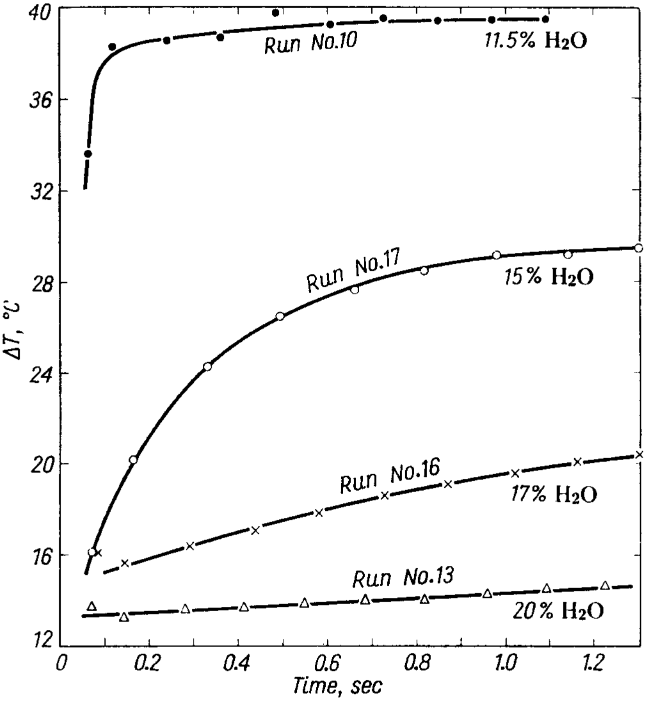


FIG. 65. Heat evolution on nitration of ethylene glycol with nitrating mixtures of variable water content (Roth, Stow and Kouba [27]).

Ropuszyński [29] reports a more elevated temperature for nitrating glycol giving a product containing less residual acid (as observed by the same author in the case of nitroglycerine)—Table 21.

TABLE 21

Temp. of nitration °C	Residual acid content		Heat test min
	% HNO_3	% H_2SO_4	
15	0.0088	0.0015	16
25	0.0041	0.0010	18

Since nitroglycol is more soluble and more volatile a marked loss of product occurs so that the yield of nitroglycol is relatively lower than that of nitroglycerine. 100 kg of glycol at 10–12°C yield 222 kg of nitroglycol, i.e. 90.5% of the theoretical yield of 245 kg.

Handling the spent acid from nitroglycol manufacturing is appreciably safer than handling spent acid from the manufacture of nitroglycerine, since nitroglycerine remains longer in contact with spent acid than nitroglycol. This factor, plus the lower sensitiveness of nitroglycol to impact and its smaller tendency to explode by ignition combine to make the manufacture of nitroglycol less dangerous than the production of nitroglycerine. That there is less danger of nitroglycol contacting spent acid as compared with nitroglycerine can also be seen from the diagram of Oehman, Camera and Cotti [42] (Fig. 26, p. 84).

In practice a mixture of glycerine and glycol in a 50/50 ratio is usually nitrated, so as to produce in one operation a product suitable for use in low-freezing dynamites.

DIETHYLENE AND TRIETHYLENE GLYCOL ESTERS

DIETHYLENE GLYCOL DINITRATE

$$CH_2ONO_2-CH_2-O-CH_2-CH_2ONO_2$$

Diethylene glycol dinitrate is also known as diglycol dinitrate and DEGDN (dinitrodiethylene glycol) or, more exactly, di-(ethyl-2-ol) ether dinitrate or 2,2′-dihydroxydiethyl ether dinitrate. Its commercial names are: Dinitrodiglycol, Nitrodiglycol and DNDG. In English speaking countries the abbreviations DEGDN, DGDN or DEGN are commonly used.

Physical properties

Dinitrodiglycol exists in two crystalline forms — a stable form melting at a temperature of +2°C and a labile one whose melting point is —10.9°C (thus resembling nitroglycerine). At 20°C it is an oily liquid of density 1.385 g/cm^3, boiling and simultaneously decomposing at 160°C. Its refractive index is 1.4517 (at 20°C).

Dinitrodiglycol is more volatile than nitroglycerine. Its vapour pressure is 0.0036 mm Hg at 20°C and 0.130 mm Hg at 60°C. Its volatility at 60°C is 0.19 mg/cm^2/hr.

Dinitrodiglycol dissolves in nitroglycerine, nitroglycol and in some organic solvents. It is scarcely miscible with ethyl alcohol, carbon tetrachloride and carbon disulphide. The solubility in 100 g water is 0.40 g at 25°C and 0.46 g at 60°C. Oehman [43] and Aubertein [44] made a detailed investigation of the solubility of dinitrodiglycol in mixed acids (Fig. 66).

Hackel and Kuboszek [30] have examined the eutectics of both forms of DEGDN with *sym*-trinitrobenzene and *α*-trinitrotoluene (Table 22).

Collodion cotton is very readily dissolved in diethylene glycol dinitrate, more so than in nitroglycerine. The viscosity of diethylene glycol dinitrate at 20°C is 8.1 cP, i.e. lower than that of nitroglycerine.

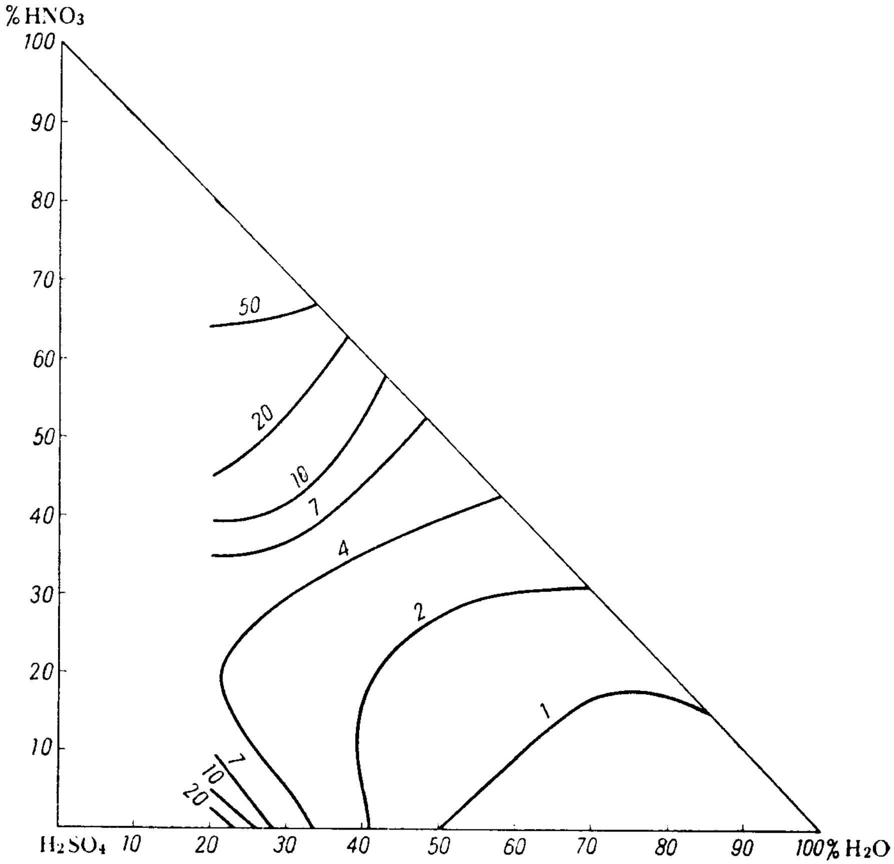


FIG. 66. Solubility of DEGDN in mixed acids [44].

TABLE 22

The second component	Eutectics			
	Stable form		Labile form	
	% of the second component	freezing temp. °C	% of the second component	freezing temp. °C
TNB	8.0	−13.2	11.5	−1.4
TNT	17.0	−15.5	20.5	−3.0

Stability and thermal decomposition

The chemical stability of dinitrodiglycol resembles that of nitroglycerine. Heated with water it undergoes hydrolysis more slowly than nitroglycerine: on being maintained for 5 days at 60°C only 0.003% is decomposed. Hydrolysis in the presence of acids (Fig. 67) or sodium hydroxide is also more difficult. On the other hand dinitrodiethylene glycol decomposes more readily than nitroglycerine when exposed to action of spent acid probably due to the presence of ether-oxygen in the molecule.

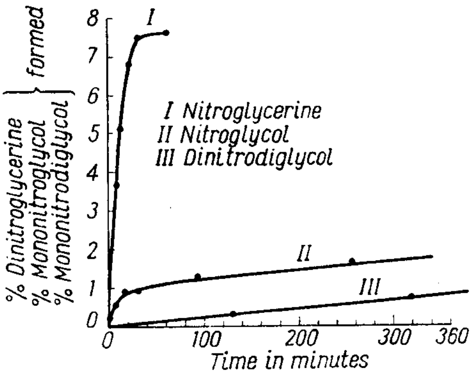


FIG. 67. Rate of denitration of nitroglycerine, nitroglycol and dinitrodiglycol with mixed acid containing 7.5–10.5% HNO_3 and 0.5–1.1% H_2O (Oehman [43]).

The relation between the chemical stability and nitrating temperature observed by Ropuszyński [29] in the instance of nitroglycerine (p. 43) and nitroglycol (p. 148) has been also confirmed with dinitrodiglycol. Diglycol nitrated at a higher temperature demonstrates improved stability owing to its lower content of residual acids. The relevant data are shown in Table 23.

TABLE 23

THE RELATION BETWEEN THE NITRATING TEMPERATURE AND RESIDUAL ACID CONTENT

Nitrating temperature °C	Residual acid content		Heat test min
	%HNO_3	%H_2SO_4	
15	0.138	0.0025	22
25	0.0069	0.0015	30

Dinitrodiglycol is as toxic as nitroglycerine. It explodes at a temperature of 200°C developing a relatively small heat of detonation that amounts to 1070 kcal/kg. Advantage is taken of this property in the manufacture of flashless and non-errosive low calorific smokeless ("double base") powder.

Dinitrodiglycol is incomparably less sensitive to shock than nitroglycerine, in this respect approaching nitrocompounds, such as TNT. It explodes on impact with a 2-kg weight dropped from a height of 160 cm. It is ignited by a direct flame with some difficulty and having been ignited it does not explode like nitroglycerine.

It follows from the investigations of Andreyev [17] that dinitrodiglycol is less capable of burning than nitroglycerine. Thus in glass tubes of 5–6 mm dia. it does not burn at 15°C. To obtain burning the tube diameter must be increased to 8 mm or the initial temperature to 40°C. The linear velocity of burning is at that time only half that of nitroglycol.

The increments of pressure required to increase the velocity of burning can be determined by the following equation:

$$U = 0.0162 + 0.0122p$$

At a pressure of 55 kg/cm^2 the burning acquires a pulsating character and its velocity increases rapidly. This behaviour is similar to that of the majority of nitric esters.

Explosive properties

Dinitrodiglycol detonates either at a high velocity of 6800 m/sec, or at a low velocity of 1800–2300 m/sec. Its ability to detonate is less than that of nitroglycerine. Its lead block expansion value is 425 cm^3, i.e. about 70% that of nitroglycerine.

Diglycol dinitrate is widely used in the explosives industry owing to its excellent capacity of dissolving nitrocellulose, the relative safety of handling it and most of all to its comparatively low price, which is less than that of nitroglycol and only slightly higher than that of nitroglycerine. Its weak point is its particular tendency to decompose in the presence of acid, so that storing spent acid is more dangerous than in nitroglycerine manufacture.

Methods of production

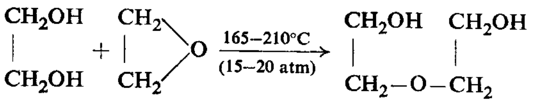
The raw material for the production of dinitrodiglycol, i.e. diethylene glycol, was synthesized as early as 1859 by Wurtz who saturated water and glycol with ethylene oxide at a temperature of 100°C. He tried to nitrate diethylene glycol, but the reaction yielded solely oxidation and hydrolysis products: glycolic acid, oxalic acid and other acids, probably because the temperature was too high. Rinkenbach [8a] published the first description of the properties of dinitrodiethylene glycol, while the industrial nitration process was originally reported by Rinkenbach and Aaronson [31]. These authors established that the largest yield was obtained by using a mixture of acids composed of

50%	HNO_3
45%	H_2SO_4
5%	H_2O

in the proportion of 367 parts of mixed acid to 100 parts by weight of diethylene glycol at a temperature of 10–15°C.

In this way, from 100 parts of diethylene glycol, these authors obtained 158 parts of the product. This is 85.4% of the theoretical yield. Laboratory scale nitration can give 93% yield [42].

In the factory at Krümmel [28] the first stage of manufacturing dinitrodiethylene glycol was the conversion of glycol and ethylene oxide into diethylene glycol according to the equation:



(9)

Diethylene glycol was separated from the reaction product by fractional distillation. Its properties should meet the following standard requirements. It must be an odourless, transparent, colourless or slightly coloured liquid, with a specific gravity of 1.1157–1.1165 at 20°C and maximum water content of 0.5%. Under a pressure of 760 mm Hg 99 parts by weight should distil within temperatures of 241.0°C (at the beginning of distillation) and 246.5°C, the residual 1% coming over below 250°C. The whole distillation should take 25 min. (For barometric pressure a correction of 0.05° for every millimeter of mercury is applicable). Acidity lower than 0.02% (as H_2SO_4) is required, the saponification value may bé up to 0.05% (as Na_2O), chlorides can be present only in traces, reducing agents must be absent and the maximum permissible glycol content is 2%.

Diethylene glycol is highly hygroscopic (more so than ethylene glycol), and so must be stored in sealed containers. The viscosity of diethylene glycol is a little higher than that of ethylene glycol, but it is appreciably less viscous than nitroglycerine, hence it is not necessary to heat diethylene glycol before feeding it into the nitrator.

At Krümmel [28] the mixed acid composed of

65%	HNO_3
35%	H_2SO_4

was prepared by mixing nitric acid of 98–99% with oleum 26% and with sulphuric acid. The nitrating acid should be freed from oxides of nitrogen as carefully as possible.

The nitration was carried out by a batch method, each charge comprising 420 kg diglycol and 1218 kg mixed acid. As a safety precaution for storing the spent acid, an excess of 293 kg HNO_3 was added to the mixed acid (theoretically 499 kg of HNO_3 are necessary for nitrating 420 kg of diglycol).

The nitration process was performed in the usual equipment, controlling the temperature, which should not exceed 25°C, by cooling with a 35% sodium nitrate solution, the temperature of which was −15°C. Under these conditions nitration lasted about 25 min. When the nitration was completed, the contents of the nitrator were cooled down to 15°C and transferred to a separator. The separation was accomplished within 7 min and the spent acid was immediately sent to the denitration unit. Special care had to be taken to ensure that no spent acid remained in the tank, because decomposition of the residual dinitrodiethylene glycol may start within a few hours. None the less such decomposition is less hazardous than that of nitroglycerine, since dinitrodiethylene glycol produces a spontaneous explosion only in the instance when the tank is confined.

The spent acid consisted of:

HNO_3	28–29%
H_2SO_4	44–46%
H_2O	20–24%
Dinitrodiglycol	4–5%

The high proportion of nitric acid in the spent acid inhibits hydrolytic decomposition of DEGDN.

Diethylene glycol dinitrate was washed twice after separation, the primary washing being carried out with some 300 l. of water, to give an acid wash water containing

3–4%	HNO_3
5%	H_2SO_4
2–3%	dinitrodiglycol

When the dinitrodiglycol has been separated, the washings were transferred for denitration.

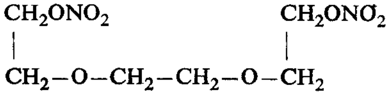
For the second, final washing, 500 l. of cold water were used, after which the product is neutralized with 150 l. of a 5% sodium carbonate solution heated to a temperature of 60°C, and then washed using 500 l. of water.

A sample of dinitrodiglycol subjected to the heat test should withstand a temperature of 82°C for 20 min. Should the product fail the test washing with sodium carbonate solution and water should be repeated.

From each nitration charge 710–715 kg of dinitrodiethylene glycol were produced, i.e. about 92% of the theoretical yield.

TRIETHYLENE GLYCOL DINITRATE

Triethylene glycol dinitrate (dinitrotriethylene glycol, nitrotriglycol, dinitrotriglycol or triglycol dinitrate):



$$\begin{array}{ccccc} CH_2ONO_2 & & & & CH_2ONO_2 \\ | & & & & | \\ CH_2 & -O- & CH_2-CH_2 & -O- & CH_2 \end{array}$$

is an oily liquid, with a specific gravity of 1.335. It is characterized by a wholly insignificant sensitiveness to shock, resembling that of dinitrobenzene. Its stability is similar to that of dinitrodiethylene glycol. Its heat of detonation is 750 kcal/kg.

The raw material for manufacturing dinitrotriethylene glycol i.e. triethylene glycol ("triglycol"), should meet the following requirements. It should be a transparent liquid of yellowish colour, with a faint smell. It should not contain glycol and the maximum content of water should be 0.1%. Specific gravity should be 1.1217 at 20°C, and the refractive index at 20°C should be 1.4552. On distillation 95.2 parts by volume should distill over within the temperatures range of 278.8 to 310°C, leaving a solid residue not exceeding 0.001%. Maximum acid content should be 0.005% (as H_2SO_4), the maximum saponification value 0.632% (as Na_2O), chlorine may be present only in traces, and reducing agents must be absent.

According to information from the factory at Krümmel [28] triethylene glycol was nitrated with an acid mixed in the proportion:

HNO_3	70%
H_2SO_4	30%

For a 500 kg charge of triglycol, 1250 kg of nitrating acid were used, nitration being carried out during a period of 30 min.

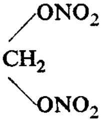
The solubility of dinitrotriethylene glycol in the spent acid is exceptionally high amounting to 8–9%. Denitrating such an acid can be hazardous in view of the presence of such a large amount of an explosive substance. Separation takes place slowly and lasts over half an hour. This is an added hazard, since dinitrotriglycol readily decomposes in the presence of spent acid. It is therefore necessary to add water to the spent acid before the oily explosive material is separated, and the residual spent acid is transferred to the denitration unit. The separated oil is washed twice with water, then with a sodium carbonate solution and finally with water. A sample of washed and neutralized triethylene glycol dinitrate should withstand the heat test for 20 min at 82°C.

From 500 kg of triglycol, 650 kg of dinitrotriethylene glycol, i.e. 72.6% are obtained.

A laboratory scale reaction can give 86–87% yield [43].

ESTERS OF OTHER GLYCOLS

METHYLENE GLYCOL DINITRATE



$$CH_2(ONO_2)_2$$

Methylene glycol dinitrate, or "nitromethylene glycol", is an oily liquid having a boiling point of 75–77°C at 20 mm Hg.

It is a strong explosive, capable of dissolving collodion cotton. However it is not stable, being readily hydrolysed and therefore it is of no practical significance.

A method of obtaining this explosive, by the nitration of moist paraformaldehyde was patented by Travagli and Torboli [32]. They utilised the well-known property of formaldehyde of reacting like methylene glycol in the presence of water.

According to Travagli [33] methylene glycol dinitrate is obtained as follows: paraformaldehyde is dissolved in sulphuric acid and added drop-wise at 3–5°C into a mixture of nitric and sulphuric acid. The resulting oil is separated and washed with water to give a final yield of 35%.

TRIMETHYLENE GLYCOL DINITRATE

Trimethylene glycol dinitrate, 1,3-propylene glycol dinitrate (1,3-propanediol dinitrate) or nitropropylene glycol

$$O_2NO-CH_2-CH_2-CH_2-ONO_2$$

is an oily liquid boiling at 180°C under 10 mm Hg, with a specific gravity of 1.393 at 20°C. It is more volatile and less viscous than nitroglycerine. It is miscible with the same solvents as nitroglycerine. It dissolves collodion cotton fairly well. For the various physical constants of 1,3-propylene glycol dinitrate (such as viscosity, refractive index, dielectric constant, dipole moment) — see Tables 2, 3, and 4 (pp. 3 and 4).

Concentrated nitric acid decomposes it with oxidation.

The chemical stability of trimethylene glycol dinitrate is excellent. A sample kept at a temperature of 75°C for a period of 25 days does not decompose. In the heat test, the iodide–starch paper is coloured only because of the volatility of the substance.

Nitropropylene glycol is a strong explosive. According to Naoúm [4] the heat of detonation is 1138.5 kcal/kg (water as vapour). When heated it explodes at 225°C. Its sensitiveness to impact is very low: a 2-kg weight falling from a height of 100 cm fails to initiate an explosion. According to Naoúm it gives an expansion of 540 cm^3 in the lead block with water tamping, which is equivalent to 90% of that produced by nitroglycerine. The expansion produced by a 93% blasting gelatine made from trimethylene glycol dinitrate is 470 cm^3, i.e. 80% of the effect produced by the same gelatine made from nitroglycerine.

Trimethylene glycol dinitrate aroused interest during World War I, since a considerable amount of trimethylene glycol occurs in glycerine obtained by the fermentation method. Furthermore glycerine may be converted to trimethylene glycol by bacterial action, as demonstrated by Freund [34] as early as 1881. It has been established that the amount of glycol formed during glycerol fermentation is insignificant and that it is formed mainly from glycerine as a result of secondary fermentation processes. A high concentration of sulphite in the fermentation vats prevents the formation of glycol, but its formation is stimulated by decreasing the sugar content of the mash.

Most of the trimethylene glycol can be separated from glycerine by distillation since glycol has a significantly lower boiling point.

The presence of glycol does not have any adverse effect on nitration, it merely reduces the yield.

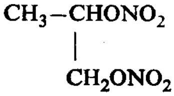
Pure trimethylene glycol boils at 211°C, its specific gravity is 1.0526 (at 18°C). Trimethylene glycol distilled from fermentation glycerine contains a certain amount of sulphur compounds (0.6–0.7% expressed as sulphur).

According to Naoúm [4] the nitration of trimethylene glycol requires a lower temperature than that used for nitrating glycerine, because the central methylene group is readily oxidized at a higher temperature. A temperature between 0 and 10°C is recommended since decomposition is possible even at 15°C, while at 20°C yellow fumes are evolved. Separating the product from the spent acid occurs with ease at 10°C. From 100 parts of trimethylene glycol, 198 parts of dinitrate are produced corresponding to 90.6% of the theoretical yield.

The spent acid behaves differently from that remaining after the nitration of nitroglycerine, since after an interval of time the glycol dinitrate contained in the solution undergoes oxidation, accompanied by a temperature rise of as much as 30°C and by the evolution of oxides of nitrogen, and carbon dioxide.

As shown by Naoúm [4] a mixture of glycerine with 5–10% trimethylene glycol can be nitrated without difficulty at 30°C, the mixture behaving like pure glycerine. Nevertheless, if the proportion of trimethylene glycol amounts to 20%, the inclination to oxidation is evident initially at a temperature of 20°C but if the reaction is carefully controlled it is possible to perform the nitration at 25°C. The spent acid that remains after nitrating such mixtures behaves like the acid resulting from the nitration of glycerine, except that its content of NO_2 developed by the oxidation processes is greater.

METHYL GLYCOL DINITRATE



$$\begin{array}{l} CH_3-CHONO_2 \\ \qquad\quad | \\ \qquad\ CH_2ONO_2 \end{array}$$

Methyl glycol dinitrate (propylene-1,2-glycol dinitrate or 1,2-propanediol dinitrate) is an oily liquid, boiling at 92°C at 10 mm Hg. Its specific gravity is 1.368 (at 20°C). The liquid does not freeze at a temperature of —20°C. It is more volatile than the isomeric propylene-1,3-glycol dinitrate.

Various physical constants of 1,2-propyleneglycol dinitrate (such as viscosity, refractive index, dielectric constant, dipole moment) are given in Tables 2 and 4 (pp. 3 and 4).

In physical properties and explosive parameters methyl glycol dinitrate resembles its isomer. The heat of detonation as 1110 kcal/kg (water as vapour). The expansion produced in the lead block with water tamping is 540 cm^3 [4].

As early as in 1904 the substance was proposed [35] as an additive to lower the freezing temperature of nitroglycerine, but its practical application on a large scale was hindered by lack of the raw material, propan-1,2-diol. It is only recently that the synthesis of glycol from ethylene led to the development of a method for producing methyl glycol from propylene via chlorohydrin. Even so, propylene-1,2-glycol is somewhat more expensive than glycols derived from ethylene.

1,2-Propylene glycol was nitrated by Naoúm [4] using mixed acid composed of

40%	HNO_3
60%	H_2SO_4

at a temperature of 20°C to produce 187 parts of product from 100 parts of glycol, i.e. an 86% yield.

A mixed acid containing

47.5%	HNO_3
45.5%	H_2SO_4
7%	H_2O

was used by Matignon, Moureau and Dode [36] at 10°C. By using 10% excess of HNO_3 they achieved a yield of 91–93%.

1,3-BUTYLENE GLYCOL DINITRATE

$$CH_3{-}CHONO_2{-}CH_2{-}CH_2ONO_2$$

Butylene-1,3-glycol dinitrate (1,3-butanediol dinitrate), also called "dinitrobutylene glycol", is an oily liquid (at 15°C) which does not freeze at a temperature of —20°C. Its specific gravity is 1.32. Dinitrobutylene glycol is more volatile than nitroglycerine, but less so than nitroglycol. Collodion cotton dissolves in it fairly easily [4,37].

For other physical constants of 1,3-butanediol dinitrate see Tables 2 and 4 (pp. 3 and 4).

The substance is characterized by excellent chemical stability. Its explosive strength, as measured by the expansion produced in the lead block, is equivalent to about 75% of the explosive strength of nitroglycerine.

As early as in 1911 butylene-1,3-glycol dinitrate was suggested [38] as a component of explosives either alone or blended with nitroglycerine.

Its raw material, 1,3-butylene glycol, is produced from acetaldehyde by conversion into acetaldol and reduction to the glycol:

$$2CH_3CHO \longrightarrow CH_3 \cdot CHOH \cdot CH_2 \cdot CHO \longrightarrow CH_3CHOH \cdot CH_2 \cdot CHOH \quad (10)$$

Naoúm [4] nitrated 1,3-butylene glycol and obtained a yield of 93.7%, i.e. from 100 parts of butylene glycol, 187.5 parts of dinitrate were obtained. (See also Matignon *et al.* [36], Aubry [37]). Aubertein [42], however, pointed out the difficulty of nitrating 1,3-butylene glycol with nitric–sulphuric acid mixtures.

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CHAPTER VI

MONOHYDROXYLIC ALCOHOL ESTERS

METHYL NITRATE

For a long time methyl nitrate CH_3ONO_2 has aroused interest, for it is the simplest ester of nitric acid and at the same time one of the strongest explosives. However, its high volatility and low boiling point prevented practical application until World War II, though it was used in the nineteenth century for a certain time in the organic chemical industry as a methylating reagent, e.g. instead of methyl sulphate. This application soon ceased owing to the danger of handling the substance. During World War II, it was used in Germany under the name myrol as a rocket fuel.

PHYSICAL PROPERTIES

Naoúm [1] describes methyl nitrate as a colourless liquid boiling at 65–66°C, very mobile and possessing a viscosity lower than that of water. Its specific gravity is 1.21.

Pauling and Brockway [2] established the structure of methyl nitrate and the length and bond angles, using the electron diffraction method (p. 2).

It is slightly miscible with water: 100 ml of water dissolve 3.85 g of methyl nitrate at room temperature. Methyl nitrate is capable of dissolving collodion cotton and higher nitrated cellulose with the greatest ease. It has a distinctive, agreeable odour. Breathing vapours of methyl nitrate causes headaches. The physiological action is similar to the effect of inhaling nitroglycerine, with the difference that the symptoms are noticeable in a very short time and that they disappear more swiftly. Vapours of methyl nitrate are inflammable: heating to a temperature of 150°C causes explosion.

Many investigations have been made into the mechanism of its explosive decomposition in the gaseous phase on heating to a sufficiently high temperature, e.g. 250–300°C, or by a spark or irradiation.

STABILITY AND THERMAL DECOMPOSITION

Decomposition of methyl nitrate under these conditions produces a spontaneous explosion. Apin, Khariton and Todes [3] on the basis of original experiments in this field, suggested that the spontaneous decomposition is caused by the exothermic character of the reaction:

$$2CH_3ONO_2 \longrightarrow CH_3OH + CH_2O + 2NO_2 \qquad (1)$$

The explosion of gaseous methyl nitrate subjected to the influence of an electric spark at 25°C was investigated by Zeldovich and Shaoulov [4] who found that it differs from an explosion initiated by heat. According to these authors, the following equations express the decomposition reaction caused by an electric spark:

$$\text{induction: } CH_3ONO_2 \longrightarrow CO + NO + H_2O + \tfrac{1}{2}H_2 \qquad (2)$$

$$\text{explosion: } CH_3ONO_2 \longrightarrow \tfrac{1}{2}CO + \tfrac{3}{2}H_2O + \tfrac{1}{2}CO_2 + \tfrac{1}{2}N_2 \qquad (3)$$

The thermal decomposition of methyl nitrate has been studied by Phillips [5], who suggested that the reactions occurring at the initial stages of decomposition of methyl nitrate and of other simple nitric esters are as follows:

$$RCH_2ONO_2 \rightleftarrows RCH_2O^{\ominus} + NO_2 \qquad (4)$$

$$RCH_2O^{\ominus} + RCH_2ONO_2 \longrightarrow RCH_2OH + R\overset{\ominus}{C}HONO_2 \qquad (5)$$

$$R\overset{\ominus}{C}HONO_2 \longrightarrow RCHO + NO_2 \qquad (6)$$

$$R{-}CH_2O^{\ominus} \longrightarrow \tfrac{1}{2}R{-}CHO + \tfrac{1}{2}R{-}CH_2OH \qquad (7)$$

Alternate oxidation and reduction reactions take place between the products to form such gases as nitrous oxide and carbon monoxide.

Gray and Rogers [6] have studied the decomposition of methyl nitrate induced both thermally and by irradiation. They postulate that a spontaneous decomposition occurs at 300°C, in the following stages: initiation of the reaction according to eqn. (2) is followed by oxidation reactions:

$$CO + H_2O \longrightarrow CO_2 + H_2 \qquad (8)$$

$$2NO + 2CO \longrightarrow 2CO_2 + N_2 \qquad (9)$$

$$2NO + 2H_2 \longrightarrow 2H_2O + N_2 \qquad (10)$$

Summing up, decomposition may be formulated in a single equation:

$$CH_3ONO_2 \longrightarrow 0.95\ NO + 0.025\ N_2 + 0.75\ CO + 0.25\ CO_2 + 0.7\ H_2 + 0.8\ H_2O \qquad (11)$$

The reaction induced by an electric spark proceeds according to the following equation:

$$CH_3ONO_2 \longrightarrow 0.175\ NO + 0.41\ N_2 + 0.49\ CO + 0.51\ CO_2 + 0.175\ H_2 + 1.31\ H_2O \qquad (12)$$

As for the reaction occurring as the result of irradiating methyl nitrate Gray and Rogers suggest that this chemical change may be expressed by means of the equation:

$$CH_3ONO_2 \longrightarrow 0.30\ NO + 0.35\ N_2 + 0.50\ CO + 0.50\ CO_2 + 1.2\ H_2O + 0.30\ H_2 \qquad (13)$$

Gray and Rogers are of the opinion that free radicals take part in all explosive decomposition reactions of methyl nitrate.

The thermal effect from exploding methyl nitrate (1609–1612 kcal/kg) is 1% higher than that developed by the explosion of nitroglycerine according to equations:

$$2CH_3ONO_2 \longrightarrow CO_2 + CO + 3H_2O + N_2 \tag{14}$$

$$\text{and } 2CH_3ONO_2 \longrightarrow 2CO_2 + 2H_2O + H_2 + N_2 \tag{15}$$

(Berthelot [7]).

Methyl nitrate is less sensitive to impact than nitroglycerine: it detonates under the impact of a 2-kg weight falling from a height of 40 cm. Andreyev and Purkaln [8] established that it burns in a glass tube at atmospheric pressure with a linear velocity of about 0.12 cm/sec, i.e. about 4 times faster than nitroglycerine. Burning continues to take place quietly under increased pressure until a value of 1.5 kg/cm^2 is exceeded. Under higher static pressures, pulsation becomes visible and further increase of pressure, e.g. up to 4 kg/cm^2 may produce explosion.

For pressures within the range 0.175–2.0 kg/cm^2, the linear velocity of burning may be estimated from the equation

$$U = 0.010 + 0.133\,p$$

EXPLOSIVE PROPERTIES

The sensitiveness of methyl nitrate to shock produced by detonation is one of highest ever known — it is appreciably higher than that for nitroglycerine. Thus, detonation of methyl nitrate can be initiated even by a No. 1 detonator. The lead block expansion with water tamping was found to be (Naoúm [1]):

520 cm^3 with a No. 1 detonator (nitroglycerine 190 cm^3)
615 cm^3 with a No. 8 detonator (nitroglycerine 590 cm^3)

The excellent aptitude to detonate may be explained to some extent by the exceptionally low viscosity of the substance. Similarly the low viscosity of methyl nitrate favours a high detonation rate.

Berthelot [9] has published some data concerning the rate of detonation of methyl nitrate. They are listed below:

in a glass tube dia. 3/12 mm	2480 m/sec
in a glass tube dia. 3/7 mm	2190 m/sec
in a steel tube dia. 3/15 mm	2085 m/sec

In a tube 30–40 mm dia. the detonation rate is 8000 m/sec. In a small diameter tube a detonation rate of about 1500 m/sec has been found, while in a wide tube detonation is propagated at a rate exceeding 6000 m/sec (Ratner [10]).

MANUFACTURE

On a small scale methyl nitrate can be obtained by carefully distilling a mixture of methyl alcohol with nitric acid containing urea nitrate [18] or with nitric–sulphuric acid mixture at 40 or 18°C [19].

Commercial quantities are manufactured in a way similar to nitroglycerine, except that because of the high volatility of methyl alcohol and methyl nitrate, the contents of the nitrator should not be stirred by compressed air. Thus Schmid system nitrators with mechanical stirrer were used in Germany during World War II [11]. Also, on account of the low boiling point and high volatility of methyl nitrate, hot water is not used for washing. Its low viscosity enables the product to be washed thoroughly with cold water and cold solutions.

100 parts of methyl alcohol yield 200 parts of methyl nitrate, i.e. 83% of the theoretical yield.

ETHYL NITRATE, $C_2H_5ONO_2$

PHYSICAL AND THERMOCHEMICAL PROPERTIES

Ethyl nitrate is a liquid boiling at 87°C, with a specific gravity of 1.12. It is scarcely miscible with water, but readily dissolved by organic solvents. Collodion cotton is dissolved in it with ease.

The substance aroused interest as long ago as in Berthelot's [7] day. He determined the O-nitration heat of ethanol as 6.2 kcal/mole. Thomson [12] has estimated the heat of combustion $-\Delta H_c$ to be 324.04 kcal/mole.

Naoúm [1] investigated its explosive properties (see further) and reported the heat of explosion to be 816 kcal/kg (water as liquid). Despite the fact that its appreciable explosive properties had long been recognized, no further attention was paid to ethyl nitrate for some time, because there seemed no possibility to finding a practical use for it. Very recently, however, it has been used as an ingredient of liquid rocket fuels. This has stimulated investigations designed to determine its properties more accurately.

Thus the heat of explosion (under oxygen-free conditions) has been determined by Wheeler, Whittacker and Pike [13] to be $-Q = 77.6$ kcal/mole, i.e. 853 kcal/kg, which is close to the value reported by Naoúm [1].

From the thermochemical data quoted, Gray, Pratt and Larkin [14] have calculated both the heat of formation of ethyl nitrate at 25°C and other thermochemical constants including the latent heat of evaporation. These data are collected in Table 24.

TABLE 24

THERMOCHEMICAL PROPERTIES OF ETHYL NITRATE

Property in question	Amount of heat
Heat of formation of the liquid substance at 25°C $-\Delta H_f$	45.7 kcal/mole
Heat of formation of the gaseous substance $-\Delta H_f$	37.0 kcal/mole
Latent heat of evaporation (ΔH_v) at 25°C	8.7 kcal/mole
Latent heat of evaporation (ΔH_v) at boiling point	8.1 kcal/mole
Entropy (in relation to absolute zero) of the liquid substance at 25°C	59.08 cal/mole/degree
Entropy of formation of the liquid at 25°C	−118.1 cal/mole/degree
Gibbs free energy of formation ΔF_f^0 of the liquid substance at 25°C	−10.5 kcal/mole

These authors have also determined the vapour pressure over the range 0 to 68°C. They found the following values:

temperature °C	0	20	30	40	50	60
pressure, mm Hg	16.3	49.9	81.8	129	197	292

These values fit the equation of Antoine

$$\log_{10} p \text{ (mm)} = 7.145 - \frac{1329}{t^{\circ}\text{C} + 224^{\circ}\text{C}}$$

EXPLOSIVE PROPERTIES

According to Naoúm [1] the expansion produced by ethyl nitrate in the lead block with water tamping is 345 cm^3, the rate of detonation in wide diameter tubes being of the order of 6000–7000 m/sec. Médard [15] has reported that the substance can be detonated in thick-walled metal tubes by strong initiation, for instance by about 40 g of PETN. Using a tube of 27 mm inner dia., the rate of detonation was found to be 5800 m/sec, while in a tube 60 mm diameter it was 6020 m/sec. Attempts to detonate ethyl nitrate in glass tubes 10 mm dia. were unsuccessful. The lead block expansion caused by explosion of ethyl nitrate is about 20% greater than that of picric acid. According to Médard the sensitiveness of ethyl nitrate to shock is not very high: drop tests with a 2-kg weight falling from a height of 50 cm caused explosion in 50%.

The use of ethyl nitrate as a component of rocket fuel involves the problem of thermal decomposition. Levy [16] has studied the decomposition of ethyl nitrate in the gaseous phase, in the temperature range 161 and 201°C under a pressure of a few centimeters of mercury. He found that ethyl nitrite is the main decomposition product. By-products include methyl nitrite, nitromethane, nitrogen dioxide and nitrous oxide.

At 181°C the yield of nitromethane corresponds to 8–9% of the decomposed ethyl nitrate.

Nitromethane and methyl nitrite are probably synthesized from free methyl radicals which react with NO_2.

Using their own data on the decomposition of ethyl nitrate between 180 and 215°C under pressures of 30–50 mm Hg, Adams and Bawn [17] have calculated the activation energy E and the constant B:

$$E = 39.90 \text{ kcal}, \qquad \log_{10} B = 15.8$$

Ethyl nitrate is produced [1] by disssolving ethyl alcohol in the cold in concentrated nitric acid (density 1.41 g/cm^3) free from nitrogen oxides followed by distillation of the product.

In the presence of nitrogen oxides, ethyl alcohol is readily oxidized to acetaldehyde and this chemical change can upset the nitration reaction, if the acid contains appreciable amounts of nitrogen dioxide.

n-PROPYL NITRATE, n-$C_3H_7ONO_2$

n-Propyl nitrate is a liquid boiling at 110.5°C. Its specific gravity is 1.063. Its explosive properties are not marked and it can be detonated only with great difficulty. The calculated heat of detonation is 549 kcal/kg (water as vapour). Expansion in the lead block test is only 15 cm^3, after correction for the expansion produced by the detonator. When mixed with kieselguhr in the proportions of 71.5–28.5, however, it produces a distinct detonation and in a lead block test it gives an expansion of 230 cm^3 [1]. n-Propyl nitrate is prepared in the same way as ethyl nitrate.

ISOPROPYL NITRATE

The boiling point of isopropyl nitrate is 101–102°C. It can only be obtained indirectly from isopropyl iodide and silver nitrate. Direct nitration of isopropyl alcohol is difficult due to oxidation at the carbon atom carrying the secondary hydroxyl group.

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CHAPTER VII

POLYHYDROXYLIC ALCOHOL ESTERS

BUTANE-1,2,4-TRIOL TRINITRATE

$$CH_2ONO_2{-}CHONO_2{-}CH_2{-}CH_2ONO_2$$

BUTANE-1,2,4-TRIOL trinitrate, also called "nitrobutanetriol", is a good solvent of collodion cotton. It is less volatile than nitroglycerine and a chemically stable compound. Its explosive strength is not much inferior to that of nitroglycerine. Its heat of explosion is 1440 kcal/kg [1].

During World War II, it was produced in Germany on a semi-commercial scale.

Its manufacture largely depends on the availability of the raw material, 1,2,4-butanetriol, which is produced from acetylene by a sequence of chemical changes as outlined below [2]:

$$CH{\equiv}CH + 2CH_2O \xrightarrow{Cu_2C_2} HOCH_2{-}C{\equiv}C{-}CH_2OH \xrightarrow[H_2SO_4 + HgSO_4]{+H_2O}$$
$$\longrightarrow HOCH_2{-}CO{-}CH_2{-}CH_2OH \xrightarrow{H_2} HOCH_2{-}CHOH{-}CH_2{-}CH_2OH \qquad (1)$$

BUTANE-1,2,3-TRIOL TRINITRATE

$$CH_2ONO_2{-}CHONO_2{-}CHONO_2 - CH_3$$

Groll [3] suggested the manufacture of butane-1,2,3-triol trinitrate for use as an explosive. The possibility of using it in practice depends upon the industrial synthesis of the raw material, butane-1,2,3-triol. Reppe [2] has suggested the following method:

$$CH{\equiv}CH + CH_3CHO \xrightarrow{Cu_2C_2} CH{\equiv}C{-}CHOH{-}CH_3 \xrightarrow{H_2}$$
$$\longrightarrow CH_2{=}CH{-}CHOH{-}CH_3 \xrightarrow{HOCl} CH_2OH{-}CHCl{-}CHOH{-}CH_3 \xrightarrow{NaOH}$$
$$\longrightarrow CH_2OH{-}CHOH{-}CHOH{-}CH_3 \qquad (2)$$

ERYTHRITOL TETRANITRATE

Erythritol tetranitrate (butanetetraol tetranitrate), also called "nitroerythrite", is a solid melting at 61°C. It was obtained as early as in 1849 by Stenhouse [4], by dissolving erythritol in nitric acid in the cold and afterwards precipitating the product by means of sulphuric acid. It is readily crystallized from an alcoholic solution.

According to T. Urbański [5, 6, 7] it forms a number of eutectics with nitro compounds and nitric esters. The composition of some of these and their melting points are given in Table 25.

TABLE 25

The second component	Eutectics		
	Content of erythritol tetranitrate, wt. %	m.p. °C	Literature
p-Nitrotoluene	47	32.4	T. Urbański [5]
m-Dinitrobenzene	70	42.4	T. Urbański [5]
2,4-Dinitrotoluene	61	40.1	T. Urbański [7]
sym-Trinitrobenzene	67	45.8	T. Urbański [7]
Pentaerythritol tetranitrate	95	59.5	T. Urbański [5]

It also forms molecular addition compounds with α-trinitrotoluene and 2,4,6-trinitroanisole (T. Urbański [6, 7]).

Compounds of erythritol tetranitrate:

with 2,4,6-trinitroanisole 2:1 mol., m.p. 61.6°C
with α-trinitrotoluene 4:1 mol., m.p. *ca.* 65.5°C
(non-homogeneous melting)

Its chemical stability and sensitiveness to impact resembles those of nitroglycerine. It is an extremely strong explosive possessing a positive oxygen balance [8]:

$$C_4H_6(ONO_2)_4 \longrightarrow 4CO_2 + 3H_2O + 2N_2 + \tfrac{1}{2}O_2 + 1414 \text{ kcal/kg} \quad (3)$$

Wide practical application of erythritol tetranitrate has been prevented by the lack of readily available raw material. The main sources of erythritol are certain kinds of moss and sea-weeds, though chemical synthesis from acetylene, according to the following scheme, has been suggested by Reppe [2]:

$$CH{\equiv}CH + 2CH_2O \xrightarrow{Cu_2C_2} HOCH_2{-}C{\equiv}C{-}CH_2OH \xrightarrow{H_2}$$

$$\longrightarrow HOCH_2{-}CH{=}CH{-}CH_2OH \xrightarrow{HOCl + H_2O_2} HOCH_2{-}CHOH{-}CHOH{-}CH_2OH \quad (4)$$

Nitroerythrite is used in medicine in place of nitroglycerine, its physiological effect being similar but slower and more prolonged.

PENTITOL PENTANITRATES

$CH_2ONO_2-(CHONO_2)_3-CH_2ONO_2$

A number of pentitols (xylitol, ribitol and arabinitol) have been nitrated by I. G. Wright and Hayward [9] to yield the pentanitrates.

The melting points of the nitrates are:

ribitol pentanitrate	33.5–34.0°C
xylitol pentanitrate	37–40°C
L-(−)arabinitol pentanitrate	26.5–27.5°C

The pentanitrates can be partially and fully denitrated by warming with pyridine and by hydrogenating with hydrogen over palladium-on-charcoal catalyst respectively. In the latter case the original pentitols were recovered.

D-MANNITOL HEXANITRATE ("NITROMANNITOL")

$CH_2ONO_2-(CHONO_2)_4-CH_2ONO_2$

D-Mannitol hexanitrate, "nitromannitol" or "nitromannite" was obtained by Sobrero [10] by nitrating D-mannitol. In view of its high sensitiveness to impact and great ease of detonation Sobrero suggested that it could act as an initiator. However, experiments carried out in the arsenal at Torino, Italy, have not confirmed this. Nitromannitol has also been obtained by Domonte and Ménard [11].

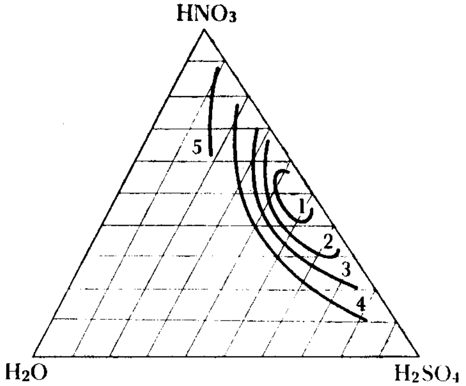


FIG. 68. Nitration of mannitol according to Kunz and Giber [16b]. Nitrogen content: *1*—over 18%; *2*—17.8–18.0%; *3*—17.6–17.8%; *4*—16.6–17.6%; *5*—16.0–16.6%.

Owing to the ease of preparation and purification, the chemical and explosive properties of mannitol hexanitrate have been thoroughly investigated. The following papers are worth attention: Sokolov [12], Berthelot [13], Sarrau and Vieille [14], Wigner [15], C. Taylor and Rinkenbach [16], Médard [16a].

The widest investigation on nitration of D-mannitol in nitric acid–sulphuric acid nitration mixture at 0°C was recently reported by Kunz and Giber [16b]. The authors built a triangle diagram (Fig. 68) known as "Sapozhnikov diagram" described in detail in the chapter dedicated to nitrocellulose (p. 333). The curves of equal nitrogen content showed shapes similar to those of nitrocellulose. The highest nitrogen content (17.8–18.0%) was obtained with the nitrating mixture of 44% HNO_3, 48% H_2SO_4 and 8% H_2O.

The curves of yield possess a similar shape as those of nitrogen content.

The rate of O-nitration of D-mannitol depends mainly on the activity of nitric acid in the acid mixtures.

PHYSICAL AND CHEMICAL PROPERTIES

D-Mannitol hexanitrate crystallizes from ethyl alcohol in the form of needles melting at 112–113°C. Its specific gravity is 1.604. It is immiscible with water, dissolves readily in ether and hot ethanol and with difficulty in cold ethyl alcohol. With aromatic mononitro compounds, e.g. nitrobenzene, *p*-nitrotoluene, *p*-nitroanisole, *α*-nitronaphthalene, mannitol hexanitrate forms addition compounds melting in a non-homogeneous way, as shown by T. Urbański [5, 6, 7, 17].

The main data are collected in Table 26.

TABLE 26

Second component	Compound		
	Mole ratio nitro compound : nitromannitol	Bent	
		weight % of nitromannitol	m.p., °C
o-Nitroanisole	2:1	34	45.5
p-Nitroanisole	2:1	58	78
Nitrobenzene	2:1	50	60
α-Nitronaphthalene	1:1	27	56
o-Nitrotoluene	2:1	39	51
m-Nitrotoluene	2:1	43	58
p-Nitrotoluene	2:1	54	71

The thermal analysis of these systems can be represented by a general curve — Fig. 69,

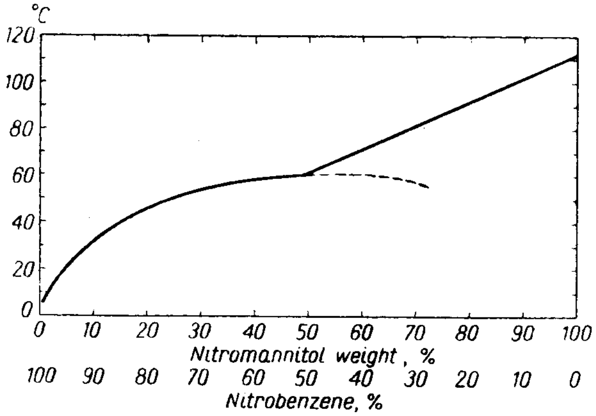


FIG. 69. Nitromannitol and nitrobenzene system melting points (T. Urbański [17]).

Ordinary eutectics are formed by nitromannitol with higher nitrated aromatic compounds (Table 27).

TABLE 27

Second component	Eutectics	
	Weight % of nitromannitol	m.p., °C
m-Dinitrobenzene	52.5	65.5
2,4-Dinitrotoluene	40.0	56.2
sym-Trinitrobenzene	55.0	78.7
α-Trinitrotoluene	42.5	62.8

Heated in a test tube, nitromannitol explodes at a temperature of 160–170°C. There is a divergence of opinion concerning its chemical stability. The stability of a very carefully purified, repeatedly crystallized sample is high, resembling that of nitroglycerine (Guastalla and Racciu [18]). However, a product crystallized only once or twice withstands heating at 75°C for only a few hours, after which brown fumes start to develop.

According to a report of Tikhanovich [19] nitromannitol in contact with an ethereal solution of ammonia undergoes a partial denitration to form D-mannitol pentanitrate (m.p. 81–82°C) together with derivatives of an ether–alcohol mannitane $C_6H_8(OH)_4$, namely mannitane tetranitrate $C_6H_8O(ONO_2)_4$ (an oily liquid) and crystalline mannitane tetramine $C_6H_8O(NH_2)_4$.

Later, Wigner [15] found that by heating with pyridine nitromannitol is denitrated to mannitol pentanitrate, and Hayward [20] has confirmed the denitration to pentanitrate by means of pyridine, occurring even at room temperature. After some 15 hr about a 65% yield is obtained.

Hayward produced evidence that the pentanitrate so obtained has the structure of D-mannitol-1,2,3,5,6-pentanitrate. Methylation of the pentanitrate with silver oxide and methyl iodide gave 4-methyl-D-mannitol pentanitrate (m.p. 111–112°C).

EXPLOSIVE PROPERTIES

Nitromannitol is a strong explosive with a positive oxygen balance. Its decomposition proceeds according to the equation:

$$C_6H_8(ONO_2)_6 \longrightarrow 6CO_2 + 4H_2O + 3N_2 + O_2 + 1512 \text{ kcal/kg}$$

It is initiated by shock as readily as nitroglycerine: a two kilogram weight dropped from a height of 4 cm causes a sample to explode. In direct contact with flame it melts and burns in the open air with difficulty. It burns evenly only after it has been warmed up. Andreyev [21] has reported that nitromannitol burns with appreciably more difficulty than nitroglycerine. In order to cause it to burn in a glass tube it was necessary to heat it to 95°C and to reduce the pressure to 85 mm Hg.

The rate of burning is thereafter rather high: 0.104 g/sec/cm^2, appreciably higher than that of nitroglycerine burning under the same conditions. Once it is kindled mannitol hexanitrate burns rapidly and large quantities may explode. In the lead block with water tamping an expansion of 560 cm^3 is produced, i.e. 93% of that produced by nitroglycerine.

The rate of detonation is:

for a loading density 0.9 g/cm^3 in an iron pipe dia. 25/35 mm	5600 m/sec (Naoúm [8])
for a loading density 1.5 g/cm^3 in an iron pipe dia. 4 mm	7000 m/sec (Berthelot [13])
for a loading density of 1.75 g/cm^3 in an iron pipe dia. 12.8 mm	8260 m/sec (Kast [21a])

Formerly the raw material for the production of nitromannitol, i.e. mannitol, was prepared from the juice of berries, in particular from *Traxinus ornus* (manna). At present it is produced by reducing D-mannose or D-fructose; in the latter case D-sorbitol is also formed.

Nitromannitol can be obtained by nitrating mannitol with a mixture of nitric acid and sulphuric acid. The method is inconvenient, however, since the reaction produces a thick crystalline mass and the nitration proceeds unevenly [8]. Generally therefore, mannitol is dissolved in a five-fold amount of nitric acid ($d = 1.51$) at a temperature below 0°C, which is maintained while a ten-fold quantity of sulphuric acid ($d = 1.84$) is added to the solution. Fine crystals of the product are precipitated which were separated on a vacuum filter. The product is slightly impure due to the presence of mannitol pentanitrate. The acid product is drowned quickly in cold water, filtered again, washed with cold water, neutralized by means of dilute sodium bicarbonate solution and once again washed with water. Nitromannitol is crystallized from alcohol, to which a stabilizer (diphenylamine) is added.

Mannitol hexanitrate is now used as a secondary charge in some detonators, instead of tetryl. Thus it is used in detonators in which the primary initiator is diazonitrophenol. There also exist detonators wherein nitromannitol is used with tetrazene. Such a blend behaves as an initiator.

On crystallization nitromannitol forms needles which easily felt together into an unpourable mass which makes filling the detonators practically impossible. The crystallization process is therefore carried out so as to precipitate the product as granules, by adding protective colloids, triphenylmethane dyestuffs or similar substances.

Nitromannitol is used for medicinal purposes instead of nitroglycerine, since its physiological effect is slower and longer lasting.

DULCITOL HEXANITRATE ("NITRODULCITOL")

Dulcitol hexanitrate, D- or L-galactitol hexanitrate, "nitrodulcite" or "nitrodulcitol", is a crystalline product, melting at 94–95°C. It was obtained as early as 1860 by Béchamp [22]. Dulcitol is an isomer of mannitol, hence the properties of nitrodulcite are similar to those of nitromannite (Wigner [15], Taylor and Rinkenbach [16], Patterson and Todd [23]).

Dulcitol occurs in plants (manna from Madagascar). It can also be obtained by reduction of D-galactose or lactose.

The preparation and chemical properties of dulcitol hexanitrate were studied in detail by Hayward and McKeown [24]. They found that the hexanitrate is partly denitrated by warming to 50°C with pyridine. The denitration product was characterized as D- or L-galactitol-1,2,4,5,6-pentanitrate (m.p. 85–86°C).

D-SORBITOL HEXANITRATE

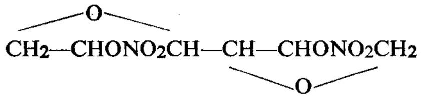
Sorbitol hexanitrate, or nitrosorbitol, is an isomer of nitromannitol. In normal conditions it is a crystalline material melting at 55°C. It has been obtained by Bergheim [25] and by Tettamanzi and Arnaldi [26].

Davis [27] has described its physical state as an oily liquid, which was used in the United States as an additive to nitroglycerine in low-freezing dynamites.

The discrepancy has been explained by the experiments of T. Urbański and Kwiatkowska [28] who found that by dissolving sorbitol in a five-fold quantity of concentrated nitric acid ($d = 1.52$) at 0°C followed by precipitating the product with the help of a ten-fold amount of 20% oleum at +5°C, hexanitrate only slightly contaminated with pentanitrate was formed. When, however, the temperature of nitration and precipitation is −10°C an oily mixture of sorbitol hexa- and pentanitrates was produced. Most probably it was a mixture of this kind that Davis described, as sorbitol pentanitrate exists under normal conditions in the form of an oil. The explosive properties of nitrosorbitol resemble those of nitromannitol.

Sorbitol is at present manufactured commercially by catalytic reduction of D-glucose. Hence the nitrated product may attain greater practical importance.

DINITRATES OF DIANHYDROHEXITOLS



$$CH_2{-}CHONO_2CH{-}CH{-}CHONO_2CH_2 \quad (\text{with } O \text{ bridges})$$

2,5-Dinitrates of 1,4;3,6-dianhydrohexitols have been prepared by Formann, Carr and Krantz [29] in an attempt to obtain vasodilatory substances. Jackson and Hayward [30] studied their chemical properties.

They prepared 1,4;3,6-dianhydrides of D-mannitol, D-glucitol and L-iditol:

isomannide dinitrate, m.p.	64.5–65.5°C
isosorbide dinitrate, m.p.	50.5–51.5°C
iso-idide dinitrate, m.p.	68–69°C

POLYVINYL NITRATE

Attempts to obtain polyvinyl alcohol nitrate, (polyvinyl nitrate), were made with the object of producing a synthetic polymer capable of replacing nitrocellulose.

The earliest experiments began in 1929 when Börschman and Funk [31] dissolved polyvinyl alcohol in concentrated sulphuric acid at a temperature of *ca.* 0°C and then introduced the solution slowly into the nitrating mixture which was heated gradually to 40–50°C, polyvinyl nitrate being precipitated. The originally plastic precipitate, after being filtered and washed changes into a brittle substance which can be pulverized readily. The product contains *ca.* 10% of nitrogen. Burrows and Filbert [32] reacted polyvinyl alcohol with nitric acid at 10–20°C to obtain the nitrate. The authors pointed out that the alcohol is readily oxidized and that measures to counteract this are necessary.

Noma, Oya and Nakamura [33] examined the reaction of nitrating polyvinyl alcohol and concluded that neither nitration with a mixture of nitric and sulphuric acid, nor nitration with nitric and acetic acid can bring about the esterification of all the hydroxyl group. This is probably due to simultaneous hydrolysis. They recommend nitrating either with a composition of nitric acid and acetic anhydride or a solution of nitric acid in carbon tetrachloride, where by a higher nitrated product, softening at a temperature of 40–50°C, is obtained.

According to Deans and Nicholls [34] polyvinyl nitrate of 13–15% N content produced a lead block expansion of 153–342 cm^3 (TNT produced 255 cm^3).

Le Roux and Sartorius [35] have determined the content of nitrogen in polyvinyl alcohol nitrate to be 13.5–14.5%, whereas its theoretical maximum content of nitrogen is 15.75%. The detonation of polyvinyl alcohol nitrate is propagated with a rate similar to that of nitrocellulose of the same nitrogen content. The rate of detonation of polyvinyl nitrate, containing 13.4% of nitrogen, in cardboard cartridges 30 mm dia. is:

at a loading density	
0.3 g/cm^3	2030 m/sec
0.6 g/cm^3	3450–3520 m/sec
1.0 g/cm^3	4920–5020 m/sec
1.4 g/cm^3	6090 m/sec
1.5 g/cm^3	6560 m/sec

Polyvinyl nitrate is a readily inflammable substance which burns without melting. It has not been used industrially on account of its poor chemical stability. Further, unlike nitrocellulose, it cannot form solutions which after evaporation of the solvent, leave a film of high mechanical strength. This is probably the result of lack of orientation of the molecular chains.

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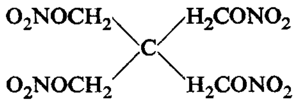
CHAPTER VIII

POLYHYDROXYLIC BRANCHED-CHAIN AND CYCLIC ALCOHOL ESTERS

PENTAERYTHRITOL TETRANITRATE (PETN)



Pentaerythritol tetranitrate ("nitropentaerythrite") also has numerous trade names which are different in various countries: PETN, Penthrite, Penta (English speaking countries), Pentrit, Niperyth, Nitropenta, NP (Germany), Pentryt, NP (Poland), Ten (U.S.S.R.). PETN was first obtained by the Rheinisch-Westfälische Sprengstoff A.G. in 1894 [1], by nitrating pentaerythritol.

PENTAERYTHRITOL

Pentaerythritol was obtained by Tollens and Wigand in 1891 [2] from acetaldehyde and formaldehyde according to the following reaction:

$$CH_3CHO + 4CH_2O + \tfrac{1}{2}Ca(OH)_2 \longrightarrow C(CH_2OH)_4 + \tfrac{1}{2}(HCOO)_2Ca \qquad (1)$$

Addition of copper salts permits substantial improvement of yield. The reaction appears to proceed in two stages. Initially an aldol condensation occurs between three molecules of formaldehyde and one molecule of acetaldehyde:

$$3CH_2O + CH_3CHO \xrightarrow{(OH^{\ominus})} C(CH_2OH)_3CHO \qquad (2)$$

Afterwards the pentaerythrose reacts with a fourth molecule of formaldehyde according to Cannizzaro's reaction:

$$CH_2O + C(CH_2OH)_3CHO + \frac{Ca}{2}OH \longrightarrow C(CH_2OH)_4 + HCOO\frac{Ca}{2} \qquad (3)$$

This reaction scheme was proposed by Tollens and Wigand [2].

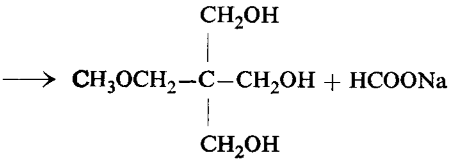
More recent investigations into the mechanism of formation of pentaerythritol have been made both by Wawzonek and Rees [3] and by Barth, Snow and Wood [4]. Both groups tried to explain the process in terms of the formation of *sym*-pentaerythritol ether (dipentaerythritol), and other ethers, e.g. the methyl ether. The latter is produced whenever the formaldehyde used for the reaction contains methyl alcohol:

$$CH_2O + H_2O \longrightarrow HOCH_2OH \qquad (4a)$$

$$CH_3OH + HOCH_2OH \longrightarrow CH_3OCH_2OH + H_2O \qquad (4b)$$

$$CH_3OCH_2OH + CH_3CHO \xrightarrow{OH^\ominus} CH_3OCH_2CH_2CHO$$

$$CH_3OCH_2CH_2CHO + 3\,CH_2O + NaOH \longrightarrow$$



$$\longrightarrow CH_3OCH_2-\overset{\displaystyle CH_2OH \atop |}{\underset{| \atop \displaystyle CH_2OH}{C}}-CH_2OH + HCOONa \qquad (4c)$$

Numerous investigations have been carried out with the aim of increasing the yield of pentaerythritol. These are reviewed in the monograph of Berlow, Barth and Snow [5]. Recently the use of basic ion exchange resins instead of calcium hydroxide was recommended [5a]. Some *sym*-pentaerythritol ether (dipentaerythritol) is produced along with pentaerythritol as shown by Friedrich and Brün [6]. The proportion of this substance depends upon the reaction conditions (see p. 195).

In spite of its great explosive strength and high chemical stability large-scale production of PETN could not be achieved until formaldehyde and acetaldehyde became available industrially. Therefore during World War I PETN was only of theoretical interest. During World War II it was used for filling detonators as the secondary high explosive charge instead of tetryl boosters, detonating fuses, small arms (e.g. 20 mm) ammunition and for making blends with various explosives. Some 1440 tons of pentaerythritol tetranitrate per month were produced in Germany during this period.

PETN. PHYSICAL PROPERTIES

PETN is a white crystalline substance which melts at 140–141°C. The melting point of the pure chemical substance is 141.3°C. Its boiling point was reported by Belayev and Yuzefovich [7] to be

160°C at 2 mm Hg
180°C at 50 mm Hg
200°C at 760 mm Hg

The ultra-violet absorption spectrum of a single crystal of PETN is characterized by a marked absorption at wave lengths above 280 mμ (Deb [8], Fig. 70).

PETN usually forms needle or column-shaped crystals, in which state it pours with difficulty. It is however possible to produce cubic crystals, which pour easily, by recrystallization from ethyl acetate. PETN has been subjected to many crystallographic studies. On the basis of X-ray measurements carried out by Booth and Llewellyn [9] the interatomic distances have been shown to be:

$$\text{C—C} = 1.50\ \text{Å}, \quad \text{C—O} = 1.37\ \text{Å}, \quad \text{O—N} = 1.36\ \text{Å},$$
$$\text{N—O (nitro group)} = 1.27\ \text{Å}$$

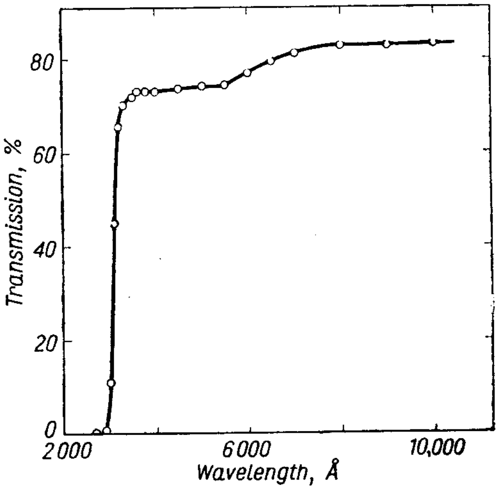


FIG. 70. Ultra-violet absorption spectrum of a single crystal of PETN (Deb, according to Bowden and Yoffe [29]).

The vapour pressure, according Edwards [10], is:

temperature, °C	pressure, cm Hg
97.0	8.38×10^{-5}
110.6	3.12×10^{-4}
121.0	1.09×10^{-3}
131.6	3.76×10^{-3}
138.8	7.08×10^{-3}

From these data Edwards has deduced an empirical equation:

$$\log p = 16.73 - 7750\frac{1}{T}$$

where p — the vapour pressure in cm Hg

T — absolute temperature.

PETN is practically insoluble in water. According to Desvergnes [11], 100 g water dissolve 0.01 g of PETN at 50°C and 0.035 g at 100°C. It is soluble in most organic solvents. Values for the solubility of pentaerythritol tetranitrate (expressed in g dissolved in 100 g of solution) found by T. Urbański and Kwiatkowski [12] are tabulated in Table 28.

TABLE 28

SOLUBILITY OF PENTAERYTHRITOL TETRANITRATE IN ORGANIC SOLVENTS

Temperature °C	PETN (g) dissolved in 100 g of solution				
	Ethyl alcohol	Ether	Acetone	Benzene	Toluene
0	0.070	0.200	14.37	—	0.150
10	0.085	0.225	16.43	0.150	0.170
20	0.115	0.250	20.26	0.300	0.230
30	0.275	0.340	24.95	0.450	0.430
40	—	0.450	—	—	—
40	0.415	—	36.16	1.60	0.620
50	0.705	—	—	2.010	1.100
60	1.205	—	—	3.350	2.490
62	—	—	42.68	—	—
70	2.225	—	—	5.400	3.290
78.4	3.795	—	—	5.400	—
80.2	—	—	—	7.900	—
90	—	—	—	—	9.120
113	—	—	—	—	30.960

Values for its solubility in ethyl acetate and pyridine, as reported by Desvergnes, are given in Table 29.

TABLE 29

SOLUBILITY OF PENTAERYTHRITOL TETRANITRATE (DESVERGNES [11])

Temperature °C	PETN (g) dissolved in 100 g of solvent	
	Ethyl acetate	Pyridine
19	6.322	5.436
50	17.868	8.567

It is of special importance for industrial practice to know the solubility of PETN in mixtures of acetone with water. Data reported by Aubertein [13] are listed in Table 30.

The recently published solubility data of Roberts and Dinger [14] agree well with those reported by T. Urbański and Kwiatkowski. The differences are only apparent, owing to the fact that the solubility is reported by the latter authors as grammes of pentaerythritol tetranitrate dissolved in 100 g of solvent (Table 31).

TABLE 30

SOLUBILITY OF PENTAERYTHRITOL TETRANITRATE IN ACETONE–WATER MIXTURES (AUBERTEIN [13])

Amount of PETN dissolved in 100 g of solvent g	Acetone concentration				
	55%	70%	80%	90%	92%
	Temperature of solution, °C				
1	41	—	—	—	—
2	52	—	—	—	—
2.5	—	24.5	—	—	—
4	62	—	—	—	—
5	—	41.5	22	—	—
10	—	54.5	38.5	15	10
15	—	62	48	24.5	20.5
17.5	—	65	—	—	—
20	—	—	54	34.5	29
25	—	—	59	41.5	34
30	—	—	63	46.5	40.5
35	—	—	—	51.5	45
40	—	—	—	55	50
45	—	—	—	58.5	54
50	—	—	—	61.5	57.5
55	—	—	—	—	60.5
60	—	—	—	—	62.5

TABLE 31

SOLUBILITY OF PENTAERYTHRITOL TETRANITRATE (AFTER ROBERTS and DINGER [14])

Temperature °C	Acetone	Benzene	Ethanol
15	20.81	—	—
20	24.84	0.275	0.125
25	30.56	—	—
30	34.56	0.496	0.213
40	44.92	0.834	0.378
50	58.76	1.448	0.657
60	—	2.389	1.196

Dimethylformamide is also a good solvent for PETN (Lang [15])

at 40°C 100 g of solution contain 40 g PETN
at 60°C 100 g of solution contain 50 g PETN
at 100°C 100 g of solution contain 70 g PETN

Furthermore, it dissolves in liquid or fused aromatic nitro compounds and in nitric esters to form eutectics. T. Urbański [16] has reported the composition and melting temperatures of the eutectics specified below (Fig. 71).

20% PETN with 80% *m*-dinitrobenzene	m.p. 82.4°C
10% PETN with 90% 2,4-dinitrotoluene	m.p. 67.3°C
13% PETN with 87% α-trinitrotoluene	m.p. 76.1°C
30% PETN with 70% tetryl	m.p. 111.3°C
20% PETN with 80% mannitol hexanitrate	m.p. 101.3°C

Similar systems were examined by Desseigne [105].

According to Hackel [17] PETN forms eutectics with nitroglycerine (see p. 41). With diethyldiphenylurea (centralite I) it produces an eutectic containing 12% of pentaerythritol tetranitrate, melting at 68.0°C.

Ternary systems giving eutectics composed of 16% PETN, 8.5% trinitro-*m*-xylene, 75.5% *m*-dinitrobenzene and 12.5% PETN, 71.0% *m*-dinitrobenzene and 16.5% 1,8-dinitronaphthalene were investigated by Khaybashev and Bogush [18]. The melting points of these eutectics are 79.5 and 69°C, respectively.

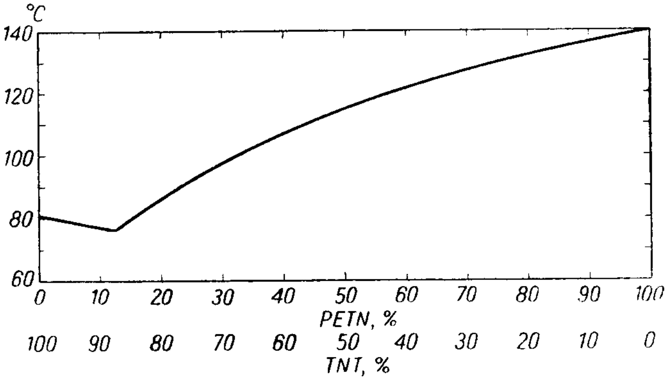


FIG. 71. PETN and TNT system melting points (T. Urbański [16]).

PETN differs from other nitric esters in failing to produce a colloid solution with nitrocellulose. This is the result of the symmetrical structure of PETN, which has a zero dipole moment. PETN is completely non-hygroscopic. Its specific gravity in crystalline form is 1.77. On compression the following density values are obtained:

pressure, kg/cm^2	density, g/cm^3
351	1.575
703	1.638
1406	1.710
2109	1.725
2812	1.740

Ebert, Eisenschütz and Hartel [19] examined the dipole moment of PETN in dilute benzene solution and found it be *ca.* 2.0 D.

Mortimer, Spedding and Springall [20] determined the dipole moments of pentaerythritol and a few of its derivatives including PETN. They found the dipole moment of pentaerythritol to be *ca.* 2.0 D and that of PETN in dioxane $\mu = 2.5$ D. This led them to conclude that there is free rotation about the C—O bond in the nitrate. It also indicates that the shortening of this bond in crystals observed by

Booth and Llewellyn [9] cannot be due to possession of any marked degree of double-bond character.

The specific heat of pentaerythritol tetranitrate is 0.4 cal/g/°C, the heat of combustion is 1974 kcal/kg, and hence the heat of formation is +390 kcal/kg or $-\Delta H_f = +123$ kcal/mole.

The heat of fusion has been estimated by Roberts and Dinger [14] to be 23–24 kcal/mole. This value has been calculated from experimental solubility data in organic solvents at different temperatures.

The latent heat of sublimation of PETN is 36.3±0.5 kcal/mole (Edwards [10]).

PETN. CHEMICAL PROPERTIES

Due to its symmetrical structure, pentaerythritol tetranitrate is characterized by high resistance to many reagents. Thus PETN, differing from the majority of nitric esters, is not readily decomposed by sodium sulphide at 50°C. On the other hand, it is decomposed quite quickly by boiling in a ferrous chloride solution. Boiling with a 2.5% solution of sodium hydroxide causes very slow decomposition, whereas nitrocellulose rapidly decomposes under these conditions.

Experiments by Aubertein and Rehling [21] have shown that treatment with water at approximately 100°C causes PETN to hydrolyse. At 125°C, and under pressure, hydrolysis proceeds quite quickly, and is considerably speeded up by the presence of 0.1% of HNO_3. Whether it occurs in water alone or in water acidified with nitric acid, the hydrolysis produces mainly pentaerythritol dinitrate. A dilute sodium hydroxide solution causes PETN to hydrolyse more rapidly than acidified water. PETN neither reduces Fehling's reagent nor enters into addition products with any aromatic nitro compound. In this respect it differs from both nitroerythritol and nitromannitol.

The chemical stability of pentaerythritol tetranitrate is very high and exceeds that of all other nitric acid esters. It withstands the heat test at 80°C for several hours. As heating continues decomposition is gradually perceptible at temperatures above the melting point, i.e. above 140°C. Aubertein and Rehling [21] have found that water is occluded in crystals of PETN purified by recrystallization from acetone–water. The presence of these occlusions has an adverse effect on the results obtained by examining the stability of penthrite at 132°C. Removal by grinding and drying the crystals improves the result of the stability test.

It has been established experimentally (T. Urbański, Kwiatkowski, Miładowski [22]) that the addition to pentaerythritol tetranitrate of such nitro compounds as nitrobenzene, nitrotoluene, dinitrobenzene, dinitrotoluene, trinitrobenzene, and trinitrotoluene, decreases its stability as determined by heating to 120–135°C. The degree of decomposition of PETN, heated alone or in mixtures, can be estimated in terms of the pH-values determining the acidity of the decomposition products (Table 32, Fig. 72).

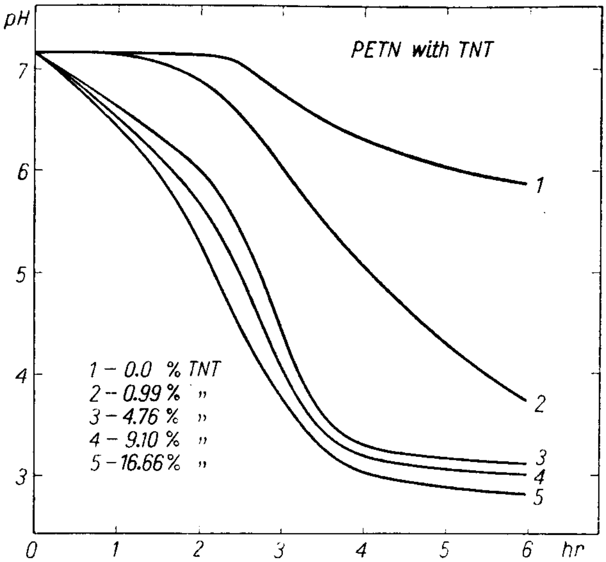


FIG. 72. Change of pH of PETN alone and with TNT on heating at 120°C (T. Urbański, Kwiatkowski, Miładowski [22]).

TABLE 32

CHANGES IN STABILITY OF PETN AT PRESENCE OF ADMIXTURES (T. URBAŃSKI, KWIATKOWSKI AND MIŁADOWSKI [22])

Admixtures	pH-Value of a water extract from the sample kept at 120°C			
	1 hr	2 hr	3 hr	6 hr
Pure PETN	7.16	7.15	6.33	5.86
9.1% *p*-nitrotoluene	5.34	3.50	3.19	1.92
9.1% 2,4-dinitrotoluene	6.30	4.20	3.13	2.92
9.1% *α*-trinitrotoluene	6.54	5.70	3.32	3.03

Similar results have been found by estimating the time needed to attain a standard pressure (300 mm Hg) due to vapours evolved on decomposition at 134.5°C (the Taliani–Goujon method, p. 28). The following times were recorded (Fig. 73)

for PETN	68.5 min
for PETN with 9.1% *p*-nitrotoluene	26.5 min
for PETN with 9.1% 2,4-dinitrotoluene	27.5 min
for PETN with 9.1% *α*-trinitrotoluene	30.5 min

The lower stability is probably due to the fall in melting point of pentaerythritol tetranitrate, and hence its transition at a relatively low temperature into the higher energy liquid state.

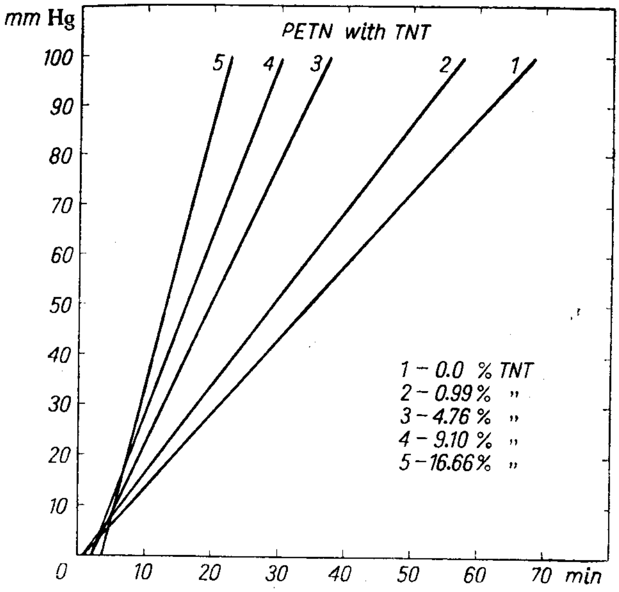


FIG. 73. Pressure evolved by PETN alone and with TNT on heating at 134.5°C (Taliani–Goujon method). (T. Urbański, Kwiatkowski, Miładowski [22]).

Other substances exert a similar influence on the stability of PETN, for example solvents capable of lowering its melting temperature.

The U.S. military specification MIL-P-387 A lays down the following technical conditions for PETN

minimum melting point		140.0°C
minimum nitrogen content		17.50 %
substances insoluble in acetone	max.	0.10 %
acid or alkali content	max.	0.003%

vacuum stability at 120°C, max. 5 ml gas evolved in a 20 hours' test.

The action of PETN on the human system is the same as that produced by all other nitric esters. Nevertheless inhalation of PETN is not dangerous, as its vapour pressure is negligible. Similarly, breathing small amounts of penthrite in the form of dust causes no deleterious effect owing to its low solubility. Lazarev [23] reports the toxicity of pentaerythritol tetranitrate to be lower than that of nitroglycerine.

PETN was introduced into clinical medicine for the treatment of angina pectoris as a long-acting coronary vasodilator [24]. The administration of PETN has very little effect on peripheral arterial vasodilation [25].

PETN. EXPLOSIVE PROPERTIES

Pure PETN heated above its melting point explodes violently at 205–225°C. In the primary stage of thermal decomposition, within the temperature range of 161–233°C, the activation energy E equals 47.0 kcal/mole, while $\log_{10} B = 19.8$, according to A. J. B. Robertson [26].

The following equation of decomposition, using a 1000 g sample of PETN, has been established by A. Schmidt [27]:

$$C_{15.8}H_{25.3}O_{38.0}N_{12.7} = 12.13CO + 3.38CO_2 + 10.35H_2O + 1.71H_2 + 0.1CH_4 +$$

$$+ 0.1C_2H_2 + 0.2NH_3 + 0.1HCN + 6.23N_2$$

heat of explosion		1530 kcal/kg
volume of gases	V_0 =	768 l./kg
temperature of explosion	t	= 4230°C

It has been found by Haid and Schmidt [28] that the equation of decomposition is practically independent on the loading density. The proportion of gaseous products resulting from the explosive decomposition of PETN under the influence of different stimuli, shown in Table 33, was determined by Bowden and Yoffe [29].

TABLE 33

GASEOUS PRODUCTS OF EXPLOSIVE DECOMPOSITION OF PETN, %

Initiation	NO_2	NO	N_2O	N_2	CO_2	CO	H_2	O_2
Detonation	—	5.3	—	22.8	37.0	26.7	6.8	1.4
Impact	—	24.3	5.3	9.4	19.1	35.4	6.5	—
Thermal decomposition at 210°C	12.0	47.6	9.5	1.6	6.3	21.0	2.0	—

Sensitiveness to shock. T. Urbański [30] has reported that PETN is exploded with a 50% probability on impact by a kinetic energy of 0.20 kgm/cm² (in comparison with about 0.95 kgm/cm³ needed for tetryl). The data of Naoúm [31] and Izzo [32] are similar. Stettbacher [33] on the other hand considered the sensitiveness to impact of PETN to be almost the same as that of tetryl. On account of its relatively high sensitiveness PETN is generally used after being desensitized ("phlegmatized") by adding 10% of montan (lignit) wax. This desensitization has practically no effect on the completeness of detonation.

PETN is not very sensitive to friction but it is characterized by a very high sensitiveness to initiation by explosion. It is detonated by 0.01 g lead azide, the minimum amount required for tetryl being 0.025 g of lead azide. PETN blended with desensitizing agents does not readily lose its aptitude for detonation. Thus, according to the researches of T. Urbański and Galas [34] PETN mixed with 40% of water can be initiated by a No. 8 detonator, which fails to detonate TNT containing barely 15% of water. Thus it is obvious why pentaerythritol tetranitrate detonates with ease when blended with 10% montan wax. On account of its high explosive power and appreciable sensitiveness, PETN is itself an excellent explosive for transmitting a detonation from an initiating explosive to a high explosive charge, i.e. as a "secondary filling" of detonating cups or as a filling for gaines (boosters).

Initiation by an electric spark. PETN can be detonated by a 2000–12000 V electric spark produced by discharging a condenser, as demonstrated by Basset and Basset [35].

Initiation by ultra-violet rays. When a crystal of PETN is subjected for a period of 1.2 msec to an intensive irradiation with ultra-violet rays, producing 900 J of energy, prompt decomposition occurs. Cracks occur on the faces of the crystal resembling those which appear in other explosives as the result of heating. PETN heated to a temperature slightly above its melting point can be exploded however by exposure for 20 μsec to irradiation producing an energy of 480 J (Deb [8]). It is decomposed by irradiation with γ-rays [104, 104a].

PETN ignites with difficulty on contact with a flame, differing this respect from straight-chain nitric esters such as nitroglycerine, nitroglycol etc. In accordance with studies of Andreyev [36] PETN does not burn even in a tube as wide as 18 mm in diameter. Only after pre-heating to 95°C is it possible to induce burning, which proceeds with the extraordinary low linear rate of 0.047 cm/sec. Under a pressure of 20 kg/cm^2 or more, it burns uniformly with a rate depending on the pressure according to the linear relationship:

$$U = 0.02 + 0.0180p$$

The rate of detonation of PETN is 8500 m/sec. Results concerning the detonation rate of pentaerythritol tetranitrate at different loading densities are collected in Table 34.

An increase of the rate of detonation can be achieved by driving out the air retained among the crystals of PETN and replacing it by a non explosive liquid, e.g. water, as shown by the investigations of T. Urbański and Galas [34]. The authors reported detonation rates for charges with a loading density of 1.45 g/cm^3 to be:

for dry PETN	rate of detonation 7295 m/sec
for PETN with 10% of water	rate of detonation 7445 m/sec

for charges with a loading density of 1.40 g/cm^3:

for dry PETN	rate of detonation 7125 m/sec
for PETN with 20% of glycerine	rate of detonation 7825 m/sec

The expansion produced by PETN in the lead block with sand tamping is 500 cm^3 and with water tamping, 560 cm^3. This is equivalent to about 93% of the strength of nitroglycerine or about 170% of that of picric acid.

THE MANUFACTURE OF PENTAERYTHRITOL TETRANITRATE

Of the various methods of manufacturing PETN, the most widely used involves pouring pentaerythritol into nitric acid ($d = 1.50$–1.52) at a temperature not exceeding 25°C. PETN is scarcely soluble in nitric acid. The product which is precipitated towards the end of the nitration, is filtered, washed with water and recrystallized from acetone.

TABLE 34

THE DETONATION RATE OF PENTAERYTHRITOL TETRANITRATE, m/sec

Specific gravity		Roth [41]	Friedrich [40]	Laffitte and Parisot [42][8]	T. Urbański and Galas [34][9]	Cook [43]
0.45		3150[2]				
0.50			3965[4]			
0.76				4200		
0.80				4400		
0.84				4860		
0.85	5330 [31][1]					
0.91		5300[3]		5120		
1.00				5320		5550
1.03			5615[5]			
1.04		5730[3]				
1.22			6355[6]			
1.35					6950	
1.40					7125	
1.45		7375[3]			7295	
1.48	6945 [39]					
1.50			7420[7]			
1.60	7200 [39]					
1.62	8000 [37]		7913[7]			
1.70						8300
1.71	8340 [38]					
1.72		8500[3]				
1.73			8350[7]			
1.75	7750 [39][4]					

[1] in an iron pipe, 25 mm dia.
[2] in a bakelite pipe 6/8.5 mm dia.
[3] in a bakelite pipe 4.5/6.3 mm dia.
[4] in a copper pipe, 15/17 mm dia.
[5] in a glass pipe, 11.4/13 mm dia.
[6] in a copper tube 10/10.6 mm dia.
[7] without confinement
[8] in a pipe, 6 mm dia.
[9] in an iron pipe 21/25 mm dia.

Certain workers (e.g. Stettbacher [44]) have suggested precipitating PETN from nitric acid by adding sulphuric acid at 20°C, filtering the product only after this operation. This method is not to be recommended, since sulphuric acid causes the precipitation of certain impurities dissolved in nitric acid, so that the slight increase in yield is offset by the diminished purity of the product.

Another method suggested by T. Urbański [45] consists in diluting the acid remaining after the nitration with water. If the final concentration of acid is 30–50% HNO_3, complete precipitation of PETN occurs, while the impurities remain in the solution. However, the method can only be used if pentaerythritol of the highest purity is available as the raw material. In practice, two methods are in use: (1)

nitration with nitric acid alone without dilution; (2) nitration followed by dilution with water.

Pentaerythritol destined for the preparation of PETN must be exceptionally pure. In Germany, nitrating grade pentaerythritol ("grade M") had to conform to the following technical specification:

The substance should contain at least 85% of crystals passing through a 2-mm sieve and retained by 0.2-mm sieve. No more than 15% may pass through the latter.

The mineral content	max.	0.5%
moisture content	less than	0.7%
dipentaerythritol content	max.	2%
reducing substances	absent	

A laboratory test nitration should produce a yield over 98%.

Pentaerythritol (LG grade) manufactured by the reaction of formaldehyde and acetaldehyde in the presence of sodium hydroxide at a temperature within the range 10–14 to 37°C was also used for nitrating purposes.

The melting point of pentaerythritol corresponding with the above mentioned specification lies within 250 and 260°C (pure pentaerythritol melts at 261–262°C). To produce it an aqueous solution of acetaldehyde is treated with formaldehyde in the presence of milk of lime, the temperature being gradually increased from 15 to 55°C. When the reaction is complete, the whole is treated with sulphuric acid sufficient to precipitate the lime as calcium sulphate. This is filtered off, and the solution concentrated under reduced pressure. The crystallized product is centrifuged and then recrystallized from water. The yield is about 62% (calculated with respect to acetaldehyde) or 51% if related to formaldehyde.

German method

The nitration of pentaerythritol to produce PETN by a semi-continuous method as used at Krümmel [46] was carried out as follows (Fig. 74).

A nitrator (*1*) of 500 l. capacity is charged with 1000 kg of concentrated nitric acid (98–99%) and 200 kg of pentaerythritol. Nitric acid passes from a storage tank into a metering tank and thence into the nitrator. Pentaerythritol is sucked by vacuum from a storage tank into a metering tank, from which a worm conveyer transfers it to the nitrator. The weighing of the raw materials takes 10 min, the nitration itself about 40 min. A temperature of 15–20°C is maintained in the nitrator by the use of a jacket and of a cooling coil refrigerated by a solution of sodium nitrate (—5 down to —10°C).

Shortly after the nitration has been started a new batch of raw material is weighed and fed gradually into the nitrator so that the contents of the nitrator (*1*) are removed by an overflow to another nitrator (*2*). This unit, with a capacity of 170 l., is cooled by means of a jacket only. In it the incoming product is cooled to 10°C.

The vapours are drawn off the nitrators via a ventilator and flow upwards into a tower where they are sprayed with water, and recovered as 20% nitric acid.

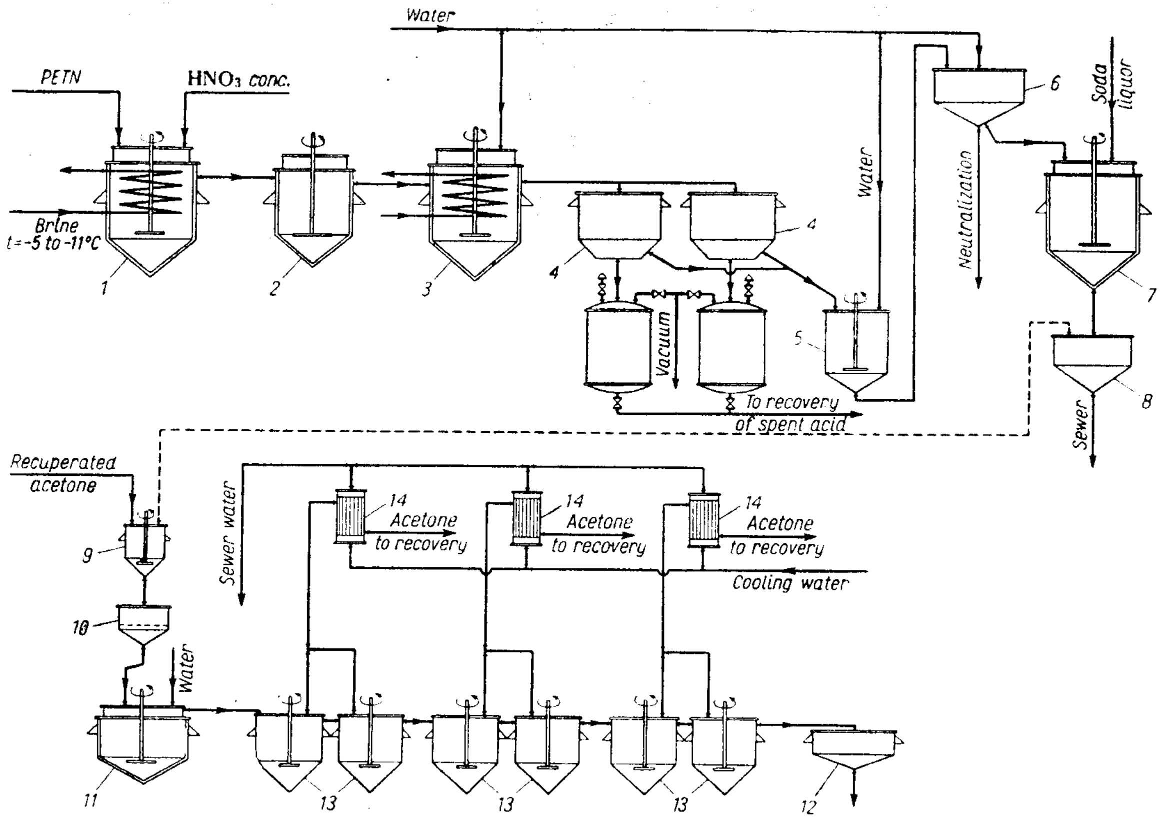


FIG. 74. Flow sheet of continuous manufacture of PETN: *1*—nitrator No. 1, *2*—nitrator No. 2. *3*—diluting vat, *4*—vacuum filter, *5*—washing vat, *6*, *8*, *10*, *12*—filters, *7*—neutralizer, *9*—vat for dissolving PETN in acetone, *11*—diluting vat, *13*—distillation apparatus, *14*—vapour condensers.

In nitrator (*2*) a suspension of PETN-crystals in 80% nitric acid is present. From here the contents pass to diluter (*3*) cooled by a coil and jacket. Here sufficient water is introduced to lower the nitric acid concentration to 30%, while the temperature is kept at 15–20°C.

The suspension of crystals of PETN contained in the diluter flows into one of a batch of vacuum filters (*4*). As each filter is filled with PETN, the stream is directed to another filter, while from the first acid is removed as completely as possible by suction, after which an outlet in the centre of the filter-floor, closed by a conical stopper is opened. The PETN is washed out of the filter with water and carried to a battery of continuously operated washers.

The first unit in the washing installation is a tank (*5*) for washing with water, from which the suspension is pumped to a vacuum filter (*6*) to extract the acid washings. After being washed, the PETN enters a neutralizer (*7*), where it is mixed with sodium carbonate solution at 60°C for 1½ hr. It is then filtered in the vacuum filter (*8*). The liquor from this filter should be alkaline.

The yield of PETN amounts 96.8%, (100 parts of pentaerythritol yield 225 parts of PETN). The raw materials required for the manufacture of 100 kg of PETN are:

44.4 kg of pentaerythritol
and 224 kg of nitric acid (98–99%)
of which 80 kg enter into the reaction
16 kg are lost
and 128 kg are recovered as 30% nitric acid.

Afterwards the crude washed PETN is purified by continuous recrystallization. PETN containing about 10% of water is transferred to a tank (*9*), where it is dissolved in acetone at 45°C. A little sodium carbonate is added (for a 200 kg nitration charge of pentaerythritol, 1000 l. of acetone and 3 kg of sodium carbonate are used). After warming up to 50°C the solution is passed through a filter (*10*). After being diluted at 60°C by adding an amount of water to obtain a concentration of acetone of 50–55% the liquor with PETN crystals suspended in it passes to a battery of six stills (*13*) equipped with stirrer and heating jacket, some also having an internal heater. Acetone is distilled off and its vapours condensed in (*14*). In the first still a temperature of 85°C and an acetone concentration of 12–15% is maintained. In the second, 3–5% of acetone is present at 90°C, while in the third, fourth and fifth stills the temperature is 100°C and only traces of acetone remain. As the acetone is distilled off the PETN crystals assume their final shape. PETN purified in this way is separated from water on the filter (*12*). The diluted acetone recovered in the condensers is purified by distillation.

The "phlegmatization" of PETN consists in thorough mixing with montan wax in the proportion of 90% PETN to 10% montan wax [47]. The process is as follows. A mixing tank, equipped with gentle stirrers, is filled with 1200 l. of water heated to 85°C. 315 kg of purified PETN which still contains 10% water is added followed by 250 ml of dilute Sudan red solution intended to distinguish the phlegmatized product, and finally the appropriate amount of melted montan wax. The whole is stirred for 10 min at 85°C, and then the contents of the vessel are cooled rapidly to 70°C by a spray of cold water. The phlegmatized product is filtered, rinsed with cold water and dried by two stages at 70°C in a convection air drier (ventilation drier). The product is thus dried first to a moisture content of 10–15%, then passed through 4-mm mesh sieve, and finally dried and passed through a 2-mm mesh sieve.

Unphlegmatized PETN is left with a water content of 10–15%, and in this form it is transported and used for the manufacture of mixtures.

Old Soviet method

The method outlined below for the manufacture of PETN was described by Shapshal and Belenkii [48].

A nitrator filled with 300 kg of 93–95% nitric acid is fed with 60 kg pentaerythritol previously dried at 100°C. By means of a cooling jacket a temperature of 20°C is maintained in the nitrator. The equipment is constructed of aluminium, and fitted with a stirrer operating at 120 r.p.m., with a funnel for adding the pentaerythritol and with an outlet for discharging the product at the bottom.

After all the pentaerythritol has been introduced the contents of nitrator are mixed for half an hour, after which the nitration product is allowed to flow to a vacuum filter. As pentaerythritol tetranitrate is present in the form of crystals, filtration is very easy and is complete in about 10–15 min. The concentration of the filtered acid is 78%, while the residual acid content in the separated PETN does not exceed 25%.

The product is transferred to a washing tank of acid-resistant steel, to be drowned in 800 l. of water, and stirred for 15 min. The washer has a double bottom, the upper porous stoneware layer acting as a filter-floor. After being washed PETN is separated on the filter where it is washed again three times with 180 l. batches of water. The washed product contains 1% of acid. It is neutralized in a special tank by means of an eight to tenfold amount of 1% sodium carbonate solution at 85–90°C, the process taking 1 hr before being centrifuged prior to crystallization. At this stage it still contains 0.3–0.5% of acid.

Crystallization is carried out as follows: 2.2 kg of acetone and twice as much sodium carbonate as needed to neutralize the acid contained in the substance are used for every 1 kg of PETN. The solution is warmed to 58°C and stirred at this temperature for 1 hr after which it is passed under a pressure of 1 atm through a filter and into a crystallizer. The filter should be heated to a temperature of 50–55°C, and the crystallizer to 45–50°C. The contents of the crystallizer are cooled very slowly: first at a rate of 1°C per 5 min, later at 2–2.5°C per 1 min. Crystallization is finished within 2 hr.

The crystalline PETN is separated from the solvent in a vacuum filter down to a 15–20% acetone content. The residual acetone is later removed by washing with a small amount of ethyl alcohol. The final product is dried at 40°C. PETN crystallized from acetone should fulfil the following conditions: m.p. 138–140°C, content of moisture and volatile components max. 0.1%, substances unsoluble in acetone max. 0.1%, mineral content (as ash) max. 0.2%. PETN should be completely free from acid. After keeping a sample at a temperature of 110°C for 8 hr, the pH-value of a water extract should lie between 5.0 and 7.0.

Japanese method

At the Maizuru plant, in Japan [49] PETN was manufactured in World War II in a plant comprising a nitrator lined with acid-resistant steel and provided with a stirrer (140 r.p.m.), a tank made from acid-resistant steel, a centrifuge, a steel crystallizer and unit for recovering acetone.

The nitrator is charged with 825 kg of concentrated nitric acid (98%) and cooled to 10–15°C, after which 150 kg of pentaerythritol are added slowly, while the temperature is kept below 15°C. The addition of pentaerythritol takes about 2½ hr. The contents of the nitrator are then allowed to stand quietly for half an hour before being drowned in some 2000 l. of water.

The aqueous solution of acid is decanted from above the penthrite and run to waste since the acid is too dilute to be worth recovering. PETN is stirred with water which is then decanted. In order to ensure thorough washing this operation is repeated five times. To the last wash aqueous sodium hydroxide solution is added to form a 0.5% solution. Next the PETN is washed again by alternate agitation with water and decantation, four times. An aqueous suspension of the washed product is run into a centrifuge by means of an impeller pump. After being centrifuged, PETN is transported to another building to be purified.

To purify the product, 60 kg of moist PETN are thrown into 150 kg of acetone warmed to 50–55°C and stirred until completely dissolved. The solution is then filtered through a cotton cloth into a vessel filled with 150 l. of water. The precipitated pentaerythritol tetranitrate is centrifuged and dried in a special room for 22 hr at 55°C.

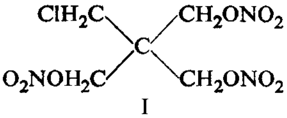
MIXED PENTAERYTHRITOL ESTERS AND ESTERIFIED ETHERS

The problem of producing asymmetric pentaerythritol tetranitrate esters of nitric acid, i.e. mixed pentaerythritol esters and pentaerythritol ether esters, is tackled from time to time in investigations which have the dual aims:

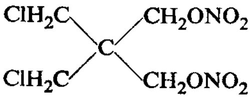
(1) To produce explosive derivatives of pentaerythritol less sensitive than pentaerythritol tetranitrate, which could be applied for desensitizing PETN and lowering its melting point, so as to make it possible to fill shells with a molten explosive mixture containing penthrite.

(2) To produce explosive derivatives of pentaerythritol which would have an asymmetrical polar structure, capable of dissolving nitrocellulose. Substances of this kind could find application as components of smokeless powder.

Patents covering a method of producing mixed pentaerythritol esters were published in 1936 by Westfälisch-Anhaltische Sprengstoff A.G. [50]. These substances, containing two or three hydroxyl groups esterified with nitric acid, possess a lower sensitiveness to impact than PETN. To produce these compounds diesters of acids other than nitric acid are nitrated. For example pentaerythritol mono- or di-chlorohydrin, pentaerythritol mono- or di-formate or pentaerythritol acetate etc. were nitrated. The first two yielded the compounds I and II.



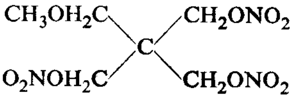
I



II

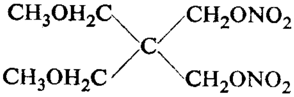
A mixture of the two substances melting at a temperature of 43–50°C gives a lead block expansion 107% that of TNT, and is less sensitive to shock than TNT. (See also Elrick, Gardner, Marans and Preckel [51]).

Particularly interesting properties have been discovered [50] in the pentaerythritol methyl ether nitrates, which are formed by nitrating monomethyl or dimethyl pentaerythritol ether.



III

Monomethyl pentaerythritol ether trinitrate (III) melts at 79–80°C, produces an expansion in the lead block of the same order as TNT, and is less sensitive to impact than TNT.

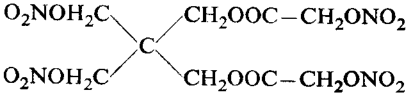


IV

Dimethyl pentaerythritol ether dinitrate (IV) which melts at 53–54°C, produces an expansion in the lead block of about 95% that of TNT. It is insensitive to impact.

Mixed pentaerythritol esters have also been described [50] that contain in their molecule hydroxyl groups substituted by organic acids, which possess nitro groups either in ester form or as C-nitro compounds joined with the acid, alongside simple nitrate ester groups.

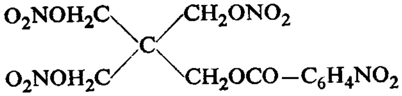
Thus, the nitration of glycolic acid pentaerythritol diester yields a tetranitrate (V):



V

This is a liquid explosive. Its strength estimated by the lead block test amounts to about 90% of the strength of TNT.

Nitration of pentaerythritol benzoate causes both esterification of hydroxyl groups with nitric acid, and a simultaneous nitration of the benzene ring to produce pentaerythritol trinitrate *p*-nitrobenzoate (pentaerythritol trinitrate ester of *p*-nitrobenzoic acid, *p*-nitrophenylenecarbonyl-pentaerythritol trinitrate) (VI):



VI

This is a crystalline substance of great explosive strength, possessing a low sensitiveness to shock.

Pentaerythritol trinitrate esters of nitrobenzoic acid have been also obtained by Marans, Elrick and Preckel [52] who have esterified pentaerythritol trinitrate by means of the corresponding nitrobenzoyl chloride.

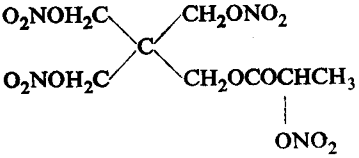
In this way they have prepared, among other esters:

pentaerythritol trinitrate *o*-nitrobenzoate	m.p. 94–95 °C
pentaerythritol trinitrate *m*-nitrobenzoate	m.p. 102–103°C
pentaerythritol trinitrate *p*-nitrobenzoate	m.p. 106–108°C
pentaerythritol trinitrate 3,5-dinitrobenzoate	m.p. 109–110°C

They also prepared pentaerythritol trinitrate formate (m.p. 62–63°C), acetate (87–88°C), propionate (m.p. 39–40°C) and their higher homologues; pentaerythritol trinitrate oxalate (m.p. 97–100°C), glutarate (m.p. 87–88°C), succinate (m.p. 88–90°C), adipate (m.p. 82–83°C), benzoate (m.p. 89–90°C) and phthalate (m.p. 125.0–126.5°C).

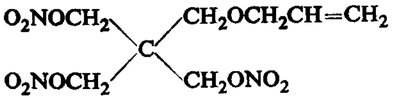
Wagner [53] prepared pentaerythritol dinitrate diacetate and pentaerythritol trinitrate monoacetate and examined their explosive properties.

Wyler [54] suggested to producing mixed esters of nitric acid and of an organic acid also containing a hydroxylic group which would also be esterified by the nitric acid (a similar ester (V) was described above). This method has been applied by Wyler to obtain (nitrate-lactoyl)-pentaerythritol trinitrate, i.e. (α-nitroxypropionyl-pentaerythritol trinitrate):

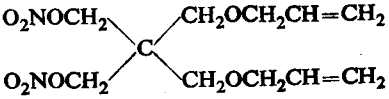


VII

Evans and Gallaghan [55] have nitrated mono- and di-allyl-pentaerythritol to produce trinitrate or dinitrate:



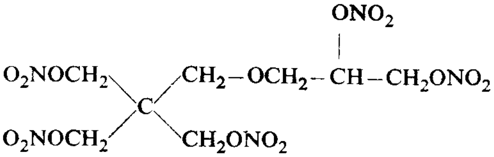
VIII



IX

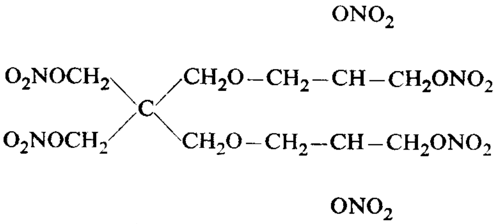
Both these ether-esters are liquids of specific gravity $d_{20}^{20} = 1.373$ and 1.191 respectively.

The same authors succeeded in obtaining glyceryl pentaerythritol ether and diglyceryl pentaerythritol ether, and converted them by nitration into pentanitrate and hexanitrate respectively:



X

(m.p. 55°C)



XI

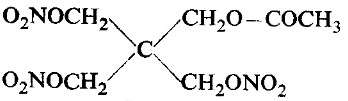
The ether-ester (XI) is an oily liquid, of specific gravity $d_{20}^{20} = 1.540$.

PENTAERYTHRITOL TRINITRATE

Initially, attempts to introduce fewer nitro groups into a molecule of pentaerythritol by means of direct nitration were unsuccessful. When less concentrated nitric acid was used the only result was a decreased yield of PETN contaminated by small quantity of pentaerythritol trinitrate.

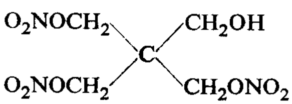
For a long time the only practicable method was the nitration of an organic acid pentaerythritol ester followed by removal of the acyl.

In this way Marans, Elrick and Preckel [52] have obtained pentaerythritol monoacetate together with certain amounts of di- and triacetate by heating pentaerythritol tetra-acetate with pentaerythritol at 180–185°C. The monoacetate was nitrated to yield pentaerythritol acetate trinitrate (XII). Careful hydrolysis of the latter produced pentaerythritol trinitrate (XIII):



XII

m.p. 87–88°C



XIII

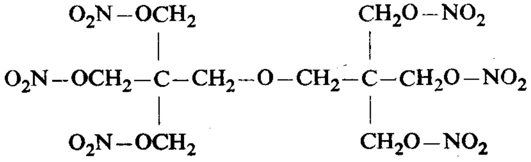
m.p. 27–28°C

However, it has been discovered that pentaerythritol trinitrate can also be produced by direct nitration of pentaerythritol with a mixed acid composed of 80% nitric acid and 80% sulphuric acid (Camp, Marans, Elrick and Preckel [56]). The nitration is performed at a temperature close to 0°C. The product, representing a mixture of PETN with trinitrate, is precipitated by adding water. To separate the components the acetone solution neutralized by means of ammonium carbonate is treated with aqueous alcohol so as to form a mixture of 7 parts of acetone, 3 parts of water and 2 parts of ethanol. PETN precipitates from this solution, while pentaerythritol trinitrate remains in the liquor to be completely separated as a precipitate by further treatment with hot water. The yield of trinitrate amounts to about 50%.

Pentaerythritol trinitrate can be used for preparing a range of mixed pentaerythritol esters.

DIPENTAERYTHRITOL HEXANITRATE (NITRODIPENTA, DiPEHN)

DiPEHN melting at 72°C, and the alcohol from which the ester is derived, have been obtained by Friedrich and Brün [6].



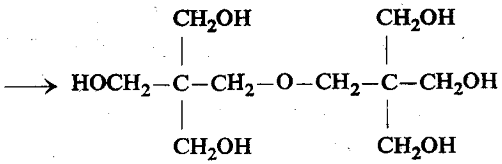
$$\begin{array}{ccc} \mathrm{O_2N{-}OCH_2} & & \mathrm{CH_2O{-}NO_2} \\ | & & | \\ \mathrm{O_2N{-}OCH_2{-}C{-}CH_2{-}O{-}CH_2{-}C{-}CH_2O{-}NO_2} \\ | & & | \\ \mathrm{O_2N{-}OCH_2} & & \mathrm{CH_2O{-}NO_2} \end{array}$$

Their work has shown that some dipentaerythritol is always produced alongside pentaerythritol during chemical combination of acetaldehyde and formaldehyde. The proportion of dipentaerythritol formed depends on the conditions under which the reaction of the two aldehydes takes place.

According to Wawzonek and Rees [3] dipentaerythritol is formed as a result of a series of reactions, in which acrolein is one of the intermediates:

$$CH_3CHO + HCHO \overset{OH^{\ominus}}{\rightleftarrows} HOCH_2CH_2CHO \rightleftarrows CH_2{=}CHCHO + H_2O$$

$$HOCH_2CH_2CHO + CH_2{=}CHCHO \rightleftarrows O(CH_2CH_2CHO)_2 \xrightarrow[OH^{\ominus}]{6CH_2O}$$

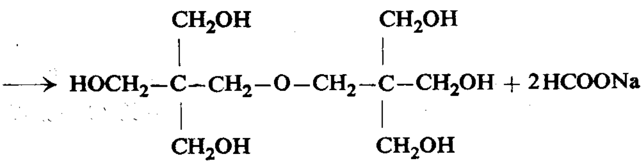


$$\begin{array}{c} \mathrm{CH_2OH} \qquad\qquad \mathrm{CH_2OH} \\ | \qquad\qquad\qquad | \\ \longrightarrow \mathrm{HOCH_2{-}C{-}CH_2{-}O{-}CH_2{-}C{-}CH_2OH} \\ | \qquad\qquad\qquad | \\ \mathrm{CH_2OH} \qquad\qquad \mathrm{CH_2OH} \end{array}$$

Barth, Snow and Wood [4] have proposed another reaction scheme approaching to that outlined by Tollens and Wigand [2], in which they assume that formaldehyde is present in the form of a polyoxymethylene chain:

$$OHC{-}CH_3 + HO{-}CH_2OCH_2OH + CH_3CHO \longrightarrow$$

$$\longrightarrow OHC{-}CH_2CH_2OCH_2CH_2{-}CHO \xrightarrow[2NaOH]{6CH_2O}$$



$$\begin{array}{c} \mathrm{CH_2OH} \qquad\qquad \mathrm{CH_2OH} \\ | \qquad\qquad\qquad | \\ \longrightarrow \mathrm{HOCH_2{-}C{-}CH_2{-}O{-}CH_2{-}C{-}CH_2OH + 2HCOONa} \\ | \qquad\qquad\qquad | \\ \mathrm{CH_2OH} \qquad\qquad \mathrm{CH_2OH} \end{array}$$

In order to produce dipenta [6] one equivalent of acetaldehyde is allowed to react with three equivalents of formaldehyde in the presence of half a mole of calcium hydroxide. In that way, pentaerythritol containing about 15% of dipentaerythritol is formed. This mixture melts at 221°C.

The melting point of pure dipentaerythritol is 221–222.5°C. From pentaerythritol and dipentaerythritol a eutectic mixture of 70% pentaerythritol and 30% dipentaerythritol melting at 190°C is formed.

Nitrodipenta resembles PETN in its physical and chemical properties. Nitrodipenta dissolves in acetone more readily than PETN, and this is used to separate the two nitrates. The specific gravity of single crystals of nitrodipenta is 1.630 at 15°C, while pellets prepared under a pressure of 2500 kg/cm^2 acquire a specific gravity of 1.589. Nitrodipenta is less sensitive to impact and to friction than PETN and its temperature of initiation is higher. In spite of this, its chemical stability at 100°C is distinctly less than that of PETN. This is the main reason why the presence of nitrodipenta in PETN is undesirable.

Besides, nitrodipenta is a less effective explosive than PETN. As determined by Brün [38] the rate of detonation is 7410 m/sec for nitrodipenta of specific gravity 1.589, the net expansion in the lead block being 75% as that of PETN.

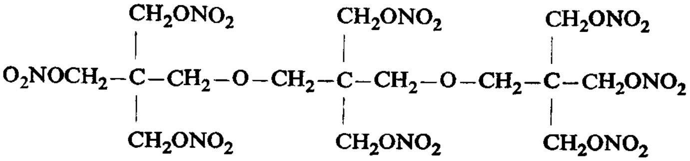
The method of preparing nitrodipenta reported by Friedrich and Brün [6] consists in nitrating pentaerythritol rich in dipentaerythritol and in afterward separating the two components by utilizing their different solubility.

The mixture of alcohols undergoes nitration with nitric acid in the same manner as pentaerythritol, after which the crude product is treated with an equal portion (by weight) of acetone. PETN is insoluble, while nitrodipenta remains in solution with a small quantity of PETN. Water added carefully causes the residual pentaerythritol tetranitrate to precipitate. The solution separates into two layers: the upper composed of fairly hydrated acetone containing a small amount of nitrodipenta, and the lower which consists of a saturated solution of nitrodipenta in acetone containing a little water. The bottom layer is removed and treated with an excess of alcohol. Almost pure dipentaerythritol hexanitrate is precipitated.

It is possible to convert hexanitrate into the original alcohol — dipentaerythritol — by treating its solution in acetone with boiling alkaline sulphide solution in alcohol.

OTHER MIXED ESTERS

Tripentaerythritol octanitrate (Nitrotripenta)



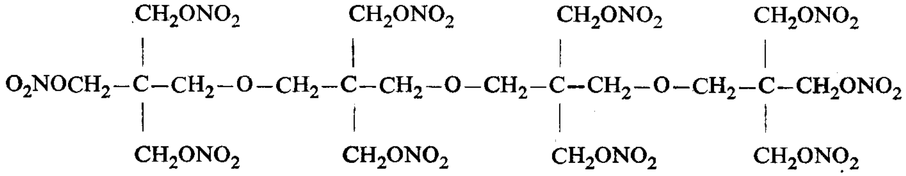
$$O_2NOCH_2-\underset{\textstyle CH_2ONO_2}{\overset{\textstyle CH_2ONO_2}{C}}-CH_2-O-CH_2-\underset{\textstyle CH_2ONO_2}{\overset{\textstyle CH_2ONO_2}{C}}-CH_2-O-CH_2-\underset{\textstyle CH_2ONO_2}{\overset{\textstyle CH_2ONO_2}{C}}-CH_2ONO_2$$

Tripentaerythritol octanitrate (Nitrotripenta) melting at 82–83°C was prepared by Wyler [57] by nitrating tripentaerythritol (m.p. 248–250°C), another by-product of the pentaerythritol reaction.

The formation of tripentaerythritol is favoured by keeping high alkalinity in the pentaerythritol reaction, by using potassium hydroxide or by carrying out the pentaerythritol reaction in the presence of pentaerythritol or dipentaerythritol [58].

Nitrotripenta has been prepared by the nitration of tripentaerythritol with 99% nitric acid at 0–10°C. Nitrotripenta is readily soluble in hot benzene and in acetone, soluble in alcohol and chloroform, insoluble in water. Because of its relatively low melting point, nitrotripenta can be melted and poured, and can therefore be used as a coating agent and sensitizer for ammonium nitrate.

Tetrapentaerythritol decanitrate (Nitrotetrapenta)



$$O_2NOCH_2-\overset{CH_2ONO_2}{\underset{CH_2ONO_2}{\overset{|}{\underset{|}{C}}}}-CH_2-O-CH_2-\overset{CH_2ONO_2}{\underset{CH_2ONO_2}{\overset{|}{\underset{|}{C}}}}-CH_2-O-CH_2-\overset{CH_2ONO_2}{\underset{CH_2ONO_2}{\overset{|}{\underset{|}{C}}}}-CH_2-O-CH_2-\overset{CH_2ONO_2}{\underset{CH_2ONO_2}{\overset{|}{\underset{|}{C}}}}-CH_2ONO_2$$

Tetrapentaerythritol decanitrate (Nitrotetrapenta) m.p. 70°C was prepared by Wyler [59] by nitrating tetrapentaerythritol (m.p. 234°C).

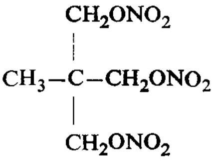
Tetrapentaerythritol was isolated by the same author from technical pentaerythritol by fractional crystallization. It was nitrated with 98% nitric acid at —5 to +5°C. It is readily soluble in acetone and ethylene dichloride. It has been suggested as a coating agent and sensitizer for ammonium nitrate.

Dihydrated pentaerythritol nitrate

Pentaerythritol has been converted to polymeric ethers by the action of heat, preferably in presence of small amounts of acids [60]. Wyler [61] nitrated it and obtained an explosive of the formula $[(C_5H_8)(ONO_2)_2O]_x$, where x has a value between 1 and 7.

1,1,1-Trimethylolethane trinitrate

1,1,1-Trimethylolethane trinitrate (trimethylolmethylmethane trinitrate, nitropentaglycerine, “nitrometriol“)



$$CH_3-\overset{CH_2ONO_2}{\underset{CH_2ONO_2}{\overset{|}{\underset{|}{C}}}}-CH_2ONO_2$$

has been proposed by Hertz [62] as an explosive capable of partly or totally replacing nitroglycerine.

Colson [63] has described it as a liquid freezing at —60°C with a specific gravity of 1.4685 at 20°C, and a refractive index of 1.4760 at 17.5°C. Its solubility in water at 19°C is 0.516 g/l. while at 36°C it is 0.685 g/l. According to Médard [64] the melting point of pure nitrometriol is 51°C.

Collodion cotton is readily dissolved by nitrometriol, which in this respect differs from PETN. The heat of explosion is 1270 kcal/kg. The lead block expansion is about 85% that of penthrite and 115% that of picric acid.

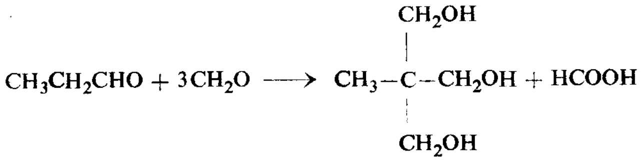
According to Médard [64] the rates of detonation developed with non confined nitrometriol cartridges, 30 mm dia., were:

density, g cm^3	1.39	1.48	1.50
rate, m/sec	6750	7040	7060

After being fused the explosive solidifies to form a mass having a density of 1.48 to 1.50 g/cm^3, which needs a very strong initiation by about 30 g PETN to detonate under these conditions with a rate of estimately 6300 m/sec. Being less sensitive to mechanical shock than PETN, methyltrimethylolmethane trinitrate explodes under an impact energy more or less like that needed for tetryl.

Médard has suggested using it in blends with ammonium nitrate (see Vol. III).

During the last war a certain amount was manufactured in Germany for use as a component of smokeless (double-base) powder. The extent of production was limited, however, due to inadequate supplies of propionaldehyde. Trimethylolmethylmethane is produced in an analogous way to pentaerythritol by reacting propionaldehyde with formaldehyde:



$$CH_3CH_2CHO + 3CH_2O \longrightarrow CH_3-\underset{\underset{CH_2OH}{|}}{\overset{\overset{CH_2OH}{|}}{C}}-CH_2OH + HCOOH$$

Nitrometriol is obtained by nitrating metriol in a manner resembling the production of nitroglycerine.

Colson [63] has reported that as a result of nitrating 100 parts by weight of 1,1,1-trimethylolethane at 10°C by means of a mixed acid containing 45% HNO_3 and 55% H_2SO_4, 197–198 parts by weight of its nitric ester were obtained i.e. about 93% of the theoretical yield. The author considers that it is possible to increase the yield up to 97–98% of theoretical, by using mixed acid fortified with 20% oleum. A continuous method of nitration has also been outlined by Colson: trimethylolmethylmethane was first dissolved in sulphuric acid and then introduced into the nitrating mixture.

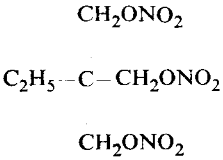
The preparation of mixed trimethylolethane esters, i.e. of acetate–nitrates, was described by Marans and Preckel [65]. By heating metriol in the presence of metriol triacetate at 175–180°C, a mixture of mono- and diacetate is obtained together with unchanged trimethylolethane.

From the nitration of metriol monoacetate metriol acetate–dinitrate is formed as an oily liquid of specific gravity $d^{25} = 1.362$. Cautious hydrolysis of this substance in contact with sodium hydroxide solution in ethanol at room temperature produces trimethylolethane dinitrate with a yield of 75%.

The dinitrate is a liquid, $d^{25} = 1.362$, $n_D^{25} = 1.4692$.

Metriol diacetate can be nitrated to yield trimethylolethane diacetate–nitrate. The latter, subjected to mild hydrolysis, yields metriol mononitrate, a crystalline substance which melts at 76–77°C.

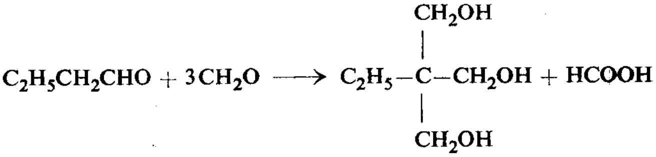
1,1,1-Trimethylolpropane trinitrate (ethyltrimethylolmethane trinitrate)



$$\begin{array}{c} CH_2ONO_2 \\ C_2H_5-C-CH_2ONO_2 \\ CH_2ONO_2 \end{array}$$

This solid melting at 45°C (Spaeth [66]) is an explosive approaching tetryl in strength. Its sensitiveness to shock lies between that of picric acid and TNT.

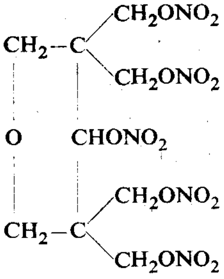
To produce the raw material, trimethylolpropane, formaldehyde is condensed with butyraldehyde in an alkaline medium:



$$C_2H_5CH_2CHO + 3CH_2O \longrightarrow C_2H_5-\overset{\displaystyle CH_2OH \atop |}{\underset{| \atop \displaystyle CH_2OH}{C}}-CH_2OH + HCOOH$$

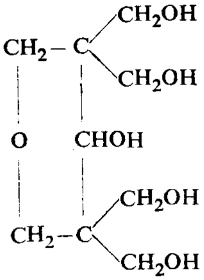
Anhydroenneaheptitol pentanitrate

Anhydroenneaheptitol pentanitrate (3,3,5,5-tetramethylol-4-hydroxypyran pentanitrate) is a derivative of an alcohol called anhydroenneaheptitol produced by esterifying it with nitric acid.



It was first obtained by Hertz [67] who proposed its use as an explosive, since (in the authors opinion) it develops greater explosive strength that PETN but is less sensitive. Tollens and Apel [68] have prepared the initial alcohol (m.p. 156°C) resulting from the reaction of acetone with formaldehyde in the presence of calcium hydroxide, to which they attributed the structure of an enneaheptitol anhydride without, however, determining which hydroxyl groups were dehydrated.

Latter this has been made clear by Mannich and Brose [69] who reported that the pyran ring structure:



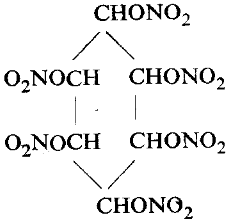
is to be regarded as most probable.

Anhydroenneaheptitol pentanitrate has found no practical application, since the yield of alcohol is low owing to the fact that in the main acetone and formaldehyde react with one another to form polymers of vinyl methyl ketone (methylene acetone) $CH_2{=}CHCOCH_3$ (Müller [70]).

CYCLIC ALCOHOL ESTERS

Inositol hexanitrate

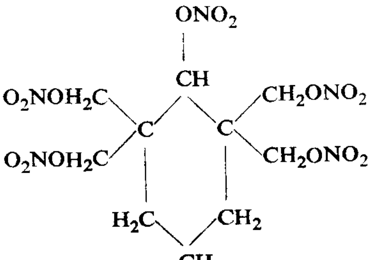
Inositol hexanitrate ("nitroinosite", "nitroinositol"), a solid melting at 132.5°C, and quebrachitol hexanitrate ("nitroquebrachite"), an oily liquid, are esters of isomeric cyclic alcohols. Their common constitutional formula is:



Both esters, and specially hexanitroinositol, were suggested by Crater [71] for use in explosives practice instead of tetryl for filling detonators and boosters. In explosive strength, sensitiveness to mechanical shock, and stability both esters are similar to nitromannite. References to quebrachitol pentanitrate can be found in the patents of Burke and McGill [72].

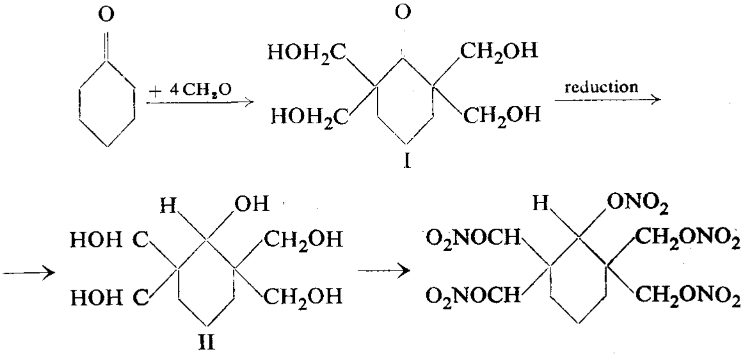
Tetramethylolcyclohexanol pentanitrate

Tetramethylolcyclohexanol pentanitrate ("nitrohexanol") is a solid, melting at 122.5°C



Attention has been drawn to this substance as an explosive by Friedrich and Flick [73]. L. Wöhler und Roth [74] have established its explosive character, determining the heat of explosion to be 900 kcal/kg, $f = 11,700$ m and the rate of detonation of a sample of density 1.44 g/cm^3 to be 7670 m/sec.

Nitrohexanol is produced as a result of nitrating the corresponding alcohol (II) obtained from cyclohexanone:

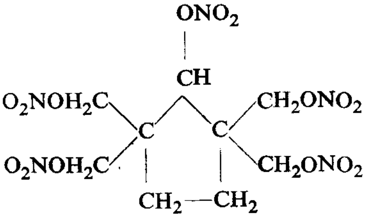


An intermediate product is tetramethylolcyclohexanone (I). Subjected to nitration, this compound yields its tetranitrate ("nitrohexanone") melting at 66°C. The heat of explosion of nitrohexanone is 825 kcal/kg, $f = 12,110$ m, rate of detonation being 7740 m/sec at a density of 1.51 g/cm^3.

Up to the present none of these substances are used in practice.

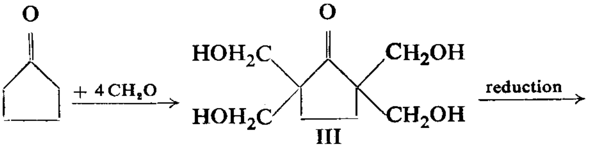
Tetramethylolcyclopentanol tetranitrate

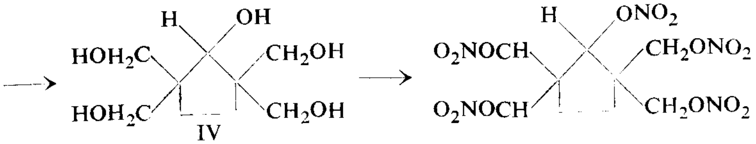
Tetramethylolcyclopentanol tetranitrate ("nitropentanol") is a solid melting at 92°C.



It was first described by Friedrich and Flick [73] and its explosive properties were examined by L. Wöhler and Roth [74]. Nitropentanol is a strong explosive: its heat of explosion is 1035 kcal/kg, the rate of detonation is 7360 m/sec at a density of 1.57 g/cm^3, $f = 12,550$ m.

It is obtained by the nitration of an alcohol (IV) obtained from cyclopentanone:



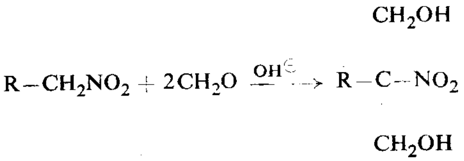


IV

Tetramethylolcyclopentanone (III) is an intermediate product in the above reaction chain. It can be nitrated to give a tetranitrate, m.p. 74°C (nitropentanone). Friedrich and Flick report the explosion heat of nitropentanone as 820 kcal/kg, $f = 10{,}680$ m and the detonation rate 7940 m/sec at a density of 1.59 g/cm^3. These substances are not in practical use at present.

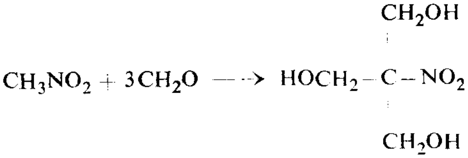
NITROALCOHOL ESTERS

Nitroalcohols are produced when nitroparaffins react with formaldehyde in an alkaline medium (Henry [75]). In the case of primary paraffins, the reaction proceeds as below:



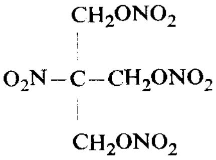
$$R-CH_2NO_2 + 2CH_2O \xrightarrow{OH^{\ominus}} R-\overset{\displaystyle CH_2OH}{\underset{\displaystyle CH_2OH}{C}}-NO_2$$

With nitromethane, a trihydric alcohol, trimethylolnitromethane, so called nitroisobutylglycerine, is formed:



$$CH_3NO_2 + 3CH_2O \longrightarrow HOCH_2-\overset{\displaystyle CH_2OH}{\underset{\displaystyle CH_2OH}{C}}-NO_2$$

Trimethylolnitromethane trinitrate



$$O_2N-\overset{\displaystyle CH_2ONO_2}{\underset{\displaystyle CH_2ONO_2}{C}}-CH_2ONO_2$$

Trimethylolnitromethane trinitrate, known also as nitroisobutylglycerine trinitrate (other names are nitroisobutanetriol trinitrate, NIB-glycerine trinitrate) is an oily liquid, freezing at —39°C (Hofwimmer [76]), but crystallizing only with the greatest difficulty. It is immiscible with water, but soluble in the most of organic solvents except petroleum ether (like nitroglycerine). It is capable of dissolving collodion cotton but not so effectively as nitroglycerine. Its specific gravity is 1.68. The substance is more viscous and less volatile than nitroglycerine.

Opinions about the chemical stability of nitroisobutylglycerine trinitrate do not agree. Naoúm [31] reported its stability between the temperatures of 70 and 80°C to be the same as that of nitroglycerine. Other sources, on the contrary, report inadequate stability which, however, can be ascribed to the presence of impurities difficult to remove (see further under preparation of the substance).

Trimethylolnitromethane trinitrate has attracted considerable interest as an explosive owing to its ideal oxygen balance. Explosive decomposition results in production of heat exceeding that produced by nitroglycerine by 7%

$$NO_2\cdot C(CH_2ONO_2)_3 \longrightarrow 4CO_2 + 3H_2O + 2N_2 + 1707 \text{ kcal/kg}$$

Its sensitiveness to impact is of the same order as that of nitroglycerine. The initiation temperature is 180°C.

In the lead block trimethylolnitromethane trinitrate produces an expansion slightly greater than that of nitroglycerine, i.e. 105–110% of the value for nitroglycerine. Blasting gelatine made from nitroisobutylglycerine trinitrate is, in spite of this, somewhat weaker than blasting gelatine from nitroglycerine because nitroglycerine applied as a component of gelatine furnishes it with some oxygen to oxidize the nitrocellulose component of this explosive. Thus, according to Naoúm [31], a 93% blasting gelatine from trimethylolnitromethane trinitrate gave a 580 cm^3 expansion in the lead block, while gelatine from nitroglycerine gave 600 cm^3.

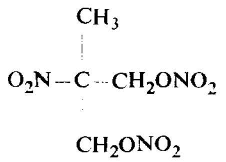
The mode of preparation of nitroisobutylglycerine trinitrate investigated particularly by Aubry [77] consists in nitrating NIB-glycerine with a mixture of nitric and sulphuric acid under conditions more or less approximating to those applied in nitroglycerine manufacture. Being more viscous the nitrated product compares unfavourably with nitroglycerine in that acids are washed out with difficulty. The yield is nearly 90% of theoretical (about 243 parts of nitrate from 100 parts of trimethylolnitromethane).

The quality of the product and especially the effectiveness of water washing are dependent on the purity of the original raw material since the presence of impurities cause the ester to form emulsions with water.

Nitroisobutylglycerine for nitrating purposes should have a melting point not lower than 150°C (the pure compound melts at 164–165°C).

Its practical application depends on the manufacture of nitromethane, which can be now obtained by vapour phase nitration (Hass *et al,* [78]; T. Urbański and Słoń [79]).

Dimethylolnitroethane dinitrate



$$O_2N-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_2ONO_2}{C}}-CH_2ONO_2$$

Dimethylolnitroethane dinitrate (2-nitro-2-methylpropanediol-1,3-dinitrate) is a solid melting at 38°C, of low volatility, dissolving nitrocellulose readily enough.

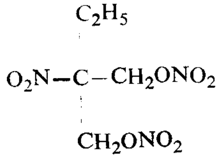
The substance was first described in a report by Bergheim [80] and afterwards by Wyler [81] and Médard [82]. It is an explosive a little weaker than nitroglycerine, but slightly stronger than cyclonite. Its heat of explosion is about 1250 kcal/kg. Its sensitiveness to impact is distinctly less than that of nitroglycerine. Wyler has estimated the sensitiveness to shock as approximately the same as TNT. Médard has reported it to be slightly higher than that of tetryl, and comparable with cyclonite.

When compressed the product can attain the following densities:

under a pressure of 1360 kg/cm^2 $d = 1.58$
under a pressure of 2760 kg/cm^2 $d = 1.61$

Médard has established that the chemical stability of this compound is insufficient for any wider use in explosives technology.

Dimethylolnitropropane dinitrate

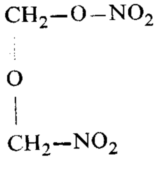


$$\begin{array}{c} C_2H_5 \\ | \\ O_2N-C-CH_2ONO_2 \\ | \\ CH_2ONO_2 \end{array}$$

Dimethylolnitropropane dinitrate (2-ethyl-2-nitropropanediol-1,3-dinitrate) is a liquid that does not dissolve nitrocellulose.

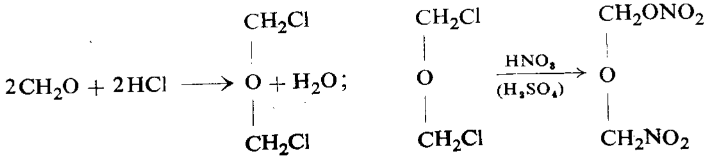
Médard [83] found that it is a stronger explosive than picric acid, producing in the lead block an expansion some 25% larger. Its sensitiveness to mechanical shock is appreciably smaller than that of picric acid.

Nitromethoxymethanol nitrate



$$\begin{array}{l} CH_2-O-NO_2 \\ | \\ O \\ | \\ CH_2-NO_2 \end{array}$$

This ester, known as methyl ether nitronitrate (more correctly as nitromethoxymethanol nitrate), is a colourless, oily liquid, boiling at 48°C at 15 mm Hg with a specific gravity 1.50 at 20°C. It readily dissolves collodion cotton, and is more volatile than nitroglycol. It was first produced by Moreschi [84] by nitrating *sym*-dichlordimethyl ether formed by reacting a 40% formaldehyde solution with gaseous hydrogen chloride:



$$2CH_2O + 2HCl \longrightarrow \begin{array}{c} CH_2Cl \\ | \\ O \\ | \\ CH_2Cl \end{array} + H_2O; \qquad \begin{array}{c} CH_2Cl \\ | \\ O \\ | \\ CH_2Cl \end{array} \xrightarrow[(H_2SO_4)]{HNO_3} \begin{array}{c} CH_2ONO_2 \\ | \\ O \\ | \\ CH_2NO_2 \end{array}$$

T. Urbański and Magiera [85] have examined the chemical stability and explosive properties of the ester and conclude that neither the substance itself nor a solution of nitrocellulose in it are sufficiently stable for practical application. Its temperature of initiation is 150°C (whereas nitroglycol is initiated at 220°C), and it is considerably more sensitive to impact than nitroglycol. They also found that an impact energy of 0.91 kgm/cm^2 is necessary to ensure a 10% probability explosion of nitroglycol, as compared with barely 0.11 kgm/cm^2 for the ester.

Nitromethoxy methanol nitrate produced a lead block expansion of 420 cm^3 whereas the net expansion produced by nitroglycol in the same series of experiments was 450 cm^3.

During the reaction between formaldehyde and hydrogen chloride a chloroether is also produced: $ClCH_2OCH_2OCH_2Cl$. According to Houben and Pfankuch [86] nitration of this substance produces a nitronitrate $O_2NOCH_2—O—CH_2OCH_2NO_2$ boiling at a temperature of 88°C under 9 mm Hg. It is less volatile than the other nitronitrate, though more volatile as nitroglycol.

T. Urbański and Magiera have found that this compound had similar explosive properties, low chemical stability, high sensitiveness to shock, and produced a large expansion in the lead block (440 cm^3).

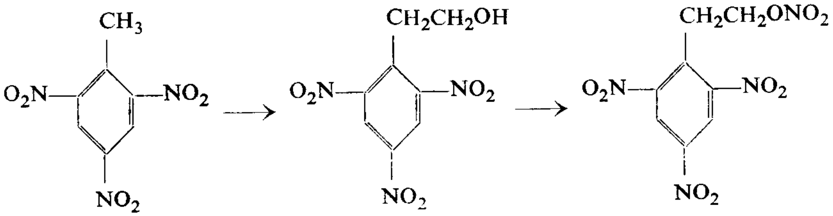
Neither of these substances has been used in practice, owing to their low stability.

NITROAROMATIC ALCOHOL NITRATES

There exists a range of explosives which are prepared by the nitration of aromatic alcohols. None of these explosives has found practical application, though this might be possible providing the costs of production were not too great and the explosive strength sufficiently high. This group of materials includes such compounds as: dinitrobenzyl nitrate [106], trinitrohydroxyethylbenzene nitrate, trinitrophenoxyethyl nitrate and the like.

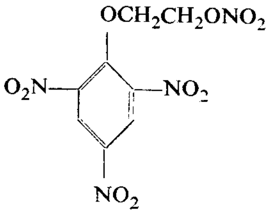
Trinitrohydroxyethylbenzene nitrate

Trinitrohydroxyethylbenzene nitrate or trinitrophenyl-β-ethyl nitrate, melting at 83°C, is obtained from trinitrotoluene, that undergoes an addition reaction with formaldehyde in an alkaline medium to produce the corresponding alcohol (m.p. 112°C), which is then nitrated (Vender [87]):



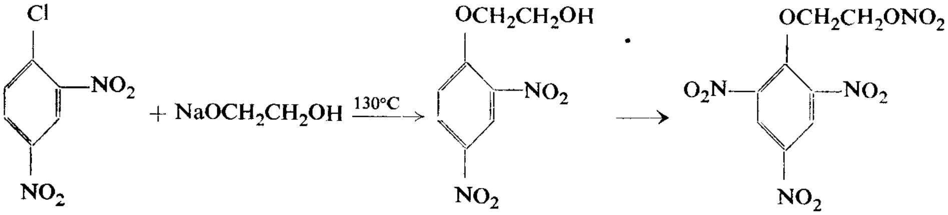
m.p. 83°C

Trinitrophenoxyethyl-ω-nitrate

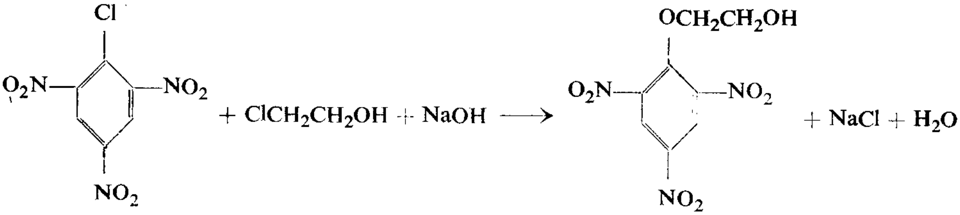


This is a white crystalline powder with a melting point of 104.5°C, soluble in acetone and capable of gelatinizing collodion cotton.

It can be obtained by reacting sodium hydrogen ethylene glyoxide and chlorodinitrobenzene followed by nitration, or chlorotrinitrobenzene, as reported by Faibourne and Toms [88]:

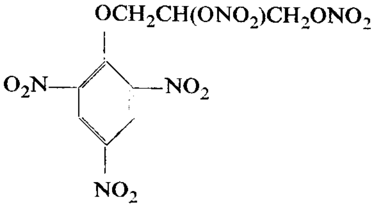


Trinitrophenoxyethyl alcohol, the parent substance of trinitrophenoxyethyl nitrate, was also obtained by Wasmer [89] in another way, namely:



Trinitrophenoxyethyl-ω-nitrate is more sensitive to impact than picric acid and less so than tetryl. Its explosive strength approaches that of tetryl, since it produces an expansion in the lead block of 350–355 cm^3.

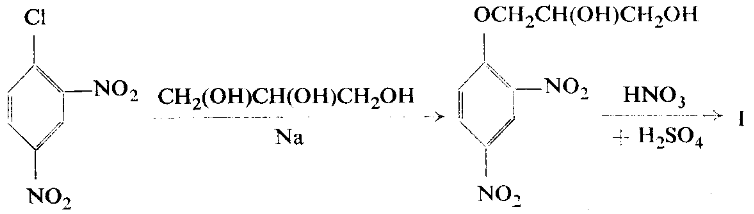
Trinitrophenyl-α-glycerol-β,γ-dinitrate (α-glyceryl-trinitrophenyl ether β,γ-dinitrate)



I

This is a white crystalline substance with a melting point of 125–127°C.

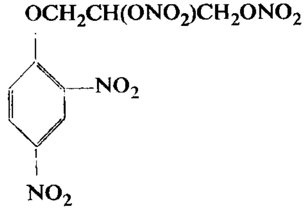
It was suggested as an explosive by Lewis [90] and later described by Desvergnes [91]. According to Willgerodt [92] it is formed by reacting chlorodinitrobenzene with glycerol in the presence of sodium hydroxide to yield dinitrophenyl-α-glycerol (II), followed by nitration:



II

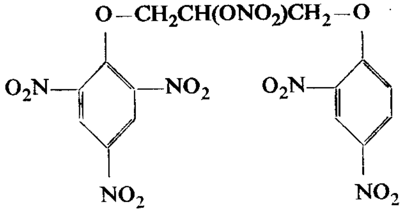
The product (I) gives an expansion in the lead block 25–30% greater than that of picric acid.

The dinitrate of (II) was also obtained [91, 93] as a substance



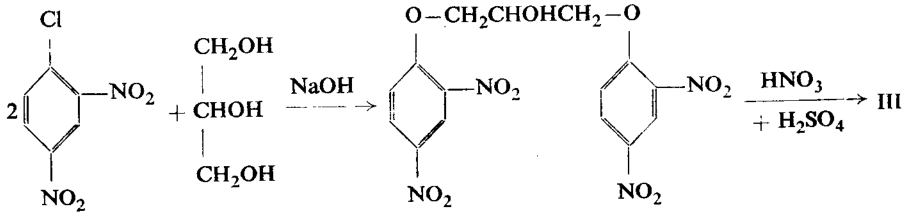
melting at 119–120°C. See also [94].

Bis(trinitrophenyl)-α,γ-glycerol-β-nitrate [α,γ-glyceryl-bis(trinitrophenyl)ether] β-nitrate



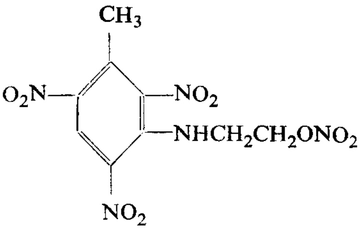
III

This is a straw yellow crystalline substance with a melting point 178–178.5°C. It was first obtained and suggested as an explosive by Dynamit A.G. [95]. Later, Desvergnes [91], Stefanović and Ćirić [94] described its preparation by the following sequence of reactions:



(m.p. 173.5–174°C)

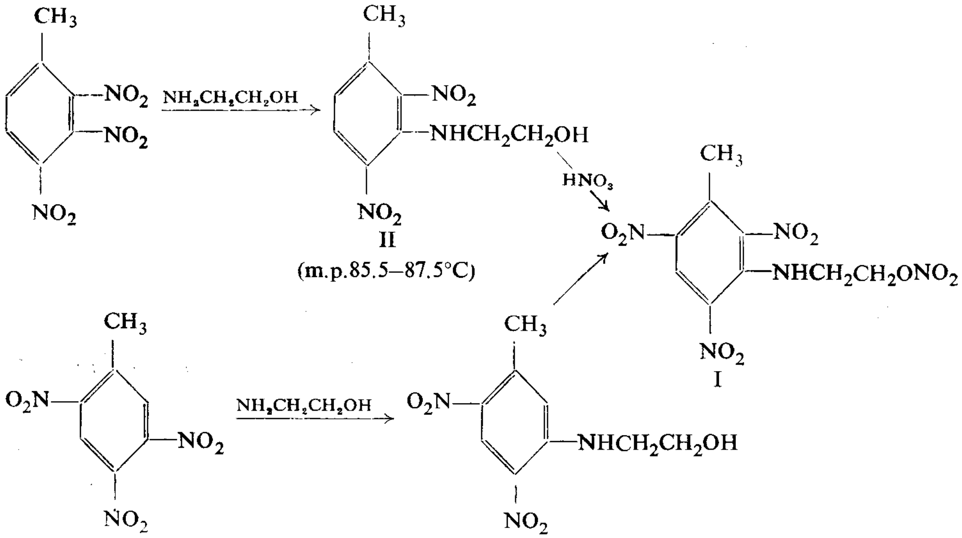
2,4,6,-Trinitro-3-(β-nitroxyethylamine)toluene



I

(m.p. 100–102.5°C)

2,4,6-Trinitro-3-(β-nitroxyethylamine)toluene was prepared by Pluciński [96] as follows:



II (m.p.85.5–87.5°C)

I

III (m.p. 115–117.5°C)

The compounds (II) and (III) are known in the literature. They were obtained and described by Racciu [97]. Further nitration of both produced (I), according to Pluciński.

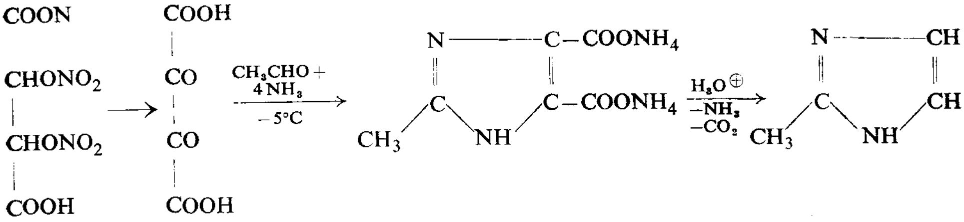
VARIOUS NITRIC ESTERS

Tartaric acid dinitrate

$$COOH-CHONO_2-CHONO_2-COOH$$

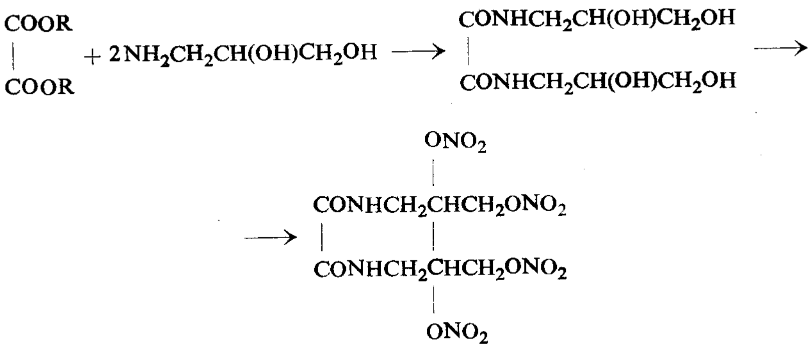
This compound was prepared by Dessaignes in 1857 [98]. The compound is unstable and is spontaneously transformed into dioxosuccinic acid (Kekulé [99], Thiele and Dralle [100] and others [101]).

The high reactivity of the dinitrate may be used to obtain heterocyclic compounds. An ingenious method of forming imidazol derivatives was developed by Payman and Fargher [102]:



Hydroxyalkylacylamide nitrates

Esters of this constitution include: di(hydroxyethyl)-oxamide dinitrate [107] and di-(β,γ-dihydroxypropyl)-oxamide tetranitrate. The latter was first prepared by Domański and Skudrzyk [103] by heating an oxalic acid ester with dihydroxypropylamine to form an amide which was then nitrated, as shown below:



$$\begin{array}{l}COOR\\ |\\ COOR\end{array} + 2NH_2CH_2CH(OH)CH_2OH \longrightarrow \begin{array}{l}CONHCH_2CH(OH)CH_2OH\\ |\\ CONHCH_2CH(OH)CH_2OH\end{array} \longrightarrow$$

$$\longrightarrow \begin{array}{l}CONHCH_2\overset{ONO_2}{\overset{|}{C}}HCH_2ONO_2\\ |\\ CONHCH_2\underset{ONO_2}{\underset{|}{C}}HCH_2ONO_2\end{array}$$

It must be pointed out that experiments intended to attach a nitro group to a nitrogen atom failed. The substance is stable, since it did not undergo decomposition after being maintained for 200 hr at 70°C, and its temperature of initiation is 187°C. Its explosive properties are as follows. At a density of 0.62 g/cm^3 it detonates with a rate of 4030 m/sec, the lead block expansion is 325 cm^3 and its relatively low sensitiveness to shock is indicated by the fact that it is exploded in a drop test by a 2-kg weight falling from a height of 60 cm.

Discussion concerning aminoalcohol esters of nitric acid which are also salts of nitric acid, is developed further in the chapter devoted to nitric salts (see p. 472).

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CHAPTER IX

CELLULOSE AND NITROCELLULOSE

THE most important of the carbohydrate esters of nitric acid are the polysaccharide nitrates, particularly cellulose nitrate or nitrocellulose (NC) and starch nitrate ("nitrostarch") which is much less used. Nitric esters prepared from other sugars such as saccharose and lactose are not of any importance as explosives.

Introduction. Today nitrocellulose is one of most important derivatives of cellulose used in industry and commerce, and a major product of the chemical industry. Its wide and manifold applications are due mainly to its extraordinary physical properties. Thus a protective coating of nitrocellulose varnish, a nitrocellulose film or a tube of smokeless powder — all are characterized by relatively high elasticity and mechanical strength. These properties are a direct consequence of the microstructure of cellulose, which is composed of highly oriented long-chain molecules of polysaccharide. Not only nitrocellulose, but also other derivatives of cellulose, such as other esters and ethers, demonstrate similar characteristics.

Today nitrocellulose is used in the manufacture of all types of smokeless powder, blasting gelatine and dynamites, celluloid, films, varnishes, and artifical leather, in the printing industry and in the pharmaceutical industry.

There exists a range of various kinds of nitrocellulose differing from one another in their physical properties according to the application intended. Nitrocellulose for smokeless powder manufacturing (guncotton) represents one type while other properties are demanded from the raw material to be used for making celluloid or artificial fibres (collodion cotton, collodion nitrocotton).

HISTORICAL

The first reference to the preparation of nitrocellulose was made by Braconnot at Nancy in 1833 [1]. He prepared a number of products he named "xyloidine" by dissolving in nitric acid a series of substances of vegetable origin. The resultant solution was passed into a large amount of water to precipitate xyloidine. Xyloidine obtained in this way was described by the discoverer as a solid, easily inflammable, burning violently and completely to leave no residue. Taking into consideration its mode of preparation, Braconnot's xyloidine probably contained only 5–6% of nitrogen.

Pelouze [2] continued the investigations of Braconnot by subjecting paper or cotton to the action of nitric acid. The difference was that in his experiments the nitrated material was not dissolved in nitric acid, but the product was similar. In later papers it was described under the name of pyroxylin. Extending his earlier researches, Pelouze [3] later established that pyroxylin was a substance differing in principle from the product obtained by nitrating starch.

At the same time some original investigations were described by Schönbein [5] of Basle. In 1845 he began to examine the properties of ozone and "active oxygen". He also investigated how various organic and inorganic substances, among them cotton, sugar etc., behave, when treated with nitric acid in the presence of sulphuric acid. He paid special attention to the properties of the product obtained from cotton which he has named guncotton in order to emphasize the possibility of using it as gunpowder. Indeed, the important contribution of Schönbein was that he indicated the practicability of the large-scale application of nitrocellulose as an explosive.

At the same time Böttger [6] announced the preparation of an explosive cotton in 1846. This was done independently of Schönbein, and Böttger's priority was admitted by Schönbein [5].

Meanwhile Otto [6] had been pursuing the same subject and reported in 1846 that he had succeeded in producing an explosive cotton similar to Schönbein's guncotton by immersing cotton in concentrated nitric acid for about half a minute, followed by washing and drying. Schönbein applied for a patent to protect his method of preparing guncotton. However, when further trials were begun to extend Schönbein's experiments and to develop production on plant scale, serious difficulties arose, mainly due to spotaneous decomposition of the nitrocellulose brought about by the low chemical stability of the product. Thus an explosion took place in 1847 in the nitrocellulose factory of Messrs John Hall and Sons at Faversham, Great Britain, which used the method based on Schönbein's patent [5]. The whole plant was destroyed. In 1848 in France storage buildings containing guncotton suffered a similar misfortune [7] and later an explosion occurred in an Austrian plant where nitrocotton manufacture had been established since 1853 by Lenk von Wolfsburg [8]. The Austrian authorities viewed the incidence of these explosions in guncotton stores with such anxiety that an edict was promulgated forbidding the manufacture of this product in Austria until its properties were thoroughly understood and production techniques firmly established.

It is now clear that the process of stabilizing nitrocellulose used by Lenk [9] that consisted in washing nitrocellulose with running water for 14 days, followed by a boil with dilute carbonate solution and a final washing with a sodium silicate solution (p. 293), was not sufficient to produce a completely stable product.

Abel takes the credit for explaining that the accidents with nitrocellulose occurred as the result of incomplete removal of readily decomposable products, i.e. they were due to inadequate purification ("stabilization") of the guncotton.

Prolonged boiling of the guncotton with water followed by pulping the substance was introduced by Abel [10]. This technique permitted the removal of the unstable products from inside the fibres. In this way Abel prepared guncotton which was chemically stable.

At that time, however, the practical application of guncotton was still limited and for a long time attempts to use it as an explosive failed.

A considerable advance in the application of guncotton for military purposes was made when Abel and Brown [11] suggested using a compressed product as a high explosive. The detonation of guncotton was brought about by means of a recently discovered detonator filled with mercury fulminate. The compressed guncotton was intended for the manufacture of demolition charges and for filling mines and torpedoes.

Another appreciable advance was the use of moist guncotton which was safer to handle. Detonation was achieved by means of a gaine (booster) made from dry guncotton initiated by a detonator.

For a time compressed guncotton was used in Russia by the artillery (1876) [12] as a shell filling. From 1890 moist guncotton was adopted for this purpose [12]. Guncotton continued to be used for a shell filling in some countries until it was replaced by the introduction of picric acid.

However, the widest military application for nitrocellulose was in the manufacture of smokeless propellants, which will be discussed in more detail in Vol. III. Between 1891 and 1895 Mendeleyev [13] sought to develop a high nitrated nitrocellulose which would dissolve in the solvent used in smokeless powder manufacture, i.e. in a mixture of alcohol and ether. Earlier work suggested that an increase in nitrogen content would cause the solubility of nitrocellulose to decrease. However, by applying suitable conditions for the nitrating process Mendeleyev prepared nitrocellulose soluble in the ether–alcohol solution despite its high nitrogen content of 12.6%. This be named pyrocollodion cotton or "pyrocellulose".

GENERAL CHARACTERISTICS OF CELLULOSE

Cellulose is one of the most widely distributed natural polymers, since it is one of the principal components of vegetable tissue. It always occurs in nature in the form of fibres varying from the knap-like fibres covering cotton seeds, to the woody substance of trees. The name cellulose is used both for cellulose isolated from the plant, and thus a chemical compound, and for cellulose *in situ* in the form normally occurring in the plant. In the second case cellulose together with hemicelluloses and lignin form the main constituents of the plant.

Little is known of the manner in which these three main components of plant tissue are bound together, whether by purely physical forces or partly by these and partly by chemical links, possibly of the ester type (Hirst [14]).

It is possible, therefore, that isolated cellulose contains some functional groups which were engaged originally in forming the linkages between cellulose and the other components of the plant. Further the isolation of cellulose inevitably causes some breakage in the long-chain molecule of cellulose, so that in general the average molecular weight of isolated cellulose is lesser than that of cellulose existing in plants. During separation and purification, cellulose oxidation reactions may occur with the formation of new functional groups in the cellulose.

Strictly speaking it is possible to isolate cellulose from any plant. However, in the selection of cellulose as raw material for industrial purposes a complex of factors is to be considered:

(a) the cellulose content in the plant, hence the yield of cellulose and the costs of isolating it;

(b) the physical and chemical properties of the cellulose and partly the characteristics of associated substances;

(c) the purpose for which the cellulose is to be used: as a textile, or in the chemical industry.

As a raw material for large-scale nitration, cellulose from cotton, alfalfa and wood pulp is used. Cellulose from annual or biennial plants such as nettle or cereals (straw pulp) etc. is seldom used.

STRUCTURE OF CELLULOSE

Cellulose can be regarded as a polymer of glucose formed by condensation through removal of water molecules. It may well be that cellulose, and also other polysaccharides, are synthesized from glucose in plants according to the equation:

$$nC_6H_{12}O_6 \longrightarrow (C_6H_{10}O_5)_n + nH_2O \tag{1}$$

This hypothesis is based mainly on the results of hydrolysis, in which glucose is the only product. In contact with dilute sulphuric acid cellulose is broken down as follows:

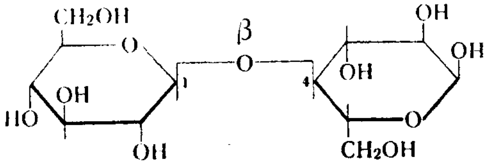
$$(C_6H_{10}O_5)_n + nH_2O \longrightarrow \underset{\text{D-Glucose}}{nC_6H_6O_{12}} \tag{2}$$

The yield of this reaction may approach the theoretical value (about 96%).

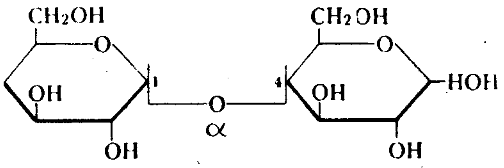
For a long time the degree of polymerization n, of the anhydroglucose units $C_6H_{10}O_5$ remained unknown. Cellulose is insoluble in all common solvents so that it was impossible to estimate its molecular weight by the usual methods, e.g. ebulliometric, cryometric, osmotic and the like. On the other hand, attempts to determine how the molecules of glucose are combined to form cellulose succeeded. As the result of treating cellulose with conc. sulphuric acid in the presence of acetic anhydride, to acetylate the hydroxyl groups and thus protect the compound against more extensive hydrolysis or breakdown, cellobiose acetate was formed. Cellodextrine acetate, composed of a few glucose units can also be formed as an intermediate product. Cellobiose acetate is a derivative of one of the bioses having the general formula $C_{12}H_{22}O_{11}$. Further hydrolysis of cellobiose results in the formation of

D-glucose. This reaction demonstrates the basic difference between the structure of starch and that of cellulose. Starch, in contact with an enzyme amylase (diastase), is broken down to form a different biose maltose, which when hydrolysed in the presence of acid is also converted into D-glucose.

The constitution of both of these bioses has been established by Haworth *et al.* [15]. It was found that the compounds differed from one another in the spacial configuration of the oxygen bond (glucosidic bond): this linkage joins the carbon atoms 1 and 4 which occupy the β-position in cellobiose, and the α-position in maltose:



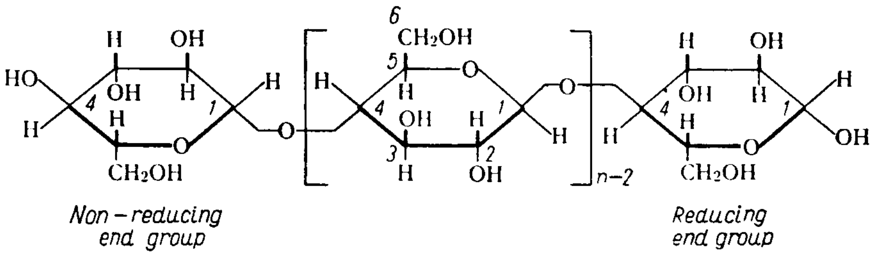
Cellobiose



Maltose

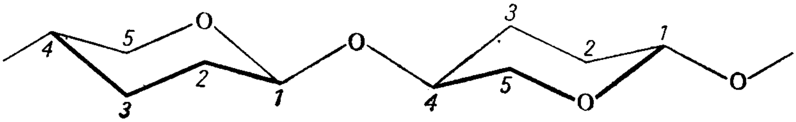
Like all carbohydrates, cellulose possesses the clearly marked prominent properties of an alcohol owing to the presence of hydroxyl (alcoholic) groups. The presence of those groups explains the ability of cellulose to form esters with nitric acid and with acetic acid which have attained great practical importance, and also with sulphuric, phosphoric and different organic acids, as well as the formation of cellulose ethers.

Formation of cellulose ethers and esters has shown that for every six carbon atoms contained in one $C_6H_{10}O_5$ group there are three free hydroxyl groups capable of undergoing esterification or forming ethers. It has also been established that the copper salts of Fehling's solution are reduced by cellulose only to a small extent. Those facts, supported by a series of studies devoted to the products of uncomplete hydrolysis of cellulose, for instance the isolation of cellotriose (Haworth, Hirst and H. A. Thomas [16]), provide sufficient evidence that a molecule of cellulose



is a straight chain composed of glucopyranose rings joined through an oxygen linkage which binds the 1- and 4-carbon atoms in the β-position (the formula is quoted from Sookne and Harris [16a]).

This formula is now regarded as a conventional one, as it is well known that non-aromatic rings of the cyclohexane type, including pyran rings, are non planar strainless rings. According to the present state of the conformation analysis a chair-form is usually attributed to the six membered rings. It follows that the anhydroglucose units form a chain, a fragment of which consisting of two rings is illustrated below. The glucoside C—O linkages joining the rings are in equatorial conformation.



The terminal glucopyranose rings of the chain contain four hydroxyl groups (two end rings of this type are shown in the formula), so that the hydrolysis of methylated cellulose would be expected to give a certain amount of tetramethylglucose together with a large amount of trimethylglucose. Among the products of hydrolysis 0.6% of tetramethylglucose has indeed been detected, resulting without question from the terminal glucopyranose nuclei, and this enabled Haworth [17] to make the first estimate of the magnitude of a cellulose molecule. He suggested that the molecule contains to some 100–200 anhydroglucose units, which would correspond with a molecular weight of 20,000–40,000.

Other methods of determining the molecular weight of cellulose include the reduction of Fehling's solution (a property of the extreme glucopyranose ring with a hemiacetal group), measurement of the viscosity of cellulose in cuprammonium solution, and estimation of the osmotic pressure of this solution or its sedimentation rate in the ultracentrifuge. The average molecular weight determined by the last three methods was higher than Haworth's original figure, namely 100,000–2,000,000.

Some data for the molecular weight of cellulose of various origins determined by ultra-centrifuging cuprammonium solution, are given in Table 35.

TABLE 35

Origin of cellulose	Molecular weight	Degree of polymerization	Author
Unbleached cotton	1,500,000	9200	Gralen and Svedberg [18]
Purified linters	1,500,000–500,000	10,000–3000	Kraemer [19]
Nettle fibre	1,760,000	10,800	
Ramie fibre	1,840,000	11,300	Gralen and Svedberg [18]
Sulphite pulp	400,000	2900	

According to Bryde and Rånby [20] the degree of polymerization of sulphite pulp varies from 845 to about 3200.

The constitutional formula and molecular weight of cellulose determined on the basis of chemical and physico-chemical experiments has been confirmed by X-ray analysis, which has also led to the discovery of the microcrystalline structure of cellulose. Today the structural model proposed by Meyer and Mark [21] and Mark and Misch [22] based on the X-ray measurements of Polanyi [23] and Sponsler and Dore [24] and taking into consideration Haworth's conclusions about the existence of the bond 1–4 in cellulose, is fully accepted. The fundamental unit of cellulose, in crystallographic measurements, consists of five cellobiose members ranged axially along the cellulose fibre. The dimensions of this unit are as follows: $a = 8.35$ Å, $b = 10.3$ Å (along the fibre axis), $c = 7.9$ Å, the angle β formed by the axes c and a being 84°. A diagram of the crystal unit is given in Fig. 75 in which three of the five cellobiose units are shown.

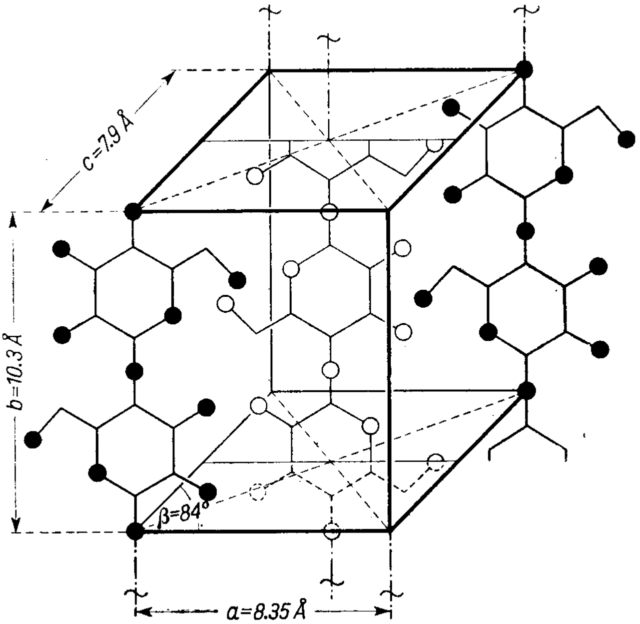


FIG. 75. Unit cell of cellulose I according to Meyer and Mark [21], Mark and Misch [22].

According to Trommel [24a] the cell dimensions of cellulose are: $a = 8.29$Å, $b = 10.5$ Å, $c = 7.93$ Å, $\beta = 84°53'$. The angle β changes to 90° in the course of the nitration.

Crystalline cellulose is believed to exist in at least four crystalline variations. Cellulose I occurs in the majority of plants. Its crystal structure conforms with the diagram in Fig. 75.

Cellulose II represents cellulose precipitated from solution or regenerated from an addition compound, for instance alkalicellulose. The essential characteristic of the microcrystalline constitution of cellulose II is a certain deformation of its crystal lattice resulting in a distortion of the β-angle, making it approximately 62° (Andress [25]).

Swelling cellulose I by means of liquid ammonia and precipitating the substance leads to the formation of cellulose III, which also differs from I by virtue of its deformed crystal lattice, in which the β-angle is approximately 58° (Legrand [26].

Regenerated cellulose (cellulose II) heated in water under pressure or in glycerine to 140–300°C yields cellulose IV giving an X-ray picture approximately the same as that of cellulose I, but with a wider β-angle of 90° (Kubo [27]).

The differences in the microcrystalline structure of the different forms of cellulose are compared in Table 36.

TABLE 36

Parameter	Cellulose I	Cellulose II	Cellulose III	Cellulose IV
Axis *a*	8.35 Å	8.1 Å	7.74 Å	8.11 Å
Axis *b*	10.3 Å	10.3 Å	10.3 Å	10.3 Å
Axis *c*	7.9 Å	9.1 Å	9.9 Å	7.9 Å
Angle β	84°	62°	58°	90°

To account for the phenomenon of chelation by intermolecular hydrogen bonds, Pierce [28] has suggested an alternative constitution for cellulose, as shown in Fig. 76.

Carbon atoms are depicted as single circlets, the oxygen atoms of the primary alcohol groups as two concentric circlets, the oxygen atoms of the secondary hydroxyl groups as two concentric circlets, the inner one being marked with a broken line, and the hydrogen bonds are indicated by the letter H.

A similar system has also been proposed by Hermans [29] who postulated that the hydroxyl groups at the carbon atoms 3 and 6 were capable of forming hydrogen bonds with neighbouring oxygen atoms. The existence of hydrogen bridges in cellulose has been demonstrated by analysing its infra-red spectrum and the spectra of its derivatives (Nikitin [30], Konkin *et al.* [30a]). This is discussed on p. 287.

The existence of hydrogen bonds joining the straight chains of cellulose explains the rigidity and mechanical strength of cellulose fibres.

Cellulose fibres are probably packed parallel to one another lengthwise along the axis to form bundles, so called micelles, which are highly oriented along the fibre axis, thus giving cellulose its characteristic mechanical properties.

On the basis of X-ray measurements it is assumed that a micelle composed of 100–170 simple cellulose chains has a length of at least 600Å and a width of 50–60Å. An outline of the micellar structure of cellulose, according to Meyer and Mark [31], is sketched in Fig. 77. The "secondary" valencies (*a*) unite individual chain-molecules while the "tertiary" valencies (*b*) join different micelles in a given system. The micellar theory of the structure of fibrous substances was suggested as early as 1858 by the Hungarian botanist Nägeli [32] while taking into consideration the double refraction of light by fibre-like substances. He published the hypothesis that substances showing a fibrous texture under the microscope were composed of smaller units, invisible under the microscope, that were also fibre-shaped particles. This theory, once forgotten, has been revived as the result of more modern studies with fibrous substances.

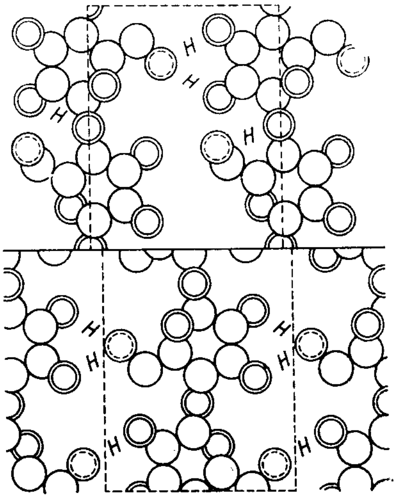


FIG. 76. Diagram of the structure of native cellulose with hydrogen bonds according to Pierce [28].

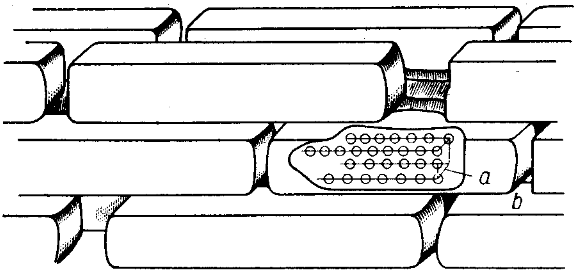


FIG. 77. Diagram of the micellar structure of cellulose according to Meyer and Mark [31].

The views of Mark and Meyer have been modified and extended by several authors, e.g. Katz [33], Rogovin [34], Kargin [35] and others [36]. The most serious objections to the Mark and Meyer's theory are: (1) the hypothesis cannot explain the process of swelling, for it does not show why micelles are not destroyed when a liquid penetrates into the fibre; (2) Staudinger's investigations on viscosity shown that cellulose micelles possess a length of the order of some 10,000 Å, a value distinct greater than that of 600 Å as estimated by X-ray experiments. An alternative concept of micellar structure emerged from this discussion, formulated by Frey-Wyssling [37], Kratky [38] and Rogovin [34]. Mark [39] and Meyer [40] accepted it and it is now generally known as the "fringe micellar theory".

According to this theory the micelles are considered as statistically distributed regions of ordered lattice, consisting of approximately parallel chain "crystalline" molecules in an "amorphous" mass. Generally speaking, cellulose fibre is a two-phase system, wherein the crystalline substance is one phase, and amorphous cellulose the other. The characteristic feature of the micellar theory of cellulose proposed by Rogovin [34], is that the term "micelle" is to be understood as an aggregation of highly oriented cellulose chains (Fig. 78) which are situated very close to one from other, hence the energy of the bonds joining the chain-molecules is high. Such aggregations are situated in a complex of non-oriented amorphous chains.

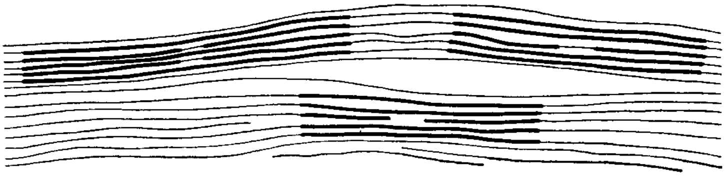


FIG. 78. Diagram of the micellar structure of cellulose according to Rogovin [34].

Non-oriented chains are indicated in the diagram by thin lines, while micelles, that is oriented parts, are marked with thicker ones. This concept made many facts explicable. Thus the spectrum of cellulose with about half its hydroxyl groups esterified with nitric or acetic acid showed an unchanged fibrous structure (Hess and Trogus [41]). To explain this, Rogovin suggests that the esterification proceeds in the non-oriented cellulose so that in effect the spectrum of the micelles remains unchanged. In the same way the swelling of cellulose fibres takes place in the amorphous phase, the micelles remaining as well oriented as before and therefore giving the distinctive X-ray diagram of the fibrous structure.

A similar theory was published by Frey-Wyssling [37] who suggested a scheme composed of two projections outlined in Fig. 79, where the crystalline phases of the cellulose fibre are marked as dotted line rectangles.

The spatial configurations proposed by Kratky [38] and Mark [39] repeat in principle the basic idea of the fringe micellar theory, according to which long cellulose chains lie lengthwise through the crystal and amorphous phases form the fibre (Fig. 80).

The letters *a*, *a'*, *b'*, represent the ends of molecules in the crystal phase of the micelle, *b*, the ends of molecules in the non-crystalline phase, *l* the length of the crystalline phase.

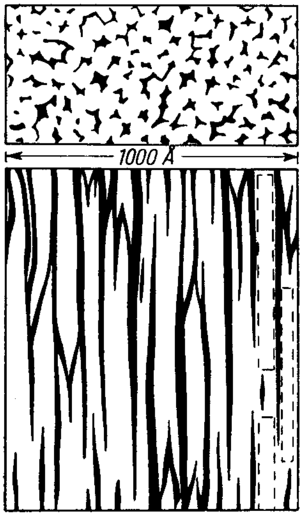


FIG. 79. Diagram of the micellar structure of cellulose according to Frey-Wyssling [37].

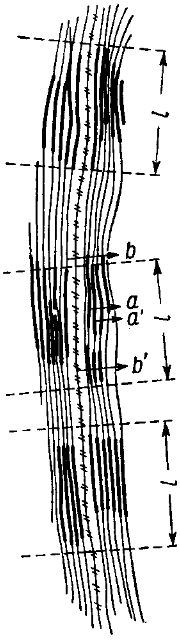


FIG. 80. Diagram of the fringe micellar structure according to Mark [39].

Figure 81 is an electron micrograph of section of cellulose fibre, enlarged 39,000 times. The micellar texture of the fibre is clearly visible.

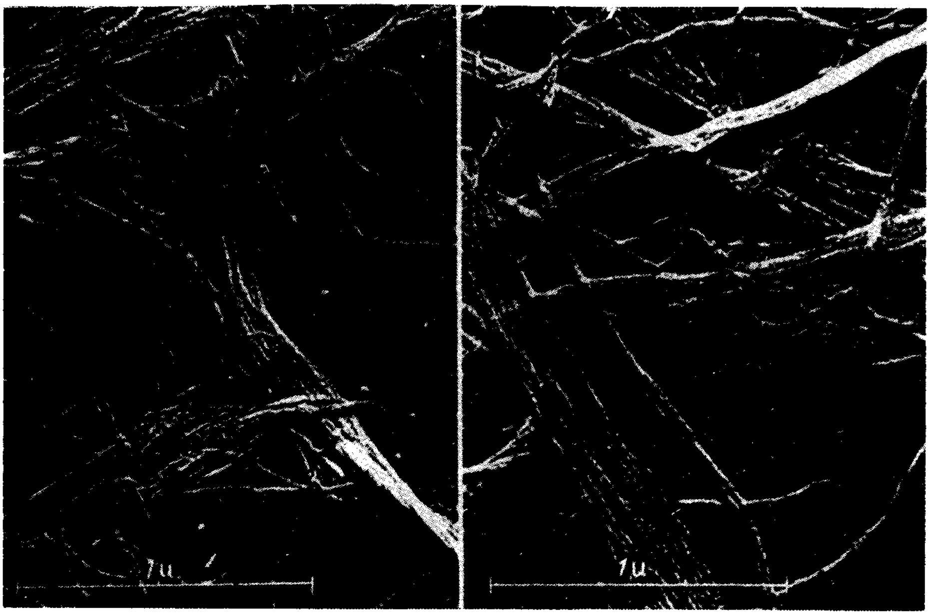


FIG. 81. Electron micrograph of cellulose fibres, from purified cotton and wood pulp respectively, magnification 39,000, according to Rånby [41a].

The Soviet authors Kargin *et al.* [35, 42] and Kozlov [43] have developed the theory of fully amorphous cellulose. Kargin and Leipunskaya [44] have drawn similar conclusions from an electron diffraction study of cellulose esters, including nitrocellulose.

At the present moment it is difficult to decide which of the two hypotheses concerning the structure of cellulose is correct: the idea of an amorpho-crystalline structure, or that postulating solely an amorphous texture. Nikitin assumes that the first hypothesis is the more probable, more especially as it is well in line with the most recent work of Zaydes and Sinitskaya [45] who conclude on the basis of electron diffraction investigations that in the natural cellulose fibre of Chinese nettle, there exist phases having a distinct microcrystalline structure. This suggests that structures shown in Figs. 78, 79 and 80 are the most probable.

Further evidence in favour of the amorpho-crystalline texture was recently provided by Rånby [46]. In a series of his papers several questions connected with the microstructure of cellulose are made clear. Cellulose to be examined in an electron microscope was initially dispersed by means of ultrasonic waves. In this way Rånby has isolated elementary thread-like micelles of about 70 Å dia. Any dimension characterizing the length of the micelle is however missing.

From an examination of α-, β-, and γ-cellulose of spruce (the classification of cellulose in α-, β-, and γ-variations is described in more detail on p. 230) Rånby arrived at the idea that the α-fraction consisted to thread-like micelles 80 Å dia. β-Cellulose has a similar structure, but with shorter micelles and seems likely to be a degraded form of α-cellulose. γ-Cellulose, however, is amorphous and contains no thread-like micelles. It appears to be composed of different polyoses including hemicelluloses together with amorphous cellulose filling the space between the micelles.

Cellulose dissolved in Schweitzer's reagent (cuprammonium) demonstrates strong laevo-rotatory optical activity. The optical activity of cellulose solutions differing in origin and of different morphological structure is the same.

CHEMICAL PROPERTIES OF CELLULOSE

Wetting and swelling. As stated above, the presence of hydroxyl groups in cellulose enables it to be esterified up to a maximum of three ester groups to every anhydroglucose unit. Further, the high content of hydroxyl groups endows cellulose with hydrophilic properties. Nevertheless, the amount of water absorbed by cellulose from an atmosphere saturated with moisture is smaller than would be expected for a substance containing so many hydroxyl groups. The maximum quantity of water taken up by cellulose is 16%. Esters of cellulose are appreciably less hygroscopic. Their hygroscopicity decreases as the number of ester groups increases though esterification does not totally eliminate hygroscopicity.

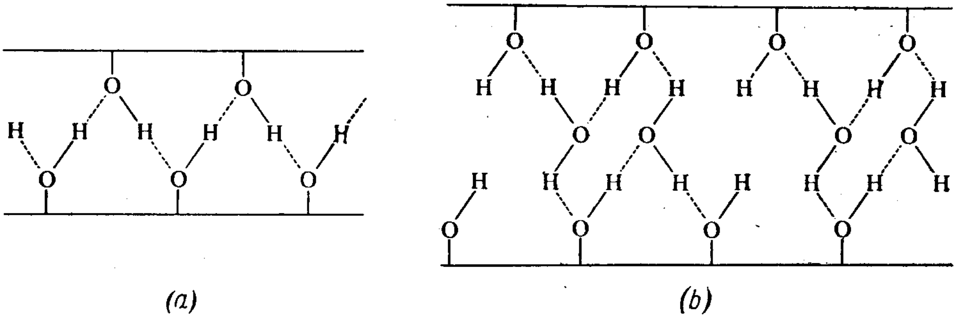


FIG. 82. Chains dry (a) and wet—swollen (b) cellulose with hydrogen bonds.

The affinity of cellulose and its derivatives for water can be explained by the existence of hydrogen bonds that bind the molecules of the cellulose chain either directly or with the help of water molecules, as outlined in Fig. 82. The existence of hydrogen bonds has been confirmed experimentally by studies of the infra-red absorption spectra of cellulose and its derivatives (the subject will be discussed later, on p. 287).

Moreover the presence of chelate bonds makes it possible to explain both certain properties of nitrocellulose and phenomena connected with the esterification reaction mechanism of cellulose, all of which will be discussed later.

According to Mark [39] the anhydroglucose units are combined along the *a*-axis (Fig. 75) by means of linkages, the energy of which amounts to *ca.* 50 kcal/mole.

The energy of hydrogen bonds is 15 kcal/mole, while that of the intermolecular (van der Waals) bond acting mainly in the direction of *c*-axis corresponds to 8 kcal/mole.

Another typical property of cellulose and its derivatives dependent on water sorption is the swelling of the fibre that occurs under the influence of certain solutions such as aqueous sodium hydroxide or an ammoniacal solution of cupric oxide, i.e. "cuprammonium". The process of swelling does not start with sorption as in the instance of water. In the first stage of swelling the liquid penetrates the molecular chains of the cellulose, gradually coming in contact with all of them so that chemical combination takes place to form alkali celluloses, $(C_6H_{10}O_5) \cdot NaOH$ and $(C_6H_{10}O_5)_2 \cdot NaOH$.

Compounds of this type are unstable, and hydrolyse in water, hence sodium hydroxide can be completely removed by water washing. In effect swollen cellulose is produced. Formerly, in view of the difficulty of removing the water contained in such cellulose by drying, it was called hydrated cellulose, the idea that it represented a water-cellulose compound, a "cellulose hydrate", being current at that time.

Cellulose hydrate is more hygroscopic than cellulose and demonstrates increased reactivity, e.g. esterification. Cellulose hydrate can also be produced by the action of dilute nitric acid.

In certain cases as for instance by treatment of cellulose with cuprammonium, swelling virtually dissolves the cellulose. (The theory of swelling and solution of nitrocellulose is developed in more detail on p. 244). During swelling a characteristic increase in the diameter of the fibre occurs, without any increase in its length.

Sorption and swelling are accompanied by the evolution of heat (Katz [33]). Water sorption causes the evolution of some 3.5–6.0 kcal/mole. The heat of swelling in the presence of sodium hydroxide depends on its concentration. When a 5–18% sodium hydroxide solution is used, the heat of swelling amounts to 13–30 cal/g of cellulose.

Degradation of cellulose. In contact with hydrolysing or oxydizing agents, cellulose undergoes hydrolysis, or oxidation accompanied by hydrolysis, to form hydrocellulose or oxycellulose.

Hydrocellulose is formed when pure cellulose is subjected to the action of cold mineral acids solutions. Hydrolysis then proceeds by stages to yield glucose as the final product. It is possible to stop the hydrolysis at any desired moment, for example by diluting the reaction mixture with water. Hydrocellulose then remains in the form of non dissolved fibres or as powder (Girard [47]). The hydrolysis is usually performed by means of hydrochloric acid or with hydrogen chloride in an anhydrous medium. In the latter case, a water-soluble addition compound $(C_6H_{10}O_5)_2 . 3HCl$ may occur as a transient product, as reported by Hess and M. Ullman [48].

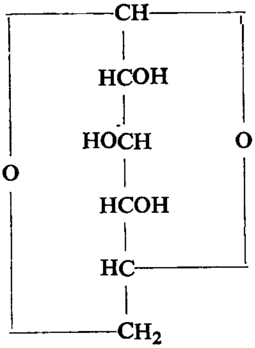
The changes that occur when cellulose is subjected to hydrolysis all follow from the destruction of the 1,4-glucoside bond. Thus the cellulose chains are shortened and a decrease in the average molecular weight takes place and the cellulose fibres lose some of their tensile strenght and elasticity. Hydrocellulose can reduce Fehling's solution, a property that accords well with the presence of hemi-acetal groups at the terminal anhydroglucose rings.

Hydrocellulose is partially soluble in sodium hydroxide solution. The stronger the reducing action of the hydrocellulose the better its solubility, which can vary from 2–10% in a solution containing 18% NaOH, at room temperature. At a low temperature, e.g. —5°C, the solubility is higher.

Oxycellulose is formed by the action of oxidizing agents such as hypochlorite solutions, hydrogen peroxide and atmospheric oxygen, acting in the presence of a sodium hydroxide solution. The properties of oxycellulose depend on its method of preparation. Oxidation in a neutral or acid medium gives a product with definite reducing properties, indicating the presence of aldehyde groups. Oxidation in an alkaline medium gives a product with acidic properties, indicating the presence of carboxylic groups. An oxycellulose of this kind is distinguished from the other by its capacity of being coloured by methylene blue.

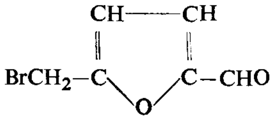
Sodium hydroxide solution partially dissolves oxycellulose. The remaining insoluble fraction does not possess reducing properties. The tensile strength of oxycellulose fibres is lower than that of cellulose fibres, but depending on the mode of preparation they may possess a higher strength than hydrocellulose fibres.

Effect of other factors on cellulose. Dry distillation at a temperature above 150°C causes cellulose to produce compounds of low molecular weight, such as water, methane, ethylene, carbon monoxide, carbon dioxide, acetic acid, and acetone. According to Pictet [49] dry distillation under reduced pressure yields a substance having the empirical formula $C_6H_{10}O_5$, laevo-glucosan which probably is *β*-D-glucopyranose anhydride:



Later on the decomposition of cellulose at high temperature was examined by a number of authors. Most of the research was devoted to the problem of the origin of coal. The experiments of T. Urbański *at al.* [50] using infra-red spectroscopic analysis for the examination of the products of thermal decomposition of cellulose are described in Vol. III. (Charcoal for blackpowder manufacture).

Cellulose brought into contact with hydrogen bromide is converted in ω-bromomethylfurfural



Cellulose can be degraded by different bacteria. One type of micro-organism causes a methane fermentation, which yields methane, carbon dioxide and lower fatty acids. A hydrogen fermentation is possible, giving H_2, CO_2 and the same acids. There is also a methane–hydrogen fermentation and nitrogen fixing bacteria which assimilate nitrogen from the atmosphere can bring about a breakdown involving the formation of nitrates. In the presence of the nitrates synthesized by these bacteria, cellulose is decomposed with evolution of nitrogen.

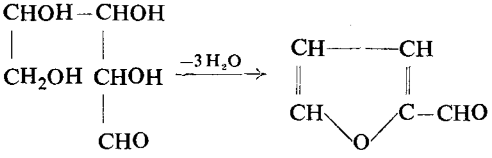
The decomposition of cellulose can be also brought about by moulds, usually by moulds such as *Aspergillus* and *Monilia*. The process is one of slow decay. Others however, for instance *Merilius domesticus*, decompose wood cellulose very quickly.

SUBSTANCES ACCOMPANYING CELLULOSE

In addition to cellulose certain related substances, namely hemicelluloses and lignin, occur widely in plants.

HEMICELLULOSES

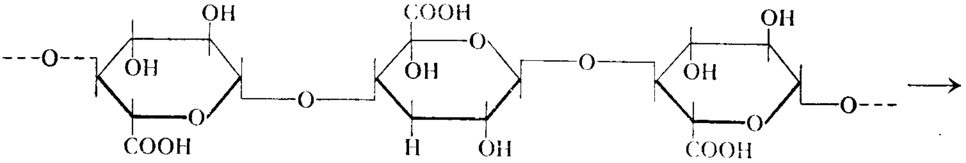
Hemicelluloses (cellulosans) is the family name of polysaccharides that includes pentosans $(C_5H_8O_4)_n$, made up of the pentose units and hexosans $(C_6H_{10}O_5)_n$ made up of hexose units. The pentosans include such substances as xylan and araban which are hydrolysed to xylose and arabinose respectively. On dehydration, furfuraldehyde is formed:



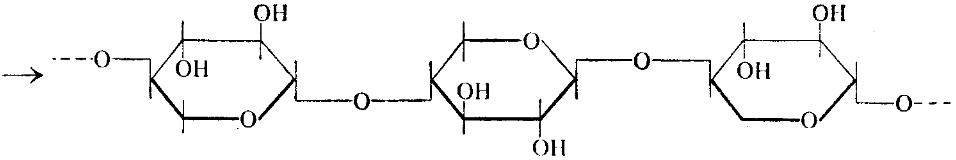
Pentose Furfural

The notable hexosans are mannan and galactan.

The hemicelluloses also include the polyuronides, or polyuronic acids, for instance a polymer of a hexuronic acid such as galacturonic acid. There is a possible generic link between the polyuronides and the pentosans since the latter might be produced as the result of the decarboxylation of hexuronic acids. The possibility of transforming hexuronic acids into pentosans by the removal of carbon dioxide molecules, and hence the conversion of hexosans into pentosans via these acids was first discussed by K. Smoleński [51]. It can be sketched as below:



Polyglucuronic acid



Xylan-(*β*-D-pyranoglucose)

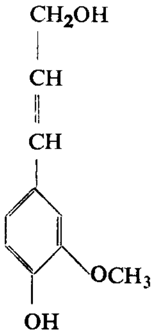
All hemicelluloses differ from cellulose in that they are soluble in dilute alkalis; it is self-evident that hexuronic acids dissolve particularly readily.

LIGNIN

Cellulose and lignin are the structural components of most plant cell walls. The constitution of lignin and its biosynthesis have been extensively studied but these problems are not yet solved.

Lignin is an ill-defined insoluble product of high molecular weight which is sensitive and therefore difficult to isolate in an unchanged form.

Already in 1897 Klason [52] suggested that gymnosperm lignin is derived from coniferyl alcohol. On the basis of experiments using isoeugenol as a model substance, Erdtman [53] advanced the hypothesis that lignin is a product of the oxidative polymerization of coniferyl alcohol:

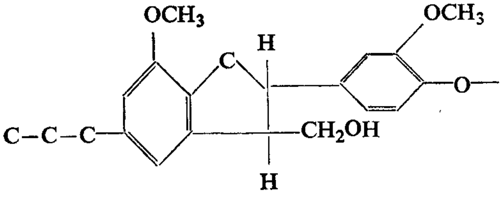


When the latter compound became easily available Freudenberg [54] studied its oxidation (mainly enzymatic) and obtained many crystalline compounds, believed to be intermediates in the conversion of coniferyl alcohol into lignin, as well as amorphous lignin-like products believed to be closely related to lignin of wood. Similar work was done by Manskaya [55]. However, degradative studies by Hibbert [56], Freudenberg [57] and many others are in agreement with the assumption that lignin is built up from phenylpropane units joined either by oxygen atoms or by carbon–carbon links.

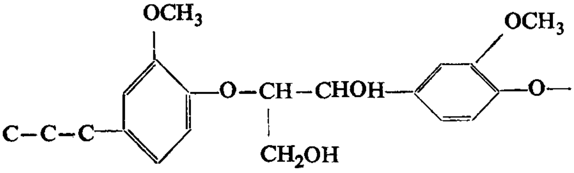
The presence of ether linkages were indicated by studies of Shorygin and Shorygina [58].

Present views on the structure of lignin are still largely speculative and in particular little is known of the non-aromatic parts of the molecules.

The occurrence in lignin of units such as:



A



B

is the subject of much discussion at the present time. Structure A shows how phenylpropane molecules could be joined by carbon–carbon links and B by ether linkages. The unit B contains a hydroxyl group in the α-position to the aromatic ring and such benzylalcoholic groups, according to Holmberg and Heden [60], account for many of the characteristic reactions of lignin, e.g. the formation of lignin sulphonic acids during the sulphite cooking process.

It is generally assumed that at least part of the lignin of wood is chemically bound to carbohydrates (hemicellulose).

Lignin gives characteristic colour reactions. With phloroglucinol and hydrochloric acid it turns red, with aniline sulphate, yellow.

CLASSIFICATION OF CELLULOSE

Cross and Bevan [59] suggested defining the pure cellulose content of a commercial cellulose in terms of its behaviour in the presence of a 17–18% aqueous sodium hydroxide solution. That part of commercial cellulose which is insoluble in this solution bears the name of α-cellulose and is the true cellulose. β- and γ-cellulose remain dissolved in the caustic soda solution. The difference between these two fractions is shown by treating the alkaline solution with acetic acid, which causes *β*-cellulose to precipitate, whereas *γ*-cellulose remains in solution.

β-Cellulose is composed of cellulose with chains shortened by chemical treatment e.g. hydrocellulose, or oxidized cellulose (oxycellulose).

γ-Cellulose is mainly a hemicellulose fraction. The division into *α*-, *β*-, and *γ*-celluloses is a conventional classification.

Recently it received a certain physico-chemical justification as the result of Rånby's [46] work (p. 224). In any case it serves a useful purpose in practice. This method of classifying being widely used, as for example in order to estimate the value of a sample of chemical wood pulp for nitrating, when certain quantitative requirements concerning the minimum *α*-cellulose content are imposed.

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CHAPTER X

GENERAL CHARACTERISTICS OF NITROCELLULOSE

STRUCTURE OF NITROCELLULOSE

NITROCELLULOSE is obtained by esterification of cellulose with nitric acid. This process is described simply as nitration or more exactly O-nitration. The nitration of cellulose can be expressed by means of the following equation:

$$C_6H_{10}O_5 + xHNO_3 \rightleftharpoons C_6H_{10-x}O_{5-x}(ONO_2)_x + xH_2O \tag{4}$$

The cellulose formula in this equation is simplified by assuming the polymerization degree $n = 1$.

As with every reaction of esterification this process is a reversible chemical change. In addition to the fundamental process of esterification the opposite reaction of hydrolysis takes place, accompanied by a series of side reactions which result in the formation of various by-products. Thus a non-uniform, highly complex product is obtained.

The greatest number of (ONO_2) groups which can be introduced in relation to every six carbon atoms is three, as explained earlier in the chapter devoted to the structure of cellulose. The theoretical nitrogen content in such nitrocellulose, called "trinitrate", is 14.15%. This nitrogen content has been calculated for an empirical cellulose formula $C_6H_{10}O_5$. In point of fact, if the terminal rings with four hydroxyl groups are taken into consideration, the calculated theoretical maximum nitrogen percentage can be slightly higher, e.g. 14.17%. The longer the nitrocellulose chain, the lower this theoretical value.

In practice experiments to obtain a nitrocellulose with the theoretical nitrogen content failed, since a product of such high nitrogen content was readily decomposed, the nitrogen content falling to 13.5%.

The possibility of attaining a nitrogen content of 14.0% by nitrating with the help of nitric anhydride was indicated by Hoitsema [1]. His experiments have since been repeated and modified by many workers, as shown in the chapter on nitrating cellulose with nitric anhydride.

Nitrocellulose of 14.04% nitrogen was obtained by Berl and Rüff [2], when they nitrated cellulose with a mixture of nitric and phosphoric acid. Later Dalmon [3] has prepared nitrocellulose containing 14.12% of nitrogen by treating cellulose with gaseous N_2O_5.

Commercially produced nitrocellulose may have all the possible number of NO_2 groups, from 0 to 3 including the fractional ones. Moreover, the nitrogen content in a series of nitrocelluloses can vary continuously: a full series of cellulose nitrates can be obtained differing only by an insignificant variation in nitrogen percentage. In view of this fact, Eder [4] advanced the hypothesis that nitrocellulose was not one individual chemical compound but a mixture of several products. Eder postulated the existence of as many as six substances of different nitrogen content, namely: 14.15, 12.75, 11.15, 9.15, 6.75 and 3.75%.

This hypothesis could not explain, however, why such physical properties as solubility and viscosity in the instance of, say, nitrocellulose containing 13.45% of nitrogen, which Eder assumed to be composed of equal parts of nitrocelluloses 14.15 and 12.75%, are not the average properties of the components. Besides Eder could not explain why high nitrated cellulose, with 14.15% N, in general a chemically unstable substance, decomposed to form a 13.5% N nitrocellulose. In accordance with Eder's views the decomposition should have gone on until the content of nitrogen was 12.75% i.e. to the nearest nitration degree.

In order to express the chemical formula of nitrocellulose, for some time formulae suggested by Vieille [5], were generally used in which a polymerization degree of nitrocellulose $n = 4$ was proposed:

$$C_{24}H_{40-x}C_{20-x}(ONO_2)_x$$

x having any value up to 12.

A more exact formula including a variable polymerization degree p, would be as follows:

$$[C_{24}H_{40-x}O_{20-x}(ONO_2)_x]_p$$

By treating cellulose with nitric acid or nitrating mixtures of different composition Vieille [5] isolated a range of nitrocellulose samples containing a number of (ONO_2) groups lying very close to the values $x = 4$ and $x = 12$. He named the different nitrocelluloses according to the parameter x by applying a suitable prefix (Table 37).

TABLE 37

x	Name	Formula	Nitrogen content, %
12	Cellulose dodecanitrate	$C_{24}H_{28}O_8(ONO_2)_{12}$	14.15
11	Cellulose endecanitrate	$C_{24}H_{29}O_9(ONO_2)_{11}$	13.45
10	Cellulose decanitrate	$C_{24}H_{30}O_{10}(ONO_2)_{10}$	12.75
9	Cellulose enneanitrate	$C_{24}H_{31}O_{11}(ONO_2)_9$	11.96
8	Cellulose octanitrate	$C_{24}H_{32}O_{12}(ONO_2)_8$	11.11
7	Cellulose heptanitrate	$C_{24}H_{33}O_{13}(ONO_2)_7$	10.16
6	Cellulose hexanitrate	$C_{24}H_{34}O_{14}(ONO_2)_6$	9.15
5	Cellulose pentanitrate	$C_{24}H_{35}O_{15}(ONO_2)_5$	8.00
4	Cellulose tetranitrate	$C_{24}H_{36}O_{16}(ONO_2)_4$	6.76

Today Vieille's formulae are regarded as purely conventional though useful in arranging various types of nitrocellulose into classes. Nevertheless, many authors have tried to isolate definite substances corresponding to Vieille's compounds. Thus de Bruin [6] claimed that he had isolated definite compounds containing 11.97 and 12.76% of nitrogen, corresponding to the enneanitrocellulose and decanitrocellulose of Vieille.

At present a less complicated nomenclature, based on the average number of (ONO_2)-groups attached to one anhydroglucose ring, is accepted:

cellulose trinitrate	$C_6H_7O_2(ONO_2)_3$	14.15% N
cellulose dinitrate	$C_6H_8O_3(ONO_2)_2$	11.11% N
cellulose mononitrate	$C_6H_9O_4(ONO_2)$	6.76% N

Nitrocellulose of 12.65% N, according to this nomenclature, is called $2\frac{1}{2}$-nitrate, etc. The degree of nitration can also be designated by the "degree of substitution" (D.S.) which is the average number of nitrated hydroxyl groups in one anhydroglucose unit.

This manner of determining the share of esterified groups results partly from the X-ray studies on nitrocellulose, because it has been proved that only the high nitrated cellulose, i.e. trinitrate, gives a wholly sharp definite picture. Other cellulose nitrates manifest a composite X-ray picture looking as if it were formed by superposing an X-ray picture of cellulose on that of its trinitrate. This observation led to the view that every cellulose with a lesser nitrogen content than cellulose trinitrate represented a mixture of trinitrate with non-nitrated cellulose. This idea was suggested by the first X-ray investigators of cellulose: Herzog and Náray-Szabó [7], Náray-Szabó and Susich [8], and particularly by Hess and Trogus [9]. The fact that neither non-nitrated cellulose nor cellulose trinitrate have ever been separated from nitrocellulose, nor even a low-nitrated cellulose is a weighty argument against this suggestion.

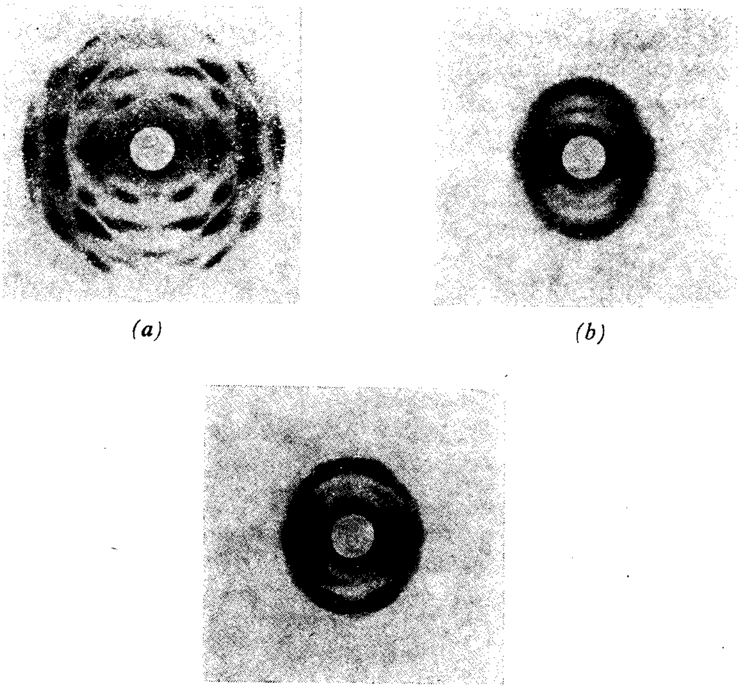
The earlier view has therefore been modified to suggest that every nitrocellulose is composed of anhydroglucose rings with three nitrate groups attached, containing 14.15% of nitrogen, and of non-nitrated and partly nitrated anhydroglucose rings. This view is generally accepted and the diagrammatic presentation shown in Figs. 86 and 89 is discussed below.

Among other X-ray investigations, the publications of Trillat [10], of Berl and Hefter [11] and of Champetier [12] should be mentioned.

The studies of Miles and Craik [13] merit special attention since they obtained the following X-ray diagrams of ramie (Chinese nettle) cellulose, which is notable for a distinctly crystalline structure (Fig. 83).

The dimensions of a nitrocellulose crystal cell depend on the degree of nitration. Values from the papers of Mathieu [14, 34] characterizing native cellulose and various nitrocelluloses are quoted in Table 38.

According to Mathieu, trinitrocellulose crystals belong to the orthorhombic system, the dimensions of the crystal cell being: $a = 12.40$ Å, $b = 25.4$ Å, $c = 9.0$ Å, angle $\beta = 90°$. Similar figures have been reported by Happey [15].


(a) (b)

(c)

FIG. 83. X-Ray diagrams (according to Miles and Craik [13]): (a) ramie cellulose, (b) ramie cellulose dinitrate, (c) ramie cellulose trinitrate.

TABLE 38

Native cellulose $a = 8.35$ Å $cb = 7.40$ Å	$A_4(002)$ $d = 3.93$ Å	$A_1(101)$ $d = 5.46$ Å $A_2(101)$ $d = 6.06$ Å
Nitrocellulose		
10.54% N	$A_2^d = 4.00$ Å	$A_1^d = 6.84$ Å
11.46		6.93
12.30		7.08
12.66		7.13
12.90		7.15

According to Trommel [15a] nitrocellulose exists in two structural forms:

(1) Intermediate structure characterized by cell dimensions $a = 13.81$ Å, $b = 10.45$ Å, $c = 7.92$ Å, $\beta = 90°$. The structure closely resembles that of cellulose and some cellulosic structural elements are present. The nitrate groups are located between the glucose rings in line with the a-axis. This structure exists between 12.3 and 13.2% N.

(2) Trinitrate structure with cell dimensions $a = 12.94$ Å, $b = 25.66$ Å, $c = 8.92$ Å. The chain molecules are paralled to the b-axis. It is formed with great difficulty but once formed it remains stable, even after denitration.

A plane projection of the crystal cell of cellulose (a) and of cellulose trinitrate (b) is outlined by the schemes in Fig. 84. Much interest was aroused in the results

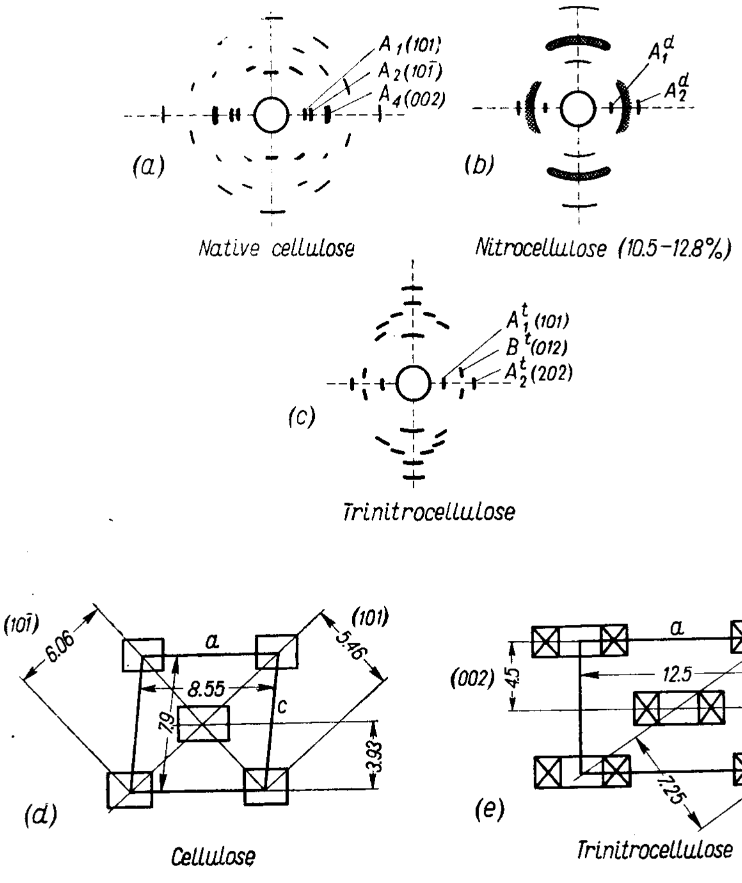


FIG. 84. X-Ray fibre diagrams (a, b and c), cell projections of cellulose (d) and cellulose trinitrate (e) by Mathieu [34].

obtained by Miles [16] who examined the crystal cell dimensions along the equatorial axis (101) for nitrocellulose obtained by nitration and denitration (Table 39).

The spatial configuration, extended in consequence of nitration, is retained despite partial denitration. This is why the cell size of a denitrated cellulose is larger than that of nitrocellulose containing the same nitrogen percentage, but obtained by a direct nitration of cellulose.

These results were confirmed by Trommel [15a] who expressed the change of the 101-spacing with increase of the nitrogen content graphically (Figs. 85 and 86).

TABLE 39

THE DIMENSIONS OF THE NITROCELLULOSE CELL UNIT ALONG THE (101) AXIS

Examined product	Nitrogen, %	*d*,Å
Cellulose nitrated to	11.14	6.67
Cellulose nitrated to	12.77	6.85
Cellulose nitrated to	13.57	7.25
Nitrocellulose 13.75% N, denitrated to	11.52	7.10
Nitrocellulose 13.75% N denitrated to	10.42	7.05

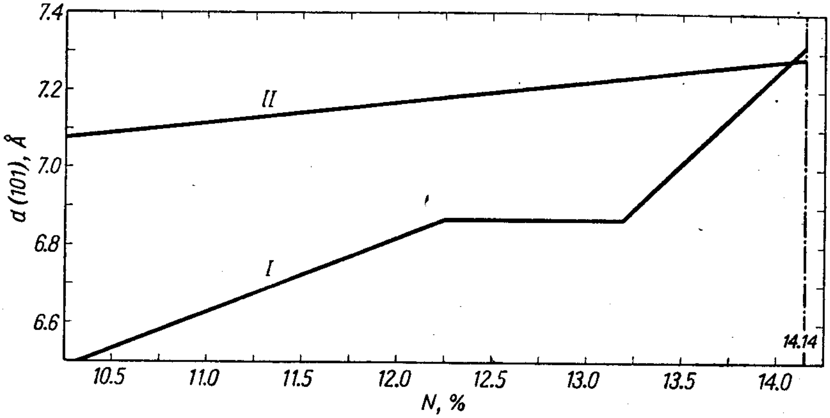


FIG. 85. 101-spacing of nitrated cellulose (*I*) and partly denitrated trinitrocellulose (*II*) according to Trommel [15a].

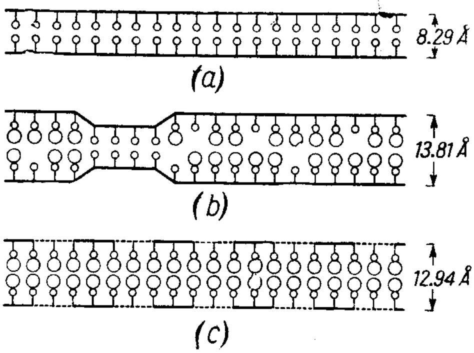
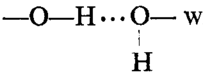


FIG. 86. Diagrammatic presentation of cellulose (a), intermediate structure (b) and trinitrate (c) chains, according to Trommel [15a].

His diagram shows the existence of the intermediate structure between 12.3 and 13.2% N and the two-phase system between 13.2 and 14.1% N, and also indicates (Fig. 85) that once the trinitrate structure has been formed, it persists even when a considerable number of nitrate groups have been removed. Because of the increase of the distance along *a*-axis, the hydrogen bonds  $-O-H\cdots\underset{\substack{| \\ H}}{O}-$ which exist in cellulose and cellulose dinitrate are not present in denitrated cellulose trinitrate, according to Trommel [15b], or are weakened. At the same time the X-ray diagrams of nitrocelluloses having a complete range of nitrogen content were studied by Miles and Craik [13]. According to these authors the products of nitration of cellulose can be divided into three classes:

(1) Those containing less than 7.5% N, which show a fibre character and give no X-ray diffraction indicating nitration, but only those of mercerized cellulose.

(2) Those containing between 7.5 and 10.5% N. They are more or less disintegrated, yielding very diffuse diffractions, apparently due in part to very small crystalline elements of mercerized cellulose.

(3) Those of more than 10.5% N giving diagrams which indicate the crystalline character of the structure, increasing as the nitrogen content increases until eventually a critical point at 12.8% is reached when the sharply defined diagram characteristic of cellulose trinitrate makes its appearance. On the basis of these experiments Miles and Craik presented the following picture of cellulose nitration. In the first stage of nitration (stage I) the nitric acid penetrates the whole of the cellulose structure (otherwise it could not be mercerized), nitration occurring only in the disordered amorphous regions. As the acid concentration is increased, the nitration gradually invades the ordered regions (stage II). At the same time the micellar arrangement is almost entirely broken down.

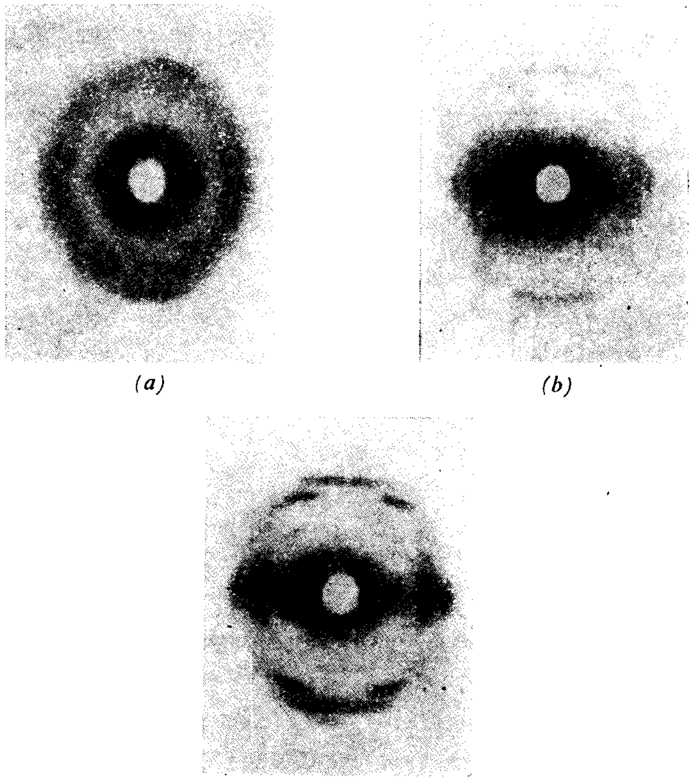
Swelling and breakdown of the micellar arrangement takes place in final stage of nitration (stage III), but to a diminished extent as the acid concentration increases. The number of the nitrate groups increases with the acid concentration but in a random manner, so that crystalline arrangement is at first difficult. It is facilitated as the nitrate groups accumulate and when 12.8% N is reached there are so many ONO_2 groups that an orderly arrangement of chains becomes possible and there is a sudden registration of the trinitrate structure.

Meyer and Mark [17] reached a similar conclusion on the basis of their own experiments and the results of other authors.

Mathieu [18] has shown that X-ray diagrams taken at frequent intervals during nitration of cellulose with N_2O_5 vapour indicate that the structure progresses through all the stages from cellulose to cellulose trinitrate.

Taking into account both their own X-ray investigations and those of other workers, Meyer and Mark [17] came to the conclusion that indistinct pictures of cellulose nitrates having a lower nitrogen content than cellulose trinitrate and hence containing free hydroxyl groups, occur due to the statistically irregular distribution of esterified hydroxyl groups. This explains why composite pictures that appear to be created by superposition of the cellulose picture upon that of trinitrate, are found in the X-ray diagrams.

The X-ray experiments of Hess and Trogus [19] have shown that nitrocellulose immediately after formation gives a very diffuse X-ray diagram with barely legible interference bands, typical for swollen cellulose and nitrocellulose. The interference bands grow more and more distinct, however, as nitrocellulose is washed, until after stabilization boiling, a picture with very sharp rings is obtained, as shown in Figs. 87 a, b and c.



(a) *(b)*

(c)

FIG. 87. X-Ray diagrams: (a) of nitrocellulose immediately after the separation from the nitrating acid, (b) of nitrocellulose after washing out the acid, (c) of stabilized nitrocellulose (Hess and Trogus [19]).

Herzog and Londberg [20] have examined the X-ray diagrams of cellulose produced by denitration of a carefully nitrated product. The picture of the regenerated cellulose was in principle identical with that of cellulose before nitration. This observation suggests that a cautious nitration of cellulose that proceeds without oxidation or hydrolysis does not change the microcrystalline structure of the cellulose, i.e. this is a topochemical reaction, in which the product preserves the same crystalline structure as the original substance. Among inorganic substances, a similar reaction is that between NaOH and cupric nitrate. The cupric hydroxide formed shows the same crystallographic properties as the original compound differing only in crystal size since one large crystal is make up of a considerable number of the small ones. Similarly ion-exchange processes depend on the ability of permutits, which are artificially produced silicates, natural crystal zeolites and ion-exchange resins, to absorb from solutions certain cations and to return to the solutions other cations contained in the silicate and the resins respectively.

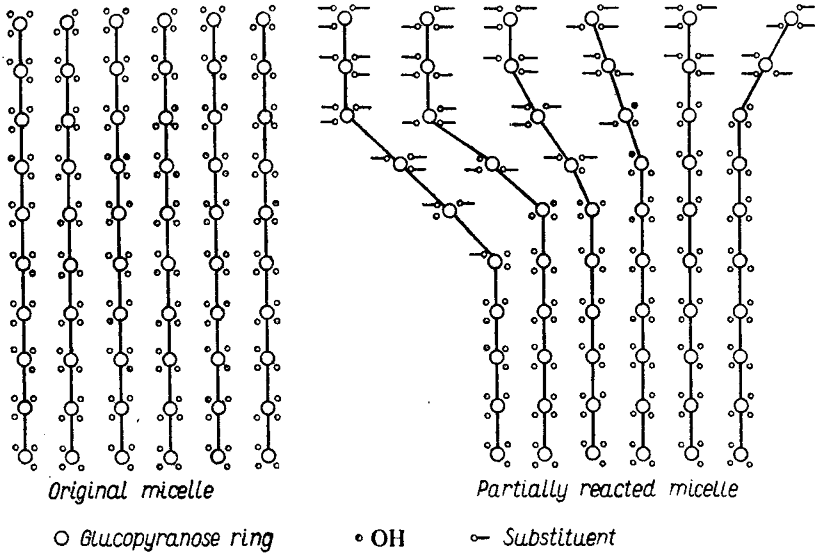


FIG. 88. Diagram of esterification of cellulose (Spurlin [21]).

The amorphous part of cellulose is regarded as more reactive than the crystalline part. When the crystalline part enters into a reaction, as for instance, in swelling or nitrating, its structure can undergo certain changes, as swelling causes the micelle chains to expand. An outline of the process suggested by Spurlin [21] showing how the micelles react with an esterifying agent is shown in Fig. 88 which indicates how the reagent attacks one end of the micelle and a gradual sliding apart the chain ensues.

PHYSICAL PROPERTIES OF NITROCELLULOSE

MELTING POINTS

Newman [22] has estimated indirectly the melting point of nitrocellulose containing 12.6% N by the following method. He determined the melting points of mixtures of nitrocellulose and γ-butyrolactone obtaining values from 39 to112°C. By extrapolation he calculated the melting point of nitrocellulose to be 890°K, i.e. 617°C.

The calculated heat of fusion is 1350 cal per anhydroglucose unit, and the corresponding entropy of fusion is 1.51 cal/°C.

SPECIFIC GRAVITY

Earlier authors: Wehrhahn [23] and Mosenthal [24], assumed that the specific gravity of nitrocellulose determined in water is independent on the nitrogen content, and is 1.66. For cellulose in alcohol, Mosenthal reports the value 1.56–1.58. The specific gravity of nitrocelluloses of different nitration degree has been determined by Brunswig [25].

For a nitrogen content of 11.10% he found the specific gravity to be 1.653, whereas for a nitrogen content of 12.30 and 13.20% N the value was 1.654 and 1.659 respectively.

Values measured later in the Chemisch-Technische Reichsanstalt [26] are well in line with those reported earlier. The increase of specific gravity accompanying the increase of nitrogen content is extremely small, namely:

nitrogen content, %	specific gravity at 15°C	
	in xylene	in water
11.61	1.616	1.655
11.73	1.622	1.655
12.20	1.630	1.655

For the specific gravity determined in a pycnometer with mercury, a series of diminishing figures has been established:

nitrogen content, %	specific gravity
11.61	1.680
11.73	1.666
12.20	1.660

The determination of the specific gravity of nitrocellulose is beset with difficulty, since the result depends to a considerable extent upon the capacity of the liquid used for measurement to penetrate into the interior of the colloidal structure of the fibre. Petitpas and Mathieu [27] have estimated the specific gravity of trinitrocellulose at 20°C in various liquids:

paraffin oil	1.608
benzene	1.636
cyclohexane	1.644
water	1.669
ethanol	1.696

For the specific gravity of nitrated products in water following data were reported by the same authors:

nitrogen content, %	specific gravity
11.52	1.654
11.9	1.659
12.2	1.674
13.1	1.662

SOLUBILITY

Esters and ethers of cellulose, and especially nitrocellulose, are most widely used in the form of a colloidal solution. This technique is applied in the manufacture of smokeless powder, nitrocellulose varnishes, film and celluloid.

Nitrocellulose will dissolve in many solvents, e.g. acetone, acetic esters, ether–alcohol. There also exist types of nitrocellulose soluble in ethyl alcohol alone.

Non-volatile solvents are usually called "gelatinizers" (or "plasticizers" in plastics technology).

The solubility of nitrocellulose in a solvent is defined by the percentage in this nitrocellulose of the fraction soluble in the solvent in question.

Thus the expression "solubility" of nitrocellulose in a certain solvent has a different meaning from the concept of solubility as applied to a crystalline substance able to form a saturated solution.

Solutions of cellulose, its esters and ethers are colloidal solutions. They are reversible lyophilic colloids. The most important characteristics of such solutions are as follows.

(1) The dissolved substance is precipitated with difficulty from the dispersing phase. Having been precipitated, it can be redissolved. The precipitated phase contains much dispersing phase.

(2) Prior to dissolution the substance undergoes swelling.

(3) The viscosity of the solutions is high, even if the concentration is low.

(4) The substance does not form saturated solutions in a single solvent, hence it has no limits of solubility in the usual sense of this term as applied to crystalline bodies. A solution resembling in its properties a saturated one can be prepared by means of a binary solvent, where a liquid immiscible with nitrocellulose is one of the two components (e.g. acetone and water).

Formerly it was believed that in their physical properties, as for instance no increase in boiling point and in osmotic pressure, colloidal solutions of cellulose derivatives were radically different from solutions of crystalline substances having small molecules. Now, however it is clear that the difference is not so considerable and that a close analogy exists between solutions of cellulose and its derivatives and those of substances of low molecular weight.

Thus analogy is visible even in the first stage of dissolution, i.e. in swelling. If acetone is added to a suspension of nitrocellulose in benzene, nitrocellulose starts to swell, increasing in volume, finally dissolving when a sufficient amount of acetone is added. The swollen nitrocellulose phase can be regarded as a solution of solvent in a solid phase. The water layer of a water–benzene system behaves the same way when alcohol is introduced to the system. Namely, as long as alcohol is added the water layer increases in volume, i.e. it "swells" whilst the benzene layer remains almost unchanged. After a certain amount of alcohol has been added the benzene layer joins with the other phase to form a homogeneous solution. Nitrocellulose can be compared with the water layer in this example.

The process of dissolving nitrocellulose fibres in non-volatile solvents, that are commonly used in small quantities to bring about the transition of nitrocellulose fibres in a solubilized state, is often called gelatinization.

Microscopic investigations of the gelatinization and dissolution of nitrocellulose seem to indicate that a protective cover exists on the surface of nitrocellulose fibres which dissolves with difficulty (Mangenot and Raison [134], Fenson and Fordham [133], p. 286).

According to investigations reported by Jenkins and G. Davies [28] and by T. Urbański [29] the dissolution and gelatinization of nitrocellulose begins at the ends of fibres cut in the beating process.

The viscosity of nitrocellulose solutions provides a further example of analogy. It has been demonstrated by examining the viscosity of solutions prepared from low-molecular substances that the higher the molecular weight, the greater the viscosity. Staudinger [30] established his rule for substances with small molecules. Subsequently it was proved that his law can also be applied to long-chain high molecular weight substances such as cellulose derivatives.

Detailed experiments on the osmotic pressure of cellulose solutions (Kratky and Musil [31]) have shown that the osmotic pressure of cellulose derivatives is subject to rules which do not differ from the laws for ideal solutions. The equation of osmotic pressure

$$\frac{P}{c}=\frac{RT}{M}(1+Bc-Cc^2+\ldots)$$

where P represents the osmotic pressure, c — concentration, M — molecular weight, and B and C are constants independent of the polymerization degree, is valid for solutions of substances of high-molecular weight as well as for those of low-molecular weight provided that the mass concentrations are uniform.

The divergencies observed with high-molecular weight substances are caused by the fact that when the value of M is large the pressure P becomes insignificant, hence the experimental error is large.

Assuming that in principle manifold similarities exist between the solutions of low-molecular weight substances and the solutions of cellulose derivatives, the hypothesis has been formulated that in a cellulose derivative solution the molecules are associated into large aggregates — micelles. In this way micelles which are assumed to be present in cellulose and its derivatives in the solid state were thought to exist also in solution, individual molecules in the solution being bound together by van der Waals or electrostatic forces. This idea has been used to explain numerous properties of colloidal solutions of inorganic substances and of soaps. Nevertheless it was realized that inorganic salts and soaps carry strong electric charges whereas nitrocellulose solutions are almost completely electrically neutral.

These views have now been abandoned in favour of the hypothesis advanced by Staudinger [30] that only individual molecules are present in a solution forming no larger aggregates. In point of fact particular molecules are capable of combining among themselves by means of residual bonds (van der Waals forces), but these linkages are unstable and are readily broken as the result of the thermal motion of the molecules.

One of the arguments against the existence of micelles in solutions of cellulose derivatives is the fact that when cellulose is converted into its derivative, e.g. an ester, the degree of polymerization remains almost unchanged. This however only occurs when ester formation is carried out under strictly controlled conditions (nitration at low temperature with nitric and phosphoric acids mixture — p. 341, or with nitric, acetic acids and acetic anhydride mixtures — p. 344). The relevent data found by Staudinger and Mohr [32] are collected in Table 40.

TABLE 40

THE DEGREE OF POLYMERIZATION OF CELLULOSE AND NITROCELLULOSE

Polymerization degree of cellulose (determined by measuring the viscosity of cuprammonium solution)	76	186	254	450	720	1540	2550
Polymerization degree of nitrocellulose (determined by measuring the viscosity of acetone)	77	170	220	440	670	1360	2500

If micelles were present in both types of solutions, we would have to assume different forces binding different cellulose derivatives, hence viscosity measurements should give different molecular weights. However the results disagree with those obtained by Gralen and Svedberg [32a], and reported on p. 343.

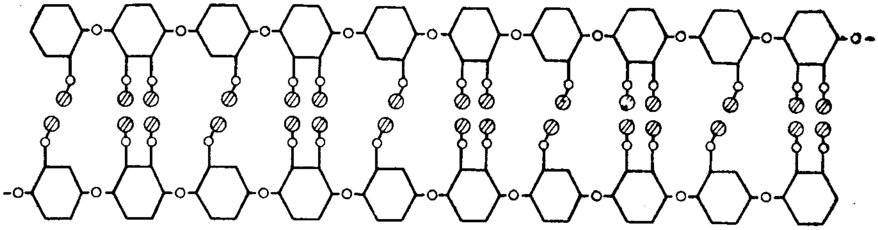
Solutions of cellulose derivatives, such as nitrocellulose, passed through a fine porous filter demonstrate neither the Tyndall effect, nor the presence of particles visible in the ultra-microscope. This is one more piece of evidence that the properties of these solutions are the same as those of substances with low molecular weight. The same holds for cellulose in ammoniacal solutions of cupric oxide ("cuprammonium").

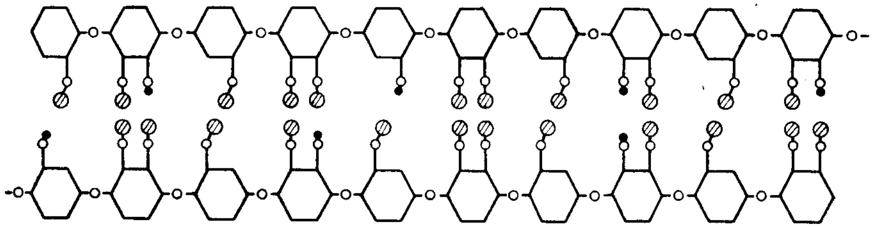
The nature of solubility and the "strength" of solvent. According to present views the dissolution of cellulose esters consists in the separation of the chain-molecules under the specific influence of the solvent until all bonds between the chains disappear. The macromolecules of polymer can slide apart even at the swelling stage. Because of their elasticity, it is possible that the chains can be pushed aside in certain places or along the entire molecules. Further, a shortening of chains occurs, but being a secondary effect it proceeds slowly.

In certain cases dissolution does not take place, the action of the solvent being limited to the production of swelling, due to insufficient "strength" of the solvent. This is possible in two events.

(1) If nitric groups are substituted for the hydrogen atoms of cellulosic hydroxyl groups only to an inappreciable extent then the constitution of the chains is regular enough to ensure a great probability that two hydrogen atoms in neighbouring macro-molecules will be close enough to link the two chains together. Hence a low nitrated cellulose may swell in contact with ether–alcohol but will not dissolve.

(2) If all or nearly all the hydroxyl groups are esterified (as in cellulose trinitrate), then the long-chain-molecules again possess a regular structure, and under the influence of forces of adhesion (van der Waals bonds) close mutual contact may be maintained (Fig. 89a). Here again the solvent may be "too weak" as to push aside such chains, and in fact high-nitrated nitrocellulose is not soluble in a mixture of alcohol and ether (Spurlin [33]).


(a) Completely substituted derivatives


(b) Derivatives of substitution 2.3

○ Oxygen ● Hydrogen ⊘ Substituents

FIG. 89. Influence of complete (a) and partial (b) esterification on contact between cellulose chains according to Spurlin (in Ott and Spurlin [33]). Only substituents between chains are shown; oxygen atoms not shown in rings.

On the other hand, in the case of cellulose dinitrate or 2¼-nitrate, the structure is generally irregular, hence no adhesion between the chains exists. With a small number of irregularly distributed hydroxyl groups there exists little probability that the macro-molecules could be joined together by means of hydrogen bonds (Fig. 89b, see also Figs. 86 and 88).

According to Trommel [15b] the cellulose dinitrate chains become more irregular after being dissolved in acetone and precipitated with water. Hence the solubility of precipitated cellulose dinitrate is increased [15c]. The proposed relationship between the solubility and regularity of the structure of nitrocellulose has been confirmed by experiments with nitrocellulose at different stages of swelling and dissolution. Thus, it has been established by Mathieu [34] and Petitpas [35] on the basis of X-ray analysis that adding small amounts of solvent, e.g. acetone, cyclopentanone, methyl nitrate, to nitrocellulose, causes an increase in the distance between the nitrocellulose chains. The distance grows larger until one molecule of solvent is absorbed in proportion to every anhydroglucose unit after which further addition of solvent does not bring about any further increase in the distance between the macro-molecules. Finally the fibrous structure disappears completely when one molecule of solvent to one (ONO_2) group-equivalent has been added.

On the other hand, numerous observations favour the opinion that the solvent enters into a chemical combination with nitrocellulose to form solvates. Some of those solvates are stable only at low temperatures. For instance, cellulose dinitrate does not dissolve in methyl alcohol at room temperature, though on cooling it does so. The cellulose nitric ester precipitates again when the solution is heated. Similar behaviour is observed with ethyl alcohol: a lower temperature causes nitrocellulose to swell or even to dissolve more readily. The solvent seems likely to be bound to free hydroxyl radicals (Highfield [36]). The hypothesis explains why nitrocellulose is soluble in a mixture of ether and alcohol, though neither of these solvents, when used separately, is capable of dissolving it. It is assumed that first an alcohol solvate of nitrocellulose is formed which then dissolves in the ether.

The hypothesis that nitrocellulose is capable of forming solvates with certain solvents has been confirmed by X-rays analysis. Hess *et al.* [37] have established that nitrocellulose reacts to form microcrystalline addition compounds with many solvents: acetone, methyl nitrate, cyclohexanone, cyclopentanone and camphor. Despite the fact that other workers (Desmaroux and Mathieu [38]) have not fully confirmed the results of Hess's experiments, they are most probably correct.

As evidence that nitrocellulose forms compounds with solvents the fact is quoted that when nitrocellulose is dissolved heat is evolved. It has been established by Okatov and Emmanuilova [39] that in the boundary layer of the solid nitrocellulose phase and the liquid ether–alcohol phase heat is developed by the following processes which occur in turn: wetting of the nitrocellulose fibres, formation of the solvate, swelling and dissolution. Those solvents which evolve the greatest heat of wetting and solvatation, are also characterized by a greater ability to bring about the swelling and dissolution of nitrocellulose. Thus, with an ether–alcohol mixture of 1:1 ratio, a considerably larger amount of solvatation heat is developed than with ether alone. The values of the heat produced by dissolving a film made from nitrocellulose of 11.9% of nitrogen content, and treated with different solvents, determined by Lipatov and Meyerson [40] are collected in Table 41. (For more details about the absorption heat of the solvent see p. 284). Investigations into the absorption isotherms of solvent in nitrocellulose are of considerable importance in relation to the problem of which essential factors cause nitrocellulose to bind solvents.

Two methods of investigating the ability of nitrocellulose to sorb substances which dissolve it are in use. One consists in placing nitrocellulose in an atmosphere

TABLE 41

HEAT OF SOLUTION OF NITROCELLULOSE

Type of film and solvent	Heat of solution (cal per gramme of the solvent) for solution of concentration:	
	15%	2%
Film including 2.4% water	—	—
CH_3COCH_3	19	13
$CH_3COOC_2H_5$	16	13
Dry film – CH_3COCH_3	20	19

containing vapours of the solvent being examined at a vapour pressure lower than the saturation pressure at the temperature for which the sorption isotherm is to be determined. The other method consists in drowning nitrocellulose in a solution composed of the solvent and another non-solubilizing liquid (diluent). The amount of solvent absorbed by nitrocellulose is then estimated.

It is evident that only the second of the two methods can be applied if a non-volatile solvent (gelatinizer) is being tested.

The amount of the substance absorbed (x) can be defined either as a percentage or as a proportion of the sorbent (m) thus by a ratio of $x/m \cdot 100\%$ or by x/m. Furthermore it may be expressed as the molecular ratio n_1/n_2 of the absorbed substance to the sorbent, or as the proportion of absorbed molecules to the total number of molecules: $N = n_1/(n_1+n_2)$.

The absorption isotherms of acetone in nitrocellulose containing 11.6 and 13.5% N respectively at 40°C have been studied by Desmaroux [41]. Acetone was dissolved in castor oil. In a separate series of experiments, Desmaroux has established the vapour pressure of acetone dissolved in castor oil, hence the activity of acetone vapour, defined as the ratio of acetone vapour pressure of the respective solution to the vapour pressure of pure acetone. Curves illustrating the relationship between the number of acetone equivalents absorbed by one anhydroglucose unit (C_6) equivalent of nitrocellulose, and the activity of the acetone vapours are shown in Fig. 90.

Miles [42] has followed the absorption of acetone from aqueous solutions, obtaining the results shown in Fig. 91.

The question whether the absorption of acetone vapours at 30°C was dependent on the nitrogen content of nitrocellulose was investigated by Rubenstein [43] (and Jenkins, Bennett and Rubenstein [122]). Figure 92 outlines the results: the acetone to nitrocellulose weight ratio as well as the mole proportion of acetone to anhydroglucose unit ("submole of nitrocellulose").

The experiments on the absorption of different alcohols, ether, and butyl acetate, carried out by McBain *et al.* [44] and those on absorption of ether–alcohol mixtures by Desmaroux [45] are also noteworthy.

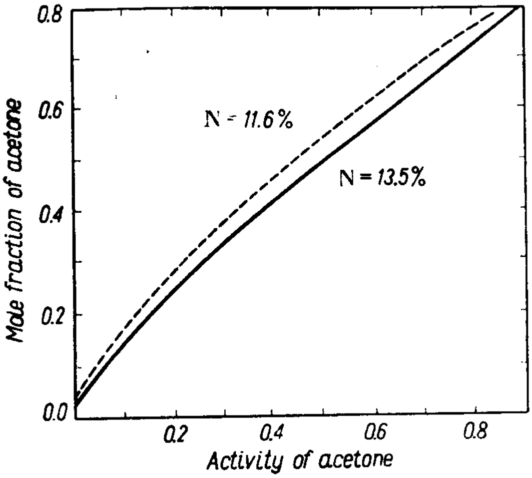
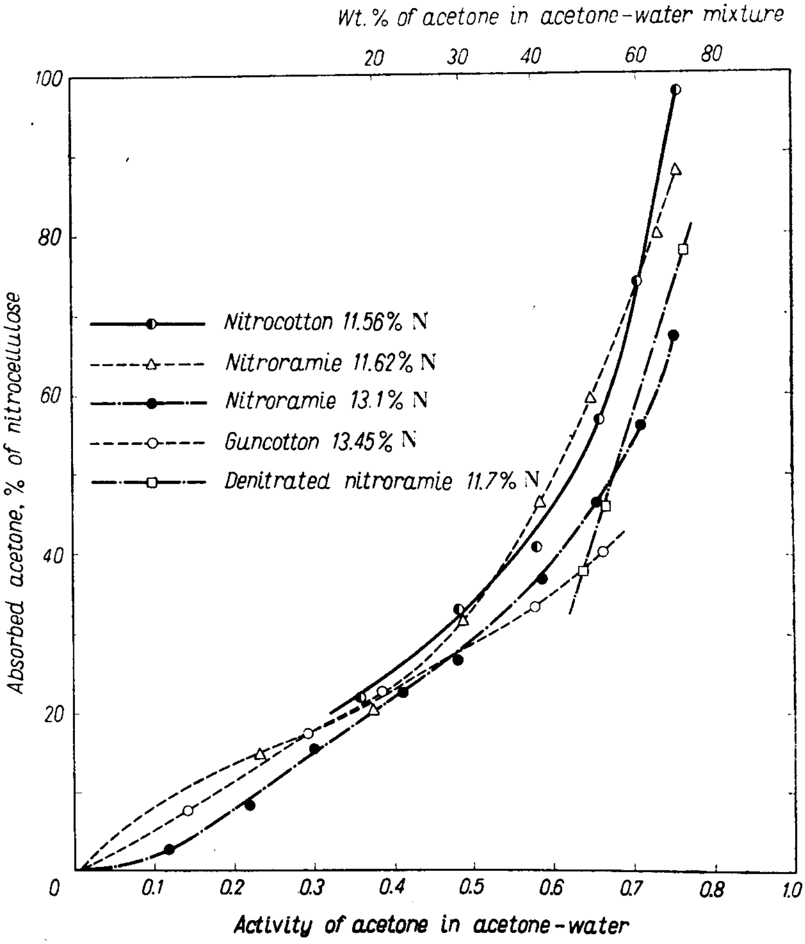


FIG. 90. Relationship between the number of moles of acetone absorbed by nitrocellulose and the activity of acetone vapour, according to Desmaroux [41].



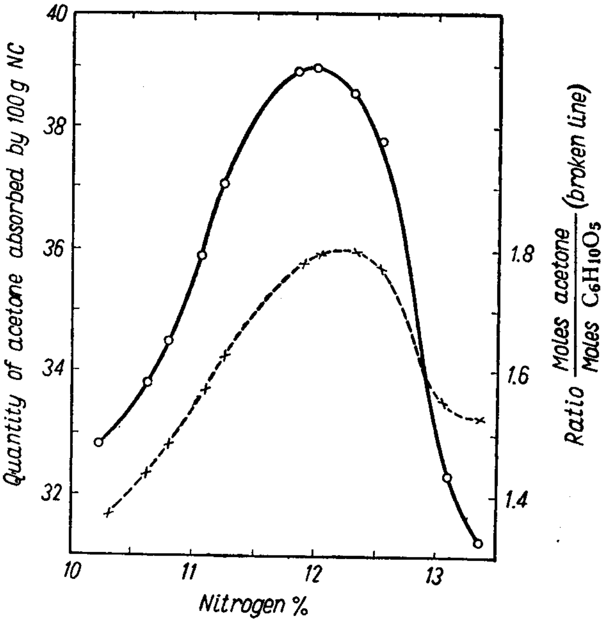


FIG. 92. Absorption of acetone by nitrocottons of various nitrogen content, at the acetone activity of 0.64 according to Rubenstein [43].

Absorption isotherms of such important gelatinizers as carbamite (centralites) and camphor in petroleum ether (Fig. 93) were published by Desmaroux [46].

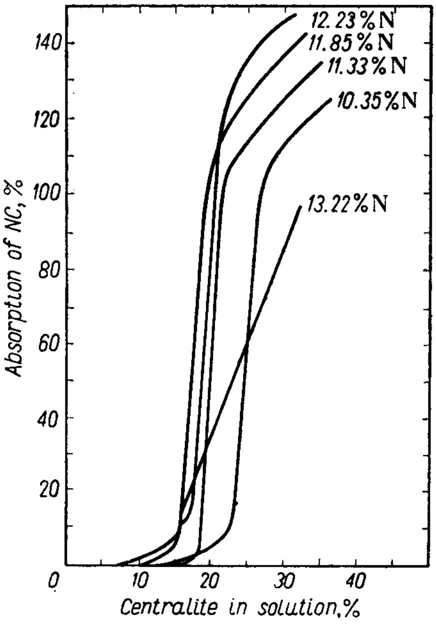


FIG. 93. Absorption isotherms of carbamite (ethyl centralite) (from hexane) by nitrocelluloses, according to Desmaroux [46].

G. G. Jones [47] has obtained similar graphs for camphor, tricresyl phosphate and dibutyl phthalate.

Desmaroux has also determined the nitroglycerine absorption isotherms from its chloroform and acetone solutions at 20°C by a nitrocellulose with a nitrogen content of 11.2–13.35 and 14.2% N (Figs. 94a and 94b respectively) as well as those of nitroglycol in an ethyl ether solution at 20°C sorbed by nitrocellulose of 12.2% N as shown in Figs. 95a and 95b.

More recently the absorption of methyl and ethyl nitrates from the gaseous phase at 40°C by nitrocellulose of 12% N, was examined, the results being shown in Fig. 96 (Petitpas and Mathieu [27]).

In order to see whether the solvent, or gelatinizer, formed addition compounds with nitrocellulose, several investigators have examined the X-ray diagrams of nitrocellulose previously treated with solvents. The first experiments in this field were those of Hess, Trogus and Tomonari [37]. They examined nitrocellulose that had absorbed acetone from its solution in ligroin ("compound I") or from its water solution ("compound II") and concluded that in both cases addition compounds were formed. This was confirmed by the fact that the X-ray diagrams of nitrocellulose treated with acetone differed from those of nitrocellulose itself. Furthermore, the diagram of "compound I" differed from that of "compound II", both with regard to the number of spots and their sharpness. According to Hess *et al.* the addition product contained three molecules of acetone to each molecule of anhydroglucose. The authors have also studied the X-ray diagrams of nitrocelluloses treated with other ketones, e.g. cyclohexanone, camphor, etc.

Later, X-ray diagrams given by nitrocelluloses with acetone prepared after the Desmaroux method by absorbing acetone from castor oil solutions, were examined by Mathieu [34]. The spacing of the plane A_1^d (101) (Fig. 84, Table 38) was 7.25 Å for trinitrocellulose, and less than 7 Å for nitrocellulose of 11.6% N. However, the distance in both types of nitrocellulose is increased considerably as acetone is absorbed, approaching 11 Å when the acetone to nitrocellulose mole ratio is 1:1, i.e. when one molecule of CH_3COCH_3 corresponds to three ONO_2 groups.

Miles [16] has reported similar results for nitrocellulose containing acetone absorbed from a water solution.

From these facts it seems beyond doubt that the crystal lattice of nitrocellulose undergoes a marked deformation as the result of absorbing a solvent or gelatinizer. For the time being it is difficult to say whether a new chemical compound is formed. Nevertheless the formation of molecular addition compounds appears likely. It is also without question that addition compound are formed by nitrocellulose and camphor. According to Hess *et al.* nitrocellulose of 13.7% N combines with camphor in a 1:1 mole ratio (one molecule camphor to one anhydroglucose unit).

The capacity of a nitrocellulose gel to bind solvents and gelatinizers should be considered as evidence that nitrocellulose yields addition compounds with those substances.

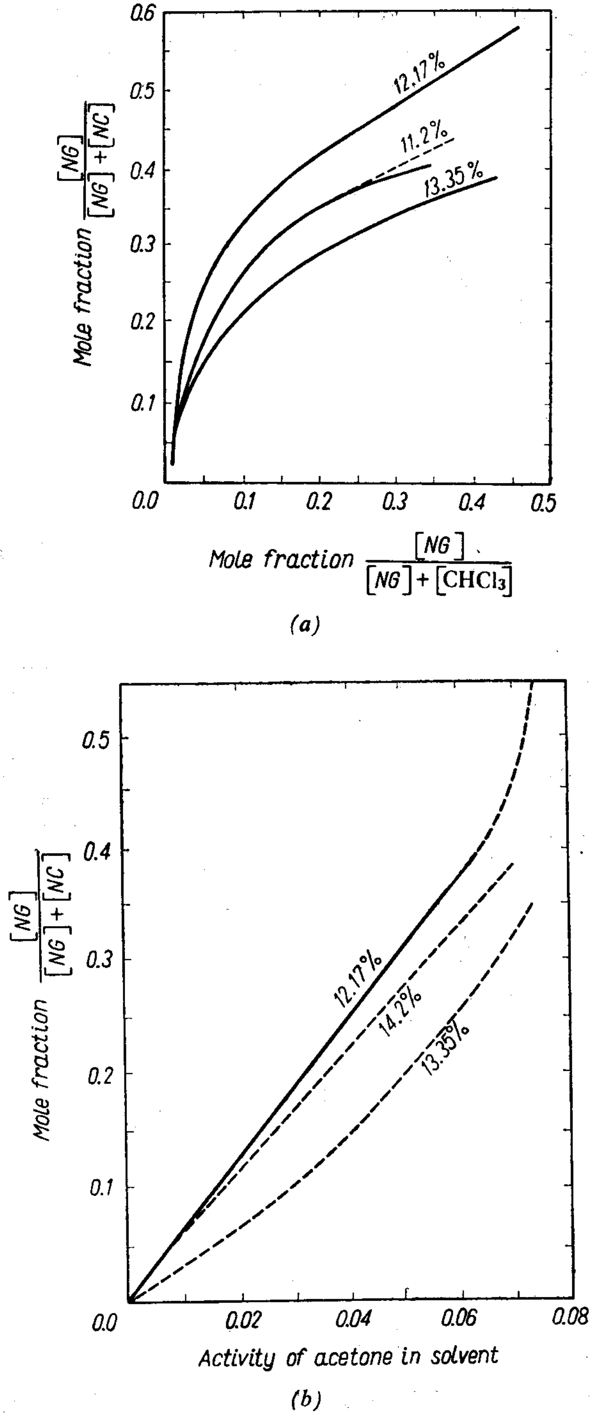
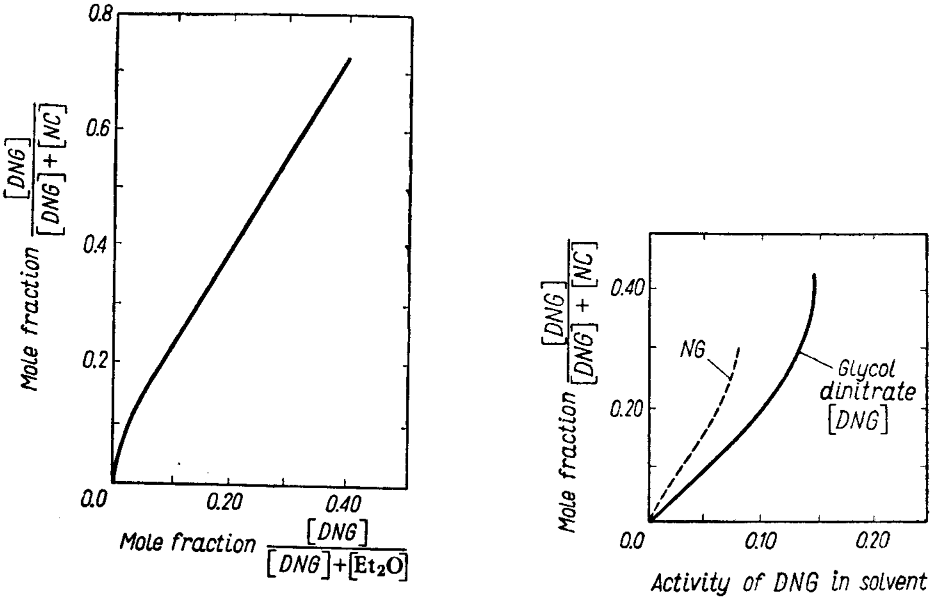


FIG. 94. Absorption isotherms of nitroglycerine (from chloroform solution) by nitrocelluloses, according to Desmaroux [46].

It is well-known in practice that about 1% of the solvent remaining in the nitrocellulose film can be removed only with difficulty. In the instance of a nitrocellulose film over 1% acetone is still retained after evaporating and drying at 70°C for 75 hr, as reported by Miles [16a].



(a) (b)

FIG. 95. Absorption isotherms of ethylene glycol dinitrate (from solution) by nitrocellulose of 12.2% N (Desmaroux [46]) as a function of concentration (a) and activity (b). Absorption of nitroglycerine (NG) is also given (b).

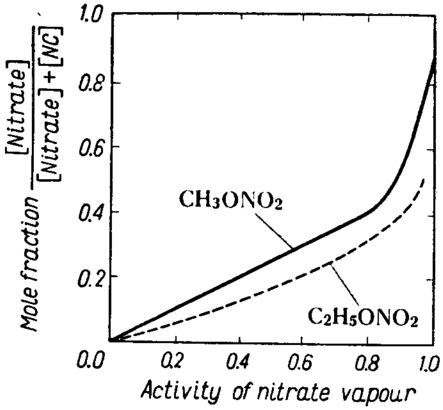


FIG. 96. Absorption of methyl and ethyl nitrates by nitrocellulose (12% N) from vapour at 40°C, according to Petitpas and Mathieu [27].

Data have been published by Baelz [48] concerning the retention of solvent by a 50 μ thick film dried at 25°C to a constant weight in air at 60% R.H. The results are shown in Fig. 97.

It is well-known that the camphor in celluloid is combined with nitrocellulose in such a stable manner that it is not removable by normal heating or evaporation under a reduced pressure.

As for the capacity of ether–alcohol to dissolve nitrocellulose, efforts have been made to explain it by assuming that the alcohol forms molecular addition compounds with the ether, these in turn acting as solvents for nitrocellulose. Desmaroux and Vandoni [49] have established that ether forms molecular addition compounds with ethanol at mole ratios of 1:1, 1:3 and 1:5. However, the compounds are stable only in the neighbourhood of the freezing point of the mixtures, that is below

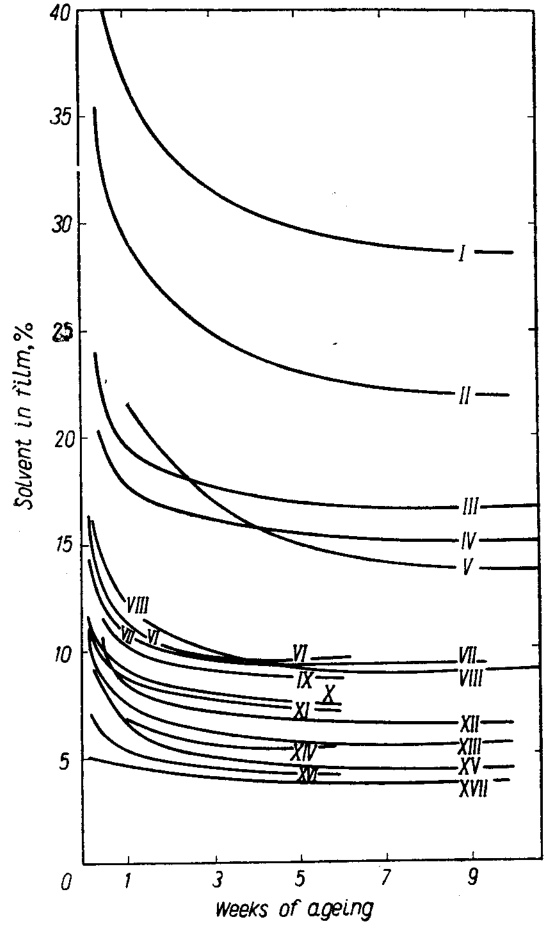


FIG. 97. Solvent retained by nitrocellulose films (50μ thickness) after exposure to air at 25°C (Baelz [48]). I—Cyclohexenyl acetate, II—methyl cyclohexanone, III—diacetone alcohol, IV—cyclohexanone, V—cellosolve acetate, VI—amyl acetate–ethyl alcohol 1 : 1, VII—amyl acetate, VIII—methyl cellosolve acetate, IX—amyl acetate–toluene 1 : 1, X—butyl acetate–ethyl alcohol 1 : 1, XI—butyl acetate, XII—cellosolve, XIII—methyl-ethyl ketone, XIV—cellosolve–toluene 1 : 1, XV—methyl cellosolve, XVI—ethyl acetate, XVII—acetone.

—100°C; at room temperature they undergo dissociation. Summing up it seems improbable that these compounds are of any importance in the dissolution process of nitrocellulose. The Highfield theory [36] (p. 248 and below) is more feasible.

General rule concerning nitrocellulose solvents. A number of suggestions for establishing a rule indicating which compounds are capable of dissolving nitrocellulose can be found in the literature. The best-known general rule is based on the principle that in order to dissolve a given substance a solvent of similar chemical constitution should be used. Thus, nitrocellulose being an ester, all esters can be used as solvents.

A more precise theory published by Highfield [36] has been mentioned already (p. 248). This author has drawn attention to the fact that having strongly polar (OH) groups and less polar (ONO_2) groups attached to a non-polar ring, nitrocellulose dissolves best either in liquids containing both polar and non-polar groups, for instance acetone, esters, acetic acid, or in a mixture of two liquids, one of which is polar, the other being non-polar or only weakly polar. As evidence supporting his view, Highfield reported that acetone mixed with 9% water is a better solvent of nitrocellulose (12.2% N) than acetone alone.

The influence of the polarity of solvents on their ability to dissolve nitrocellulose has been also demonstrated by Wo. Ostwald [50], who has introduced the value μ^2/ε as an expression characterizing the "strength" of solvent (μ—dipole moment, ε—dielectric constant). Good solvents of acetyl celluloses are characterized by a high μ^2/ε value. The physical significance of μ^2/ε is not clear, however, and its introduction has not helped to clarify the process of dissolution.

The solubility of high-nitrated cellulose (13.46% N) in a mixture of formic and acetic acid esters with ethyl alcohol was followed by T. Urbański [51]. The author established that for a range of homologous esters of both acids, the capacity of dissolving nitrocellulose increased in proportion with the value of the dipole moment of the ester. According to T. Urbański the sequence of formic acid esters corresponding with an increasing capacity to dissolve nitrocellulose is paralleled by the dipole moment values, as follows:

	μ
$HCOOCH_3$	1.21
$HCOOC_2H_5$	1.35
$HCOOC_3H_7$	1.50
$HCOO\text{-iso-}C_4H_9$	1.51
$HCOO\text{-iso-}C_5H_{11}$	1.60

Finally Papkov [52] observed that the surface tension of the solvent is a further factor influencing the solubility of cellulose esters. This worker established that the best solvents from a series of liquids resembling each other chemically, e.g. in a homologous range, were characterized by a moderate, "optimum" surface tension. Liquids having higher or lower surface tensions than this optimum value are worse solvents. The rule is also valid for mixtures. Thus a 50:50 acetone–water solution with a surface tension $\sigma = 30.4$ dyne/cm caused only a weak swelling of nitrocellulose, whereas 75:25 acetone–water solution, having the surface tension $\sigma = 26.7$ dyne/cm, produced strong swelling.

Taking into consideration both the work of Ostwald, and that of Papkov, extended investigations into the ability of solvents to dissolve esters and ethers of cellulose have been carried out by Moll [53] who has linked the results of his experiments both with the electrostatic constants and with surface tension. The results of Moll's investigations are described graphically, a typical example of his curves being shown in Fig. 98.

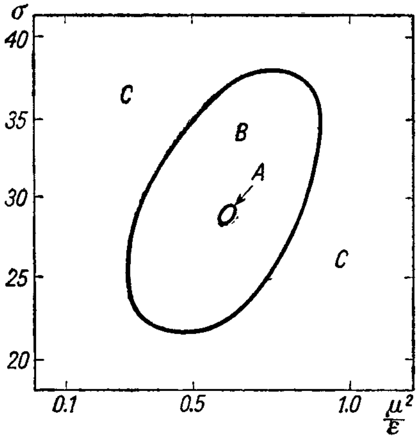


FIG. 98. Relation between μ^2/ε and surface tension σ of aliphatic liquids on their ability to dissolve cellulose trinitrate (Moll [53]).

The graph concerns cellulose trinitrate and aliphatic solvents including alcohols, ketones, esters, nitroparaffins, chloroderivatives of hydrocarbons. The liquids are ranged in respect of their μ^2/ε values and of surface tension σ.

Liquids forming highly viscous solutions are characterized by constants included within the curve *A*. These are:

ethylene glycol acetate ($\mu^2/\varepsilon = 0.62$, $\sigma = 29.0$)
methoxybutanol acetate ($\mu^2/\varepsilon = 0.64$, $\sigma = 28.8$)

Other liquids capable of dissolving trinitrate give less viscous solutions. The constants μ^2/ε and σ for those substances are situated in an area enclosed by the curve *B*. Values of both constants that lie outside the curve *B*, in the area *C*, indicate solvents which are merely able to cause cellulose trinitrate to swell (Fig. 99).

The chart in Fig. 99 concerns liquid cyclic compounds (aromatic, hydroaromatic, heterocyclic). In this graph, the curve *B* limits the area characterizing liquids that produce solutions of relatively low viscosity while the area *C* again defines liquids that cause swelling only.

On the basis of many years' experience it has been established which groups of chemical compounds are capable of dissolving nitrocellulose:

(1) Alcohols: methyl, ethyl, propyl and other alcohols (in case of low-nitrated cellulose).
(2) Aldehydes: acetaldehyde, benzaldehyde, furfural.

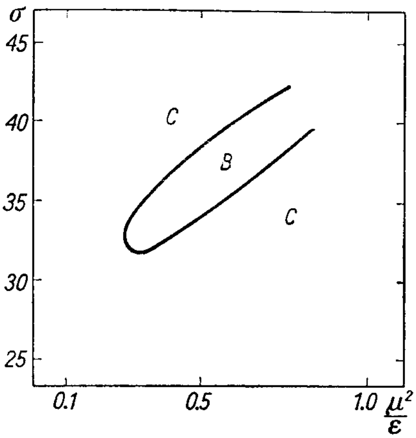


FIG. 99. Relation between μ^2/ε and surface tension σ of cyclic liquids on their ability to dissolve nitrocellulose (Moll [53]).

(3) Ketones: acetone, methyl ethyl ketone, propione, acetophenone, cyclohexanone, camphor.
(4) Ethers: methyl, ethyl, propyl, butyl etc. ethers in mixtures with alcohols.
(5) Inorganic acid esters: nitrates (e.g. methyl nitrate, nitroglycol, nitroglycerine), silicates (e.g. ethyl silicate), phosphates (e.g. triphenyl phosphate, tricresyl phosphate), mixed esters of nitric and hydrochloric acid (e.g. chlorohydrin dinitrate).
(6) Organic acid esters: carbonates (e.g. ethyl carbonate), formates, acetates (e.g. ethyl acetate, butyl acetate, amyl acetate), propionates, etc., oxalates (e.g. ethyl oxalate), maleates, phthalates (e.g. butyl phthalate); carbamates and phenylcarbamates (e.g. ethyl phenylcarbamate).
(7) N-substituted carbonamides: e.g. acetanilide, substituted urea-derivatives.
(8) Aliphatic nitro compounds: nitroparaffins (e.g. nitromethane, nitroethane, etc.).
(9) Aromatic nitro compounds: nitrobenzene, nitrotoluene, dinitrobenzene, dinitrotoluene, trinitrotoluene, nitroanisoles and nitrophenetoles, dinitroanisoles and dinitrophenetoles, nitrophenols etc.
(10) Heterocyclic compounds: pyridine, picolines (these substances cause nitrocellulose to denitrate), dimethylpyrone.

Solubility of nitrocellulose in ether–alcohol. In commercial practice, in the explosives industry, the most widely used solvent is a mixture of ether and alcohol. The solubility of nitrocellulose depends upon two factors: (1) the degree of polymerization of the nitrocellulose, (2) the nitrogen content of nitrocellulose. (1) The influence of the degree of polymerization on the solubility in ether–alcohol has not been investigated systematically, hence there exact information is lacking. However, from many years' observation in the manufacture and application of nitrocellulose is possible to take for granted the conclusion that the higher the molecular weight of the nitrocellulose the lower its solubility.

Nitrocellulose with a decreased molecular weight may be obtained as the result of depolymerization (degradation) of the cellulose before nitration, e.g. by keeping it at a temperature of 150–170°C or by treating it with acids. The resultant hydrocellulose, which usually possesses a lower molecular weight than cellulose, is then subjected to nitration to produce a more soluble substance as compared with the nitration product of a non-depolymerized raw material.

Further, the stabilization boiling of the nitrated cellulose exerts an express influence on the solubility of nitrocellulose. It causes the substance to become more soluble due to partial depolymerization and denitration. (A certain, insignificant decrease of nitrogen value occurs owing to partial hydrolysis). According to Bruley [54] the following relationship exists:

	solubility, %	nitrogen content, %
after 20 hr of boiling	5.2	12.99
after 60 hr of boiling	11.3	12.94
after 100 hr of boiling	10.9	12.95
after 140 hr of boiling	14.8	12.91
after 220 hr of boiling	21.2	12.94
after 260 hr of boiling	22.4	12.92

Likewise the solubility of nitrocellulose in ether–alcohol solution is improved by prolonged heating of the substance, accompanied by a reduction in the nitrogen content. Data from Lacape [55] show that nitrocellulose of 13.03% N and 7.0% of soluble matter, after being maintained at 108.5°C for 50 hr, has a nitrogen content of 12.65% and a solubility of 52.7%. On the other hand, nitrocellulose of 11.73% N, 98% soluble after being heated for 35 hr at 108.5°C was found to have a nitrogen content of 11.11% and its solubility fell to 92.7%.

The change of solubility in both of these instances occurs not only in consequence of depolymerization, but also owing to partial denitration.

(2) The influence of nitrogen content on the solubility of nitrocellulose in ether–alcohol has been known for a long time. Cellulose nitrates of an average nitrogen content from 10.5 to 12.2% dissolve in ether–alcohol, while nitrates containing more nitrogen (12.8–14.1%) or less than 10% are insoluble in mixtures of this kind. Some inclination towards higher or lower solubility is induced by the molecular dimensions, but the influence of this factor is rather limited.

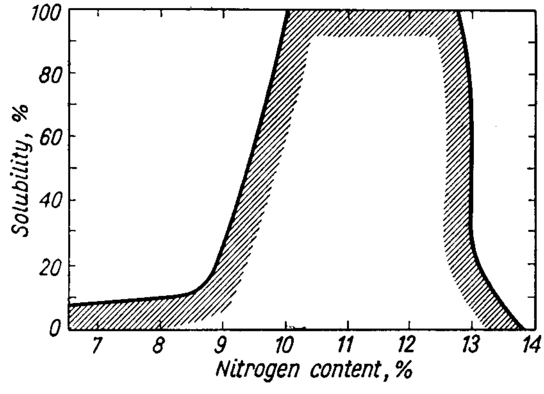


FIG. 100. Solubility of nitrocellulose in ether–alcohol against nitrogen content.

The effect of nitrogen content on the solubility of nitrocellulose in ether–alcohol (2:1) is shown in the graph in Fig. 100.

This was found by several authors. One of the latest reports on the subject is given by Trommel [55a]. He found that the solubility rapidly decreases as the nitrogen content increases from 12.9 to 13.15% N.

In his investigations into the relationship between the solubility of nitrocellulose and its nitrogen content Brunswig [55b] has claimed that the solubility is independent of the method of preparing nitrocellulose of a given nitrogen content — whether it was performed by direct esterification of cellulose, or by hydrolysing a higher nitrated cellulose with a mixture of dilute acids. By drowning nitrocellulose containing 13.2% of nitrogen, of 5% solubility in a sufficiently dilute acid mixture, the nitrogen content may be reduced to 12.6%. The solubility of the nitrocellulose thus obtained is 100%, exactly the same as that of nitrocellulose with the same nitrogen value produced by direct nitration of cellulose.

However, de Bruin and Witte [55c] found that the solubility of partly denitrated nitrocellulose is abnormal. Thus, nitrocelluloses of 13.43 and 12.98% N prepared by direct nitration had solubilities in ethanol–ether (1:2 by volume) of 5 and 100% respectively.

Nitrocellulose of the same nitrogen contents prepared by denitration had solubilities of 13 and 45% respectively.

The authors attribute this to the influence of the OH groups which in the denitrated product are not distributed randomly but are placed preferentially in such a way that the OH groups of neighbouring chains can be linked by hydrogen bonds.

The solubility of nitrocellulose depends to an appreciable extent on the conditions of nitration. Among several nitrocelluloses with roughly the same nitrogen

TABLE 42

THE SOLUBILITY OF NITROCELLULOSE IN ETHER–ALCOHOL

Water content of nitrating acid %	Nitrogen content of nitrocellulose %	Solubility %	Molecular weight of nitrocellulose (from viscosity measurements)
3.73	13.34	1.81	220,000
5.12	13.38	3.76	150,000
6.99	13.43	3.51	170,000
12.92	13.33	3.12	190,000
13.77	13.40	3.67	185,000
15.61	12.62	89.0	150,000
15.87	12.72	100.0	130,000
18.60	11.81	100.0	90,000
18.76	11.94	100.0	95,000
21.50	10.03	36.21	40,000
22.33	9.64	28.25	25,000

content (13.5–11.0% N) prepared by means of different nitrating acids the nitrocellulose with the highest solubility was the one made from the nitration mixture containing more water. Hence, in practice it is assumed that an increase of 1% in the water content of the mixed acids giving products of 13.4–12.0% N will cause the solubility of the nitrocellulose to increase considerably, while the nitrogen value is decreased only to an insignificant degree, e.g. 0.1–0.2%.

In Table 42 the effect of the water content of the mixed acid on the solubility of cellulose nitrates in ether–alcohol, mixed in a 4:3 weight ratio, taking into account also the molecular weight of the nitrocellulose, is shown according to Schiemann and Kühne [56]. (The figures also indicate the strong depolymerizing or degrading activity of water-rich nitrating acids.)

The composition of the solvent, i.e. the ether to ethyl alcohol ratio, also exerts an influence on the solubility of nitrocellulose. Gibson and McCall [57] found that the composition of ether–alcohol showing the highest solubilizing capacity differed according to the nitrogen value of the nitrocellulose. The ether–alcohol mixtures which are the best solvents for nitrocellulose of a given nitrogen content are as follows:

N content, %	the optimum volumetric ether to alcohol ratio
11.80	50:50
12.20	53:47
12.55	70:30

With solutions that have been prepared from solvents at a limiting ratio, i.e. where a small change in the proportion of the solvents may cause the dissolved nitrocellulose to coagulate, the highest viscosities are observed. The question is discussed below.

Solubility in alcohol and in other solvents. The solubility of nitrocellulose in alcohol is relatively low. In the case of nitrocellulose containing more than 11% of nitrogen the solubility in ethanol does not exceed a few per cent. Lower nitrated products are dissolved up to 100%, but further lowering the nitrogen value leads to a product that dissolves only with difficulty.

Acetone is not capable of dissolving nitrocelluloses of nitrogen value less than 10%. They can be dissolved in dilute aqueous NaOH.

In ethyl acetate and in other organic esters nitrocellulose containing 10% of N or more is completely soluble.

VISCOSITY

Viscosity, as well as solubility, is a most important characteristic for distinguishing various types of nitrocellulose. The determination of viscosity is of great theoretical importance, since it is used to study the degree of polymerization of nitrocellulose. In commercial practice viscosity frequently plays a decisive part, for it is used to assess suitability of nitrocellulose for specific purposes. Thus, in the manufacture of blasting gelatine or varnishes a nitrocellulose with the appropriate viscosity is used to make the required products. Films, protective coatings or tubes and cords of smokeless powders should neither be brittle not too soft: properties which depend mainly on the viscosity of the nitrocellulose.

With regard to their viscosity, nitrocellulose solutions demonstrate the typical properties of lyophilic colloids. The action of pressure, temperature and concentration causes anomalies to appear indicating that these solutions deviate from the classical Hagen–Poiseuille's law of viscosity. The measurement of viscosity, as carried out in practice, is discussed on p. 277.

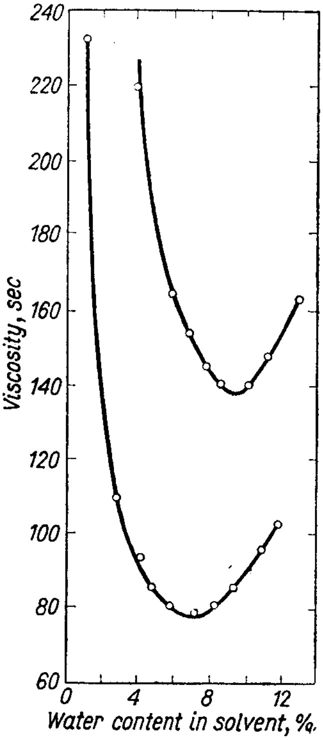


FIG. 101. Change of viscosity with addition of water to solutions of nitrocellulose in acetone (Masson and McCall [58]).

The viscosity of nitrocellulose solutions is to some extent dependent on the composition of the solvent, and on its solvent capacity or "strength". Masson and McCall [58] have examined the viscosity of nitrocellulose solutions in acetone to which different amounts of water had been added. They obtained a curve, reproduced in Fig. 101, that illustrates the effect of the water content of the acetone on the viscosity of nitrocellulose solutions.

The curve shows a distinct minimum viscosity at a water content of about 7%, since acetone containing this amount of water is a better solvent than anhydrous acetone. As the water content increases the dissolving "strength" of the solvent is diminished. Simultaneously the viscosity of the solution increases. Finally, at a 12% water content the "limit of dissolution" is achieved, and on exceeding this percentage, precipitation of nitrocellulose gel takes place.

The viscosity of nitrocellulose solutions in ether–alcohol undergoes similar changes as the composition of the solvent is modified.

The relationship between the viscosity of 3, 4 and 5% solutions and the ether to alcohol ratios is outlined in the graph (Fig. 102) reproduced after Gibson and McCall [57]. The minimum viscosity of a 4% solution corresponds to a mixture of 55 parts by volume of ether with 45 parts by volume of alcohol (1.1:1 parts by weight). A solvent composed of 75% of ether and 25% of ethanol produces a high viscosity solution. By an inappreciable decrease of the alcohol content the precipitation of nitrocellulose gel is brought about. The opposite effect, giving a high-viscosity solution on the border of gel precipitation is produced by a solvent made up from 25% ether and 75% alcohol. The gel precipitates on the addition of a small amount of alcohol.*

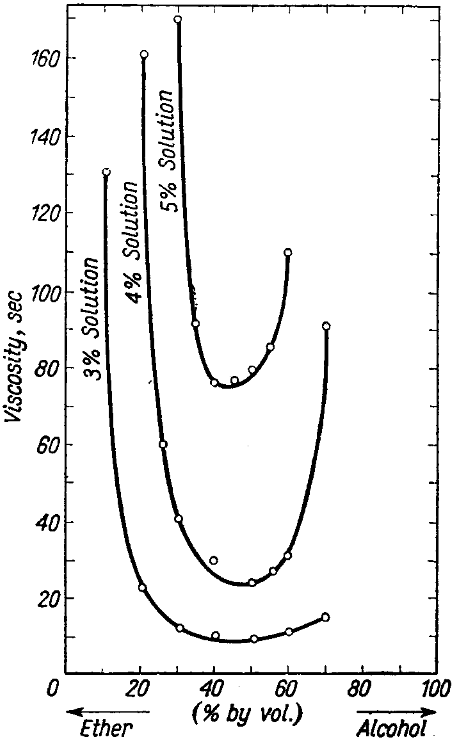


FIG. 102. Influence of the composition of the solvent (alcohol and ether) on the viscosity of nitrocellulose solutions (Gibson and McCall [57]).

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* The viscosity, expressed in seconds, represents the time needed by a steel sphere 0.793 ±0.001 cm dia., weighing 2.0385±0.0007 g, to fall through a 10 in. layer of solution contained in a tube 2.5 cm dia., 35.5 cm long at a temperature of 25°C.

The *intrinsic viscosity* [η] (dl/g or ml/g) is an important physico-chemical constant of polymers estimated by extrapolation to an infinite dilution, that is to a zero concentration of the polymer. (For the Fikentscher function k — "Eigenviscosität" — see p. 278). If the intrinsic viscosity were in fact a measure of the length of the polymer chain molecules, then it would be expected not to vary as a result of changing the solvent. Dobry [59] has determined the viscosities of 0.04% solutions of nitrocellulose (11.4% N) in different solvents and calculated the intrinsic viscosity by means of extrapolation. The results are collected in Table 43. The changes in the intrinsic viscosity brought about by varying the solvents are negligeable. Lindsley [60] has come to the same conclusion.

TABLE 43

THE INTRINSIC VISCOSITY OF NITROCELLULOSE

Solvent	[η]	Solvent	[η]
Acetic acid	0.33	Cyclohexanone	0.33
Acetone	0.29	Acetophenone + 3% of ethanol	0.32
Methyl cyanide	0.31	Ethyl benzoate + 11% of ethanol	0.32
Methanol	0.30	Methyl salicylate + 20% of methanol	0.33
Isobutyl formate	0.30		
Ethyl formate	0.32		
Nitrobenzene	0.32		

Nevertheless, such a uniformity in results has not been confirmed by all investigators. Thus G. G. Jones [61] has found a range of less uniform values for high-viscosity collodion nitrocotton HH, with 12.2% N. Some of these data are collected in Table 44.

TABLE 44

THE INTRINSIC VISCOSITY OF COLLODION COTTON

Solvent	[η]
Acetone	0.53
Methanol	0.53
Ethyl lactate	0.66
Epichlorohydrin	0.69
Benzyl acetate	0.71
Nitrobenzene	0.66

The addition of aromatic hydrocarbons to a nitrocellulose solution in amyl acetate produces an increase in the viscosity of the solutions, as shown in a diagram published by Drinberg [62] (Fig. 103).

Different plasticizers added to nitrocotton solutions can reduce their viscosity. Thus it has been established (Nisizava [63]) that the addition of camphor lowers the viscosity of nitrocellulose solutions. The same effect was reported by Wolff and Rosen [64] for nitrocellulose solutions in butyl acetate, to which additions of tricresyl phosphate and dibutyl phthalate were made.

The results published by other authors, concerning similar systems, for instance the work of Kozlov and Kalashnikova [65] on the behaviour of nitrocellulose and acetylcellulose in the presence of plasticizers, are inconsistent with the above observations. According to Kozlov and Kalashnikova on the addition of camphor or castor oil to an acetone solution of nitrocotton no change of viscosity occurred.

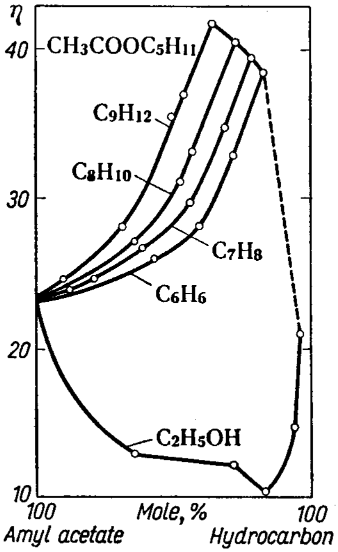

FIG. 103. Change of viscosity of nitrocellulose solution in amyl acetate with addition of aromatic hydrocarbons, according to Drinberg [62].

It is very interesting to observe the influence of aldehydes on nitrocellulose solutions. This has been done by Kozlov and Bedushevskaya [66]. This effect is most complicated, since in accordance with the said authors two processes were occurring simultaneously: the formation of cross links which produced an increase of viscosity, and a degradation of the long-chain molecules which reduced the viscosity.

An addition of diphenylamine causes a marked decrease in viscosity, as reported by Drinberg [62]. The viscosity of high-viscosity nitrocotton solution is decreased under the influence of a 5% admixture of diphenylamine (by weight of nitrocellulose) as much as 24%.

According to the work of Kozlov *et al.* [67] the viscosity of a 2% nitrocellulose (11.5% N) solution in acetone is decreased as a result of adding such electrolytes as lithium chloride up to a quantity equivalent to the number of available hydroxyl groups. The viscosity fell from 0.17 P to some 0.14–0.11 P.

When the amount of added lithium chloride was increased to a value equivalent to all the hydroxyl groups, both free and esterified, the viscosity was reduced to

0.0038 P. The change of viscosity is not brought about by any change of molecular weight, as this undergoes no diminution after treatment with LiCl.

The problems of the increase in viscosity of nitrocotton and the precipitating gel in the presence of inorganic compounds, owing to the formation of complex compounds, is discussed later (see p. 302).

The effect of temperature on the viscosity of nitrocellulose solutions has been studied by many authors, e.g. Nishida [68], Drinberg [62], E. Karrer *et al.* [69], Kozlov [70] and Goldman [71]. These experiments showed that the viscosity of concentrated nitrocellulose solutions is lowered more quickly, the higher the concentration of the solution. Attempts were made by E. Karrer, Berl and Umstätter [69] to find a formula expressing the relationship between the viscosity and the temperature (from 20 to 48°C). Shor [72] has examined the viscosity of nitrocellulose solutions within the concentrations range 14.9–17.9% and at temperatures from 0 to 40°C. On the basis of a mathematical analysis of the numerical results, the author has deduced the following formula:

$$\eta_t = \eta_0 e^{-kt}$$

where: η_t is the viscosity of the solution at a temperature t°C, η_0 is the viscosity of the solution at 0°C and k is a constant equal to about 0.05.

The determination of viscosity at 0°C is difficult to carry out, hence the author has modified his formula as follows:

$$\eta_t = \eta_{20} e^{1-0.05t}$$

where η_{20} represents the viscosity at 20°C.

Hence the formula for the temperature gradient is: $\frac{d\eta_t}{dt} = -0.05\eta_t$. Thus a change of the temperature of solution by 1°C causes the viscosity to vary by 5%. The equation has been confirmed by experiment. In the graph (Fig. 104) the calculated values fit well with the experimental data.

Ageing of nitrocellulose solutions. The tendency of nitrocellulose solutions to undergo changes in the course of time (to "age") has been known for many years. It consists mainly in a decrease of viscosity during the first ten to twenty hours after dissolution. At room temperature the decrease of viscosity stops after 1–2 days. At an elevated temperature it continues, and the viscosity approaches a certain asymptotic limiting value, that may be estimated by means of extrapolation.

The rate of decrease in viscosity, and the value of the lower limit at which the viscosity becomes stable depends on the type of nitrocellulose and on the solvent used. The higher the initial viscosity, the faster viscosity falls. However, the viscosity curves as a function of time never cross one another.

The reason why the viscosity falls is the effect of the solvent on the molecules of nitrocotton which tends to degrade the chains. The shortening of the molecular chains is relatively more marked in the case of long chains, i.e. with nitrocellulose that produces the more viscous solutions. This is an irreversible process. If from a solution that is already stabilized in respect of viscosity, nitrocellulose is precipitated and then redissolved, then the viscosity of the new solution is exactly the same as immediately before the precipitation. Addition of acids or bases to the solution hastens the degradation of nitrocellulose.

Studying this phenomenon of ageing the viscosity measurements of the nitrocellulose must always be carried out at a pre-determined time, e.g. 24 hr, after the solution has been prepared and kept at room temperature, since otherwise the results obtained are not comparable.

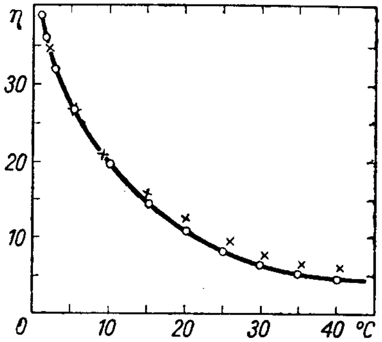

FIG. 104. Change of viscosity of nitrocellulose solution with temperature (○ —experimental and + — calculated values), according to Shor [72].

Effect of storage on viscosity. Factors such as the method of storing undissolved nitrocellulose affect the viscosity of its solutions. It has been established (Kanamaru [73]) that nitrocellulose kept in a polar liquid, e.g. water, alcohol, and tested for viscosity at stated periods by dissolving samples in acetone, shows for the first few days a rather rapid increase in viscosity, which gradually becomes slower. If cellulose is stored in a non-polar liquid, such as carbon tetrachloride, or petroleum ether, then the viscosity of solutions remains unchanged or increases only very slightly.

From samples examined by means of X-rays it has been established that the increase in viscosity is related to an improved orientation of the microcrystals along parallel axes.

Effect of the degree of polymerization on the viscosity. It has been made clear by the experiments of many authors that operations leading to the degradation of cellulose prior to nitration contributes to the production of a less viscous nitrocellulose. Moreover, the degree of polymerization of cellulose before nitrating depends upon the origin of the cellulose: the type of plant, its age and so on. The properties of the cellulose, such as polymerization degree, are passed on to the nitrocellulose, as already stressed (p. 246), to exert an influence on the viscosity of the product. Hence cotton yields nitrocellulose solutions more viscous than these from wood pulp cellulose and the solutions of the product from long fibre cellulose are more viscous than those from short fibre cellulose. Solutions prepared from nitrocellulose of older plants demonstrate a lower viscosity.

The relationship between the viscosity of nitrocellulose solutions and the age of poplar wood cellulose according to Pascal [74], is shown in Table 45.

TABLE 45

THE EFFECT OF THE AGE OF WOOD ON THE VISCOSITY OF NITROCELLULOSE SOLUTIONS

Age of poplar years	Nitrogen content %	Viscosity sec
26–48	10.5	128
24–36	10.9	201
8–24	10.9	248
8	10.8	697

As shown experimentally by Piest [75], cotton which was subjected to various operations, e.g. bleaching, treatment with alkalis or acids, strong heating prior to nitration furnishes nitrocellulose solutions of low viscosity. At the same time an increase in the solubility of the nitrocotton was also observed. This is evidence that the cellulose molecules are shortened and their content of terminal group is increased. A certain proportion of hydrocellulose and oxycellulose may result. The total effect is to bring about an increase in the reductive properties of the cellulose, i.e. an increase of the copper number.

In Tables 46 and 47 results reported by Gabillon [76] are tabulated.

TABLE 46

THE EFFECT OF HEAT TREATMENT OF CELLULOSE ON THE VISCOSITY OF NITROCELLULOSE SOLUTIONS

Cotton	Copper number	Nitrogen content %	Viscosity sec	Solubility in alcohol %
Without heating	0.25–0.27	11.82	480	3.6
Heated for 4 hr at 120°C	0.28–0.30	11.90	320	3.9
Heated for 8 hr at 120°C	0.26–0.34	11.90	270	3.5
Heated for 12 hr at 120°C	0.32–0.39	11.94	238	5.8
Heated for 4 hr at 130°C	0.31–0.37	11.92	350	5.6
Heated for 8 hr at 130°C	0.40–0.43	11.95	276	6.7

Effect of the conditions of nitration. The conditions under which the nitration was carried out exert an appreciable influence on the viscosity of nitrocellulose solutions. Thus a high nitrating temperature produces low viscosity nitrocellulose

TABLE 47

THE EFFECT OF CHEMICAL TREATMENT OF CELLULOSE ON THE PROPERTIES AND YIELD OF NITROCELLULOSE

Cotton	Copper number	Nitrogen content %	Viscosity sec	Solubility in hot alcohol %	Yield %
No treatment	0.26–0.29	12.22	78	3.1	137
Treated with caustic soda under pressure	0.44–0.41	12.08	28	10.8	125
No treatment	0.13	12.06	730–810	0.95	150
Treated with 1% hydrochloric acid at 70°C	0.57	12.03	245–250	3.9	147.5
Treated in the same way at 80°C	0.96	12.03	39–40	11.09	140

since nitration at an elevated temperature is accompanied by degradation, hydrolysis, and oxidation processes to a larger extent than at a lower temperature.

The following relationship has been given by Berl and Klaye [77]:

nitrating temperature, °C	viscosity, sec
25	1215
35	765
45	480

An exactly similar decline of viscosity is observed, according to Gabillon, on raising the temperature to 45°C. The effect of nitration at a temperature exceeding 45°C (45–65°C) produces a considerably smaller diminution though the decrease in yield is appreciable. Data quoted by Stark [78] for cotton nitrated for 30 min by means of a mixed acid composed of

38.5%	HNO_3
44.5%	H_2SO_4
17.0%	H_2O

are given in Table 48.

TABLE 48

THE INFLUENCE OF NITRATION TEMPERATURE OF CELLULOSE ON THE VISCOSITY AND SOLUBILITY OF NITROCELLULOSE SOLUTIONS

Nitration temperature °C	Nitrogen content %	Viscosity sec	Solubility in ether–alcohol %
15	10.7	330	52
18	10.9	280	68
20	10.8	260	79
22	11.2	205–290	84–98
40	11.5	28	100

Prolonged nitration favours the processes of degradation and oxidation, and hence also the reduction of viscosity. Schur and Hoos [78a] have nitrated wood pulp cellulose at various temperatures to attain results as follows (Table 49).

TABLE 49

THE TEMPERATURE OF NITRATION AND THE VISCOSITY OF NITROCELLULOSE SOLUTIONS

Temperature °C	Nitrogen content %	Viscosity sec	Yield %
40	11.09–11.19	50–80	150.7–155.2
45	11.13–11.31	15–27	146.8–150.0
50	11.25–11.35	11–14	136.5–147.2
55	11.41–11.44	5–6	125.5–134.0

In the Table 50 data have been collected from the investigation of the influence of the time of nitration by means of a mixed acid composed of:

38.2%	HNO_3
44.5%	H_2SO_4
17.3%	H_2O

at 22°C, on the viscosity of nitrocellulose solutions.

TABLE 50

THE EFFECT OF TIME OF NITRATING CELLULOSE ON THE VISCOSITY OF NITROCELLULOSE SOLUTIONS

Time of nitration min	Nitrogen content %	Viscosity sec	Solubility in ether–alcohol %
30	11.8	180	99.3
35	12	160	99.5
40	12	138	99.7
45	11.9	102	99.3
60	11.8	93	98.5

An increase of the nitrogen content is also accompanied by an increase of viscosity, providing that the nitrocotton is prepared under accurately uniform conditions. This relationship is described by Berl and Klaye [77] as tabulated below (Table 51).

In these experiments the nitrocellulose was washed (free of acid) with cold water only after being nitrated.

TABLE 51

THE RELATIONSHIP BETWEEN THE NITROGEN CONTENT AND VISCOSITY OF NITROCELLULOSE

Nitrogen content %	Viscosity sec
9.09	447
10.41	1800
12.48	16,200
13.02	18,600
13.50	322,500

It has been demonstrated in experiments by many authors that the nitrogen content has a distinct influence on the viscosity of solutions when identical conditions of nitration and purification of the nitrocellulose are used. Thus for a nitrocellulose containing 11.96% N, giving a solution of viscosity 203 sec, the molecules of nitrocellulose do not differ in chain length from those of a nitrocellulose containing 11.05% N giving a solution of only 27 sec viscosity (Krüger [79]). The molecular weight was determined by the diffusion method. Additional nitration of a lower nitrated cellulose yielded a more viscous product.

Of all the factors influencing viscosity the most important is the molecular weight of the raw material.

Okada [80] therefore suggested determining the molecular weight of cellulose by determining the viscosity of nitrocellulose derived from it. He suggested nitrating cellulose with a strong nitrating mixture (27.5% HNO_3, 63% H_2SO_4, 9.5% H_2O) and at low temperature (0°C) to yield a high nitrated product (13.0–13.2% N).

However, the conditions of nitration did not guard sufficiently against degradation, and oxidation (e.g. [146]), and a number of authors suggested nitration under conditions where the possibility of degradation and oxidation was considerably reduced. This is discussed on p. 343.

Thus Rogovin and Shlakhover [81] performed a stepwise nitration applying mixed acids composed of nitric acid, acetic anhydride and acetic acid. Nitrating mixtures of this composition do not bring about degradation, hydrolysis or oxidation of nitrocellulose during the nitration (see p. 344). Each additional nitration causes an increase of viscosity. The results are collected in Table 52.

In order to avoid the degradation of cellulose Wannow [82] used a mixture of nitric acid with phosphoric acid and water at temperatures of 0 and 20°C. The constant degree of polymerization was demonstrated by measuring the osmotic pressure. It has been confirmed that the viscosity of nitrocellulose solutions depends upon the nitrogen content of the substance (Fig. 105).

The extent to which the composition of the mixed acid influenced the viscosity of the nitrocellulose was followed by Berl and Berkenfeld [83]. They demonstrated that enriching the nitrating mixtures with sulphuric acid caused a considerable decrease in the viscosity of the nitrocellulose solutions.

TABLE 52

THE EFFECT OF AN ADDITIVE NITRATION ON THE VISCOSITY OF NITROCELLULOSE SOLUTIONS

Type of substance	Nitrogen content %	Viscosity	
		absolute, of a 2% solution in acetone sec	specific, of a 0.25% solution in acetone sec
Cellulose nitrate	11.40	93	0.78
Re-nitrated cellulose nitrate	13.39	348	1.75
Cellulose nitrate	11.28	186	0.95–1.0
Cellulose nitrate re-nitrated once	12.40	510	1.30
Cellulose nitrate re-nitrated twice	13.40	910	2.85
Cellulose nitrate	11.21	51	0.6
Re-nitrated cellulose nitrate	13.41	153	1.4

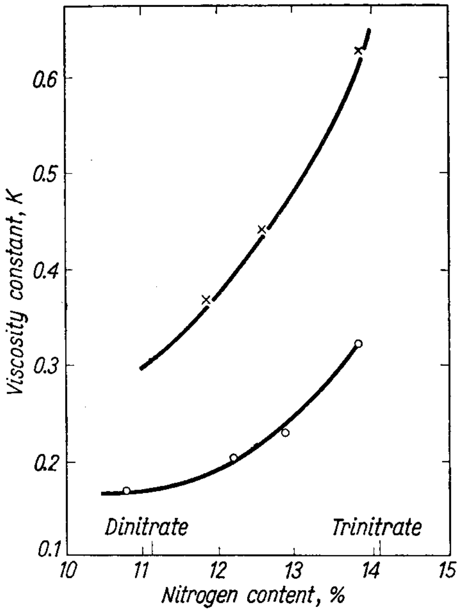

FIG. 105. Change of viscosity of nitrocellulose solutions with nitrogen content (Wannow [82]). + — Nitration at 0°C, ○ — at 20°C.

Effect of the treatment after nitration. The treatment of the nitrocellulose after nitration also exerts a major influence on the viscosity. Thus, for instance vigorous stabilization boiling leads to a decrease in viscosity. Values reported by Bruley [54] are given below:

boiling period, hr	viscosity, sec
10	703
14	454
18	424
24	389
32	279
40	254
48	237
60	140

A particularly marked change in the viscosity of nitrocellulose results from keeping it boiling in solutions of different reagents — bases and acids. In order to lower the viscosity of nitrocellulose, careful boiling in an alkaline medium is sometimes applied in practice.

Lenze, Metz and Rubens [84] reported the data assembled in Table 53.

TABLE 53

THE EFFECT OF AFTER TREATMENT WITH ALKALIS ON THE VISCOSITY OF NITROCELLULOSE SOLUTIONS

Treatment of nitrocellulose	Nitrogen content %	Viscosity of ether-alcohol solution sec	Solubility in 95% alcohol %	Copper number after denitration
Nitrocellulose untreated with alkalis	12.22	88	5.5	3.94
Nitrocellulose slightly treated with alkalis	12.18	64	5.4	4.06
Nitrocellulose treated slightly more with alkalis	12.16	29	9.2	5.71
Nitrocellulose treated strongly with alkalis	12.08	11.4	13.2	8.70
Nitrocellulose vigorously treated with alkalis	11.91	8	20.0	9.25

In view of the increase of the copper number it may be concluded that the substance undergoes strong hydrolysis and oxidation in the course of the treatment with alkali. Operations of this kind should therefore be performed with great care, since the over intensive action of these reagents and the appreciable fall in viscosity that ensues cause the gel formed after evaporation of the solvent to become brittle. In recent times therefore stabilization boiling under pressure has been widely applied.

The first references to this method were however published as early as 1899 (Schulz [85]).

Stabilization by boiling under pressure is now used:

(1) in order to shorten considerably the time of stabilization, which is usually the longest manufacturing operation;

(2) in order to attain the viscosity characterizing the collodion cotton intended for varnish making.

Various kinds of varnish collodion cotton differ widely in the viscosity of their solutions; ranging from an insignificant value to a high viscosity, achieved chiefly by means of stabilization boiling in an autoclave.

Wehr [86] reported the values tabulated below characterizing the change in viscosity brought about by keeping nitrocellulose boiling under pressure in water at 134°C (Table 54).

TABLE 54

Type of nitrocellulose	Nitrogen content %	Time of boiling at 134°C min	Intrinsic viscosity η
original	12.12	—	1.220
I	12.01	15	0.360
II	12.02	40	0.190
III	11.98	90	0.100
IV	11.98	165	0.050
V	11.97	295	0.029
IV	11.87	430	0.021

The viscosity of nitrocellulose is also affected by prolonged exposure to sunshine primarily by ultra-violet rays. It is beyond question that these cause shortening of the molecular chain. (Donald [87], Fric [88], Breguet and Caille [89], Stark [78] and others).

time of exposure to light, hr	viscosity, sec
—	335
24	320
48	305
480	270
900	240

Similar results due to irradiation were also established by Rogovin and Glasman [90]. Clément, Rivière and Beck [91] found that under the influence of the light only the viscosity of high-viscosity nitrocellulose was decreased, low-viscosity nitrocellulose did not undergo any change. In view of the experiments of Minc [92], quoted below, this observation appears to be inaccurate. Clément, Rivière and Beck observed, moreover, that the solubility was increased by irradiation. The increase of solubility may be brought about to some extent by a certain denitration that accompanies the irradiation of nitrocellulose. Denitration produced by the influence of ultra-violet rays has also been reported by other workers (see p. 312).

As shown by Minc [92], the reduction in viscosity of collodion cotton, nitrogen content 11.2% N, dissolved in acetone by ultra-violet irradiation is greater, the higher the concentration of nitrocellulose in the solution.

Thus in the instance of 1% solution exposed for an interval of 4 hr to the action of light the decrease in viscosity is 0.3–0.7%. With 10–20% solutions, on the other hand, the reduction in viscosity during the same period is 25.0–34.2%. Minc's experiments showed that in solutions of low viscosity the reduction of viscosity could remain unobserved. Claesson and Wettermark [92a] investigated the irradiation of solutions of cellulose nitrate with light of wave-length 253 mμ. The depolymerization was followed viscosimetrically and the chain breakage was found to obey the course predicted theoretically for a random process with a quantum yield of 0.01–0.02.

In their more recent paper Claesson, Palm and Wettermark [92b] investigated the magnitude of the degradation of nitrocellulose (12.2% N)

(1) at different wave-lengths,

(2) when the energy of the light was varied.

A solution of nitrocellulose in methanol (concentration 0.40–0.45%) showed depolymerization after exposure to light to the wave-length 302 mμ, whereas no depolymerization was detectable after exposure to the wave-lengths 334 and 365 mμ. Solutions of the same nitrocellulose sensitized by adding *ca.* 1% β-naphthylamine showed depolymerization at all the wave-lengths.

The viscosity of the solutions fell from $[\eta] = 4.14$ to *ca.* 2.4 dl/g during the first 50 hr exposure, after which it rapidly assumed a constant value. The decomposition of nitrocellulose by light is discussed later (see p. 312).

Ultrasonic waves also bring about a reduction in the viscosity of nitrocellulose. The effect is more marked the higher the initial viscosity, and thus the longer the nitrocellulose chains (Sollner [93]; Schmidt and Rommel [94]). For instance, nitrocellulose with a molecular weight of 123,000, estimated by means of Staudinger's viscosity equation, subjected in solution form to the action of ultrasonic waves suffered a degradation to a molecular weight of 70,000–80,000.

In more recent experiments, Edelmann [95] has followed the depolymerization of nitrocellulose in dilute (0.5%) solution. He reported that nitrocellulose of an average polymerization degree $n = 1060$, and containing considerably amounts of the $n > 2500$ fraction, was degraded after being subjected for 1 and 4 hr to the action of ultrasonic waves of 800 kc/sec to an average polymerization degree of $n = 910$ and 630 respectively. By fractionation, the presence of a small quantity of $n = 1400$ was established in the latter.

The action of ultrasonic waves seems likely to be the result of mechanical rupture of the long chain molecules of nitrocellulose on being rubbed by the violently oscillating particles of solvent. Thus it is one of rare examples of depolymerization brought about by mechanical forces. Further evidence in favour of the supposition that mechanical forces may cause the substance to depolymerize is provided by the effect of pulping nitrocellulose in beaters on the viscosity of the product. The shortening the nitrocellulose fibres that occurs reduces its viscosity. According to Bruley [54] the relation can be depicted numerically, as shown in Table 55.

TABLE 55

THE EFFECT OF BEATING NITROCELLULOSE ON THE VISCOSITY OF ITS SOLUTION

Viscosity, sec	
before beating	after beating
109	82
228	117
92	50
89	53

More recently Staudinger and Dreher [96] have confirmed these observations, by determining the effect of the time of pulping nitrocellulose in a colloid mill on its molecular weight as determined by viscosity measurement. They further established that owing to intensive milling a partial denitration of nitrocellulose took also place, as seen in Table 56.

TABLE 56

THE RELATION BETWEEN THE TIME OF BEATING NITROCELLULOSE AND ITS MOLECULAR WEIGHT

Time of beating, hr	% N	Molecular weight
0	12.95	430,000
4	12.80	125,000
8	12.46	80,000
12	11.75	47,000

Recently, the effect on the nitration product of beating the cellulose prior to nitration has been studied by Ellefsen [97] who confirmed the well-known view that beating of cellulose was accompanied by partial degradation to soluble substances. However, the molecular weight was unchanged in those fractions of cellulose that did not dissolve in water.

Sometimes an increase in the viscosity of nitrocellulose is possible, through cross links formed between free hydroxyl groups. This involves the chemical reactions of cellulose, which are discussed later (see p. 303).

It follows from the experiments of Nishida [98] and Kozlov [70] that mixing or stirring solutions of nitrocellulose causes the viscosity to increase initially and then to fall. As mentioned already (p. 261) the viscosity of nitrocellulose is of major importance for the properties of smokeless powder gel. Low viscosity solutions yield a brittle gel. Besides, the lower the viscosity the more the gel shrinks on removal of the solvent. More detailed information regarding the relationship between the viscosity of nitrocellulose and its suitability for use in powder manufacture is contained in Vol. III.

The viscosity of commercial types of nitrocellulose is tested by means of a variety of different methods in various countries.

The Ardeer Method is the most commonly used in Great Britain and in the British Commonwealth [16a]. The determinations are made in acetone of specific gravity 0.8097 at 20°C, prepared by mixing 95.0 volumes of acetone and 5.0 volumes of water, by the falling-sphere method adapted in the first place for military nitrocelluloses by Masson and McCall [58]. As mentioned already (p. 262) these authors found that the addition of a small amount of water to the acetone reduced the viscosity of the nitrocellulose solution very considerably and that a minimum viscosity was reached with a certain percentage of water, which varies from one nitrocotton to another (Fig. 101). The apparatus is calibrated with sugar solution of known absolute viscosity. The results are calculated on the assumption of specific gravity of 0.80 for all nitrocellulose solutions and are always reported in c.g.s. units (poises, P) at 20°C. The viscosity figure is always preceded by one of the following letters: X, L, M or H, which in the usual I.C.I. dual notation, indicate different ranges of both nitrogen content and viscosity. First letter (N-content): L = 10.5–11.2%, M = 11.2–11.8%, H = 11.8–12.2%. Second letter (viscosity): X = lowest, H = highest. A general idea of the viscosity range can be gathered from the concentrations quoted, for each of which a steel ball 1/16 in. in diameter has to fall through 15 cm of the solution within a period of 6 sec to 6 min. The time of fall on seconds is approximately twice the viscosity in c.g.s. units.

There are four degrees of viscosity: X, L, M, and H. In each a different concentration is used, thus for X, L, M and H the concentrations are 40, 20, 10 and 3% respectively (in g per 100 ml solvent). These ranges bear no simple relation to each other, and the general use of conversion factors to convert a viscosity determined in one range into another is quite inadmissible.

Many other formulations are in use. The most general in the United States is the Hercules Method [16a]. Determinations are also made at various concentrations, but the solvent consists of ethyl acetate, ethyl alcohol, and toluene in the proportions 20:25:55 by weight. Results are recorded in c.g.s. units, as in the Ardeer Method, but at the same time a general classification of nitrocelluloses as e.g. "5 sec", "1 sec", "$\frac{1}{2}$ sec" -product and so on is in use. These are the times of fall of a steel ball through a 10 in. layer of solution containing 12 g nitrocellulose in 100 g of solution. The smallest are derived by extrapolation from data obtained with more concentrated solutions and are fictitious. Thus commercial sorts of nitrocotton furnished by the Hercules Powder Co. possess viscosities corresponding to the following values: 1/4, 1/2, 15–20, 25–30, 30–40, 60–80 and 125–175 sec. Products used for varnish making possess the first four viscosities.

Viscosity determinations at the highest convenient concentration are of practical value, because in most of the applications of nitrocellulose, solutions of these concentrations are used, and there is usually little difference between the concentration in use and that used for the determination. All nitrocellulose solutions that are not very dilute show more or less abnormal viscosity, i.e. the rate of flow is not proportional to the applied stress or pressure. The ease of flow of a solution at one degree of stress cannot then be inferred from a "viscosity" determined at another. Nevertheless the measured viscosity of a comparatively concentrated solution is in general useful information. This advantage is sacrificed in what is the most rational of all viscosity systems, the German I.G. Method. Measurements are made in dilute solutions and the results are expressed in terms of the "Eigenviscosität" (k) of Fikentscher and Mark [99] a function which to a large extent is independent of concentration:

The Fikentscher function k can be defined by means of the expression:

$$\ln \eta_r = \frac{75k^2c}{1+1.5kc} + kc$$

c being the concentration in g/ml.

The values accepted are those of the Fikentscher k multiplied by 10,000. This system, which specifies the nitrocellulose and not its solutions, is the most scientific and consistent of all, but is limited to German practice only. For example, E510 and E950 I.G. nitrocelluloses correspond to ½–1 and 12.5 sec Hercules and X39–X140 and L125 Ardeer products respectively.

FRACTIONATION OF NITROCELLULOSE

Long ago it has been established that nitrocellulose is not a homogeneous substance. The earliest experiments in this field were made by Stepanov [100] who used the method of fractional precipitation from an acetone solution by the addition of water. Stepanov added different amounts of water stepwise to a solution of nitrocellulose in acetone to obtain fractions varying slightly, corresponding with the nitrogen content. The first and least soluble fraction contained 13.15% of nitrogen, while the N-content of the last, fifth portion, was 12.90%.

Duclaux *et al.* [101] came to other conclusions for he established that particular fractions differed only in the viscosity of solutions the nitrogen content being the same. In order to precipitate nitrocotton from its acetone solutions the authors added acetone–water mixtures, richer and richer in water until finally pure water was added. A range of fractions was separated from nitrocellulose acetone solution of viscosity 0.1 P (poises). The viscosity of the first fraction was 0.603 P, and that of the last 0.007 P (2% solutions).

Identical results of fractionating nitrocellulose by successive dissolution and precipitation have also been reported by other authors, e.g. Brunswig [102] Kumichel [103], Lacape [55], Glikman [104].

The most extensive investigations were those of Medvedev [105]. Commercial collodion cotton of 11.08% N was divided by Medvedev into four fractions. The viscosity of the acetone solutions as well as the molecular weight (osmotic method) of these were determined. The nitrogen content in all the fractions was approximately the same (Table 57).

TABLE 57

THE PROPERTIES OF COLLODION COTTON FRACTIONS

Fraction	Nitrogen content %	Specfic viscosity of solution of concentration: 2%	1%	0.25%	Molecular weight (by osmotic pressure)
I	11.4	21.56	3.9	0.39	25,000
II	*ca.* 11.8	26.37	4.67	0.43	60,000
III		24.52	4.47	0.42	40,000
IV		57.50	7.30	0.68	75,000

Lipatova and Lipatov [106] also found that the fractions of higher viscosity possessed a higher temperature coefficient of viscosity.

In other experiments, the opposite method of fractionation by dissolution was applied. In this way G. Meissner [107] prepared a soluble fraction with a nitrogen content of 10.28%, in quantity about 4% by extracting a specimen of nitrocellulose with 12.17% N using 50:50 ether–alcohol. The insoluble part was composed of nitrocellulose of 12.32% N.

Nitrocellulose has also been extracted with alcohol, the residue then being treated with a mixture of ether and ethanol (60:40 by volume, Berl and Hefter [108]). Three fractions were isolated: the *first* soluble in alcohol, the *second* soluble in ether-alcohol, and the *third* an insoluble residue. The fractions differed in nitrogen content. The lowest nitrogen content was found in the first fraction and the highest in the third fraction (Table 58).

TABLE 58

THE PROPERTIES OF NITROCELLULOSE FRACTIONS

Nitrogen content of original nitrocellulose	Solubility, %		Nitrogen content of fractions, %		
	in alcohol	in ether–alcohol	(1)	(2)	(3)
12.65	7.44	92.40	9.6	12.60	12.25
13.13	2.68	8.60	9.7	12.15	13.35
13.17	2.40	11.43	—	12.00	13.15
12.72	2.80	74.00	—	12.96	13.00

Similarly Craik and Miles [109] extracted nitrocotton by means of aqueous acetone with a gradually increasing acetone concentration. The fraction which dissolved with the greatest facility was the poorest in nitrogen, whilst the insoluble portion contained more nitrogen than the original substance. These workers also studied the viscosity of the fractions, finding that the less soluble fractions yielded the more viscous solutions.

A range of nitrocotton samples containing from 11.3 to 13.1% N, and nitroramie of 10% N prepared by denitrating nitroramie of 13% N by acting with nitric acid 80%, have been fractionated by G. G. Jones and Miles [110] by a method of successive extraction with aqueous acetone: every subsequent solvent was richer in acetone than the preceding one. They demonstrated that particular fractions differed in nitrogen content and viscosity.

The change of nitrogen content as the extraction proceeded is showed in Fig. 106. From their collected results Jones and Miles have constructed a graph (Fig. 107)

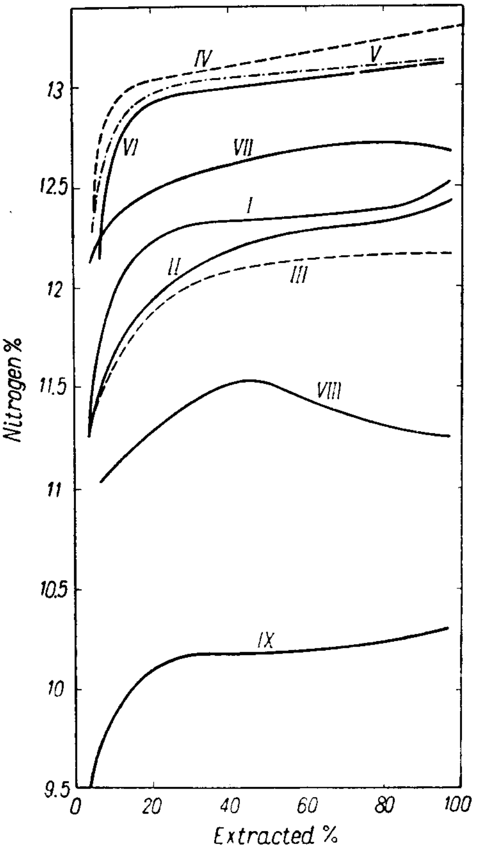

FIG. 106. Nitrogen contents of extracted nitrocellulose fractions according to G. G. Jones and Miles [16a]: (I) HH nitrocellulose, 12.20% N, high viscosity, unkiered; (II) HX nitrocellulose, 12.26% N, low viscosity; (III) HX nitrocellulose, 12.07% N, low viscosity; (IV) Guncotton, unkiered, 13.14% N; (V) Guncotton, kiered, 12.95% N; (VI) Guncotton, kiered, 12.93% N; (VII) "Pyro" nitrocellulose, 12.70% N; (VIII) Nitro-woodpulp, 11.30% N; (IX) Nitroramie (73.5% soluble in acetone), 10.00% N.

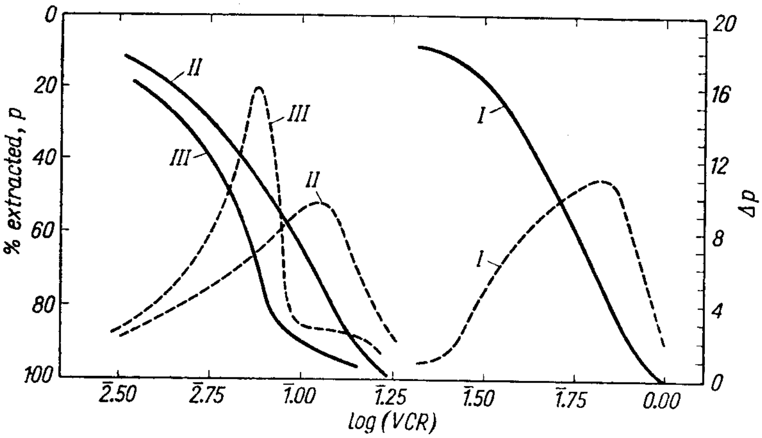

FIG. 107. Viscosity–concentration ratio ($\log_{10}$ VCR) (plain lines) and distribution of $\log_{10}$ VCR of fractions of nitrocotton (broken lines), according to G. G. Jones and Miles [16a]. Designation of samples as in Fig. 106.

to express the viscosity in terms of viscosity–concentration ratio (VCR) which is the specific viscosity, and the quantity of the component extracted, of different nitrogen content.

Extensive research into the fractional partition of nitrocellulose by means of acetone–water mixtures was carried out by Rogovin and Glasman [111]. The results of these experiments are given in the Table 59.

TABLE 59

VISCOSITY OF FRACTIONS OF NITROCELLULOSE

Nitrocellulose fractions	Viscosity of a 2% solution in acetone sec
I	16–17
II	33–34
III	54–62
IV	62–115
V	420
VI	690–1000

The method of fractionating by dissolution has also been used to determine the length of cellulose chains: nitration by means of nitric acid mixed with phosphoric acid does not bring about any degradation of practical importance. The molecular chains of nitrocellulose produced in this manner are as long as those of the original cellulose, hence different fractions do not differ with regard to their viscosity. Schieber [112] used a mixture of alcohol and ethyl acetate in which proportion of the acetate was augmented step by step.

Krüger [113] tried fractionating nitrocellulose by diffusion. The principle of the method was that a nitrocellulose solution in acetone, methyl alcohol or amyl acetate diffused into a pure solvent layer on the surface of the solution. Clearly molecules of smaller size penetrate more rapidly. A nitrocellulose solution of 12.8% N was separated into two layers in this way after 42 days' diffusion. The lower fraction comprised nitrocotton with a nitrogen content of 13.1% N, the upper layer one of 12.1% N.

Fractionating nitrocellulose by means of ultra-filtration was carried out by Duclaux and Wollmann [101]. Using filters differing in pore sizes, nitrocellulose of 11.0–12.5% N was separated into fractions of different viscosity ranging from 0.08 to 3.7. The molecular weight of the fractions, determined by the osmotic pressure method, was found to range from 21,000 to 70,000. Differences in the nitrogen content of the fractions was negligeable.

The distribution of molecular weights in nitrocellulose solutions has been studied by other methods, e.g. Svedberg's ultra-centrifuge method (Svedberg and Gralen [114] and Jullander [115]). Svedberg and Gralen have also made use of this method to determine the molecular weights of cellulose and nitrocellulose, and hence the degradation of the cellulose chain during nitrating. The results of these experiments are reported elsewhere (see. p. 343).

The fractionating of nitrocellulose by chromatographic absorption has also been described. As reported by Claesson [116] a 1.5% nitrocellulose solution in acetone was absorbed on activated charcoal in differing amounts that correspond with the molecular weight. This relationship is illustrated by the diagram (Fig. 108). The higher the molecular weight, the less it is absorbed by the charcoal. Nitrocellulose can be also fractionated on starch.

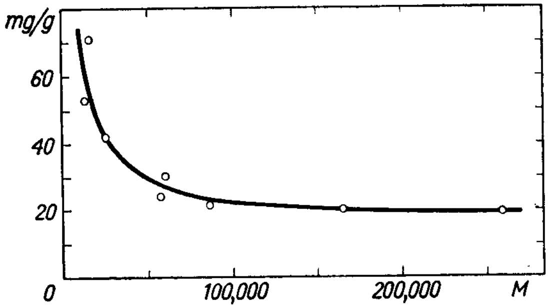

FIG. 108. Chromatographic separation of nitrocellulose fractions (quantity of fractions in mg/g and their molecular weight *M*; Claesson [116]).

There is no doubt that even the most uniform nitrocellulose, the nitro group content of which corresponds to trinitrate, is not a chemical individual in the usual sense of the term. The substance is composed of chains of different length, hence it is non-homogeneous.

HYGROSCOPICITY

As early as 1894 it was found that the lower the nitrogen content of nitrocellulose, the larger the amount of moisture it absorbs. Extensive research on the hygroscopicity of nitrocellulose was carried out by Will [117]. At an atmospheric humidity exceeding 90%, but below that at which condensation of vapour occurs on the nitrocotton owing to fluctuation of temperature, there exists a distinctive relationship between the nitrogen content of nitrocellulose and the amount of moisture absorbed. The more nitrate groups there are present in the molecule the fewer the available hydroxyl groups, and the less hygroscopic the nitrocellulose. This is due to the fact that molecules of water associate by means of hydrogen bonds with free, non-esterified HO-groups in the nitrocellulose.

It has been reported by Will that for nitrocelluloses with nitrogen content from 9.0 to 13.3%, dried to a constant weight at the temperature of 40°C, the percentage sum of the nitrogen content and of the absorbed mixture was constant equal, on average, to 14.6:

$$\%\mathrm{N} + \%\mathrm{H_2O} = 14.6$$

This simple formula has not been fully confirmed in later investigations, however. Thus Demougin [118] from his own investigations on the hygroscopicity of nitrocellulose containing from 10.94 to 14.1% of nitrogen has come to the conclusion that Will's rule could only be valid in atmospheres of low humidity. As the moisture content of the atmosphere approaches saturation point, the physical shape of the nitrocellulose, and hence the state of its surface, and the diameter and number of capillaries varied. De Pauw [119] then found that for nitrocelluloses containing 12.3 to 13.8% N the sum of the nitrogen content and of the hygroscopic moisture content was not constant, but was higher the lower the nitrogen content of the nitrocellulose. So for nitrocellulose with a 12.3% N the sum amounts to 17.1, whereas for 13.8% N it is 16.4.

In spite of the variability of the sum calculated from the nitrogen content and hygroscopicity the effect of the nitrogen content on the hygroscopicity can be expressed by a straight line. In Fig. 109 (after de Pauw) straight-lines corresponding with different relative moistness of atmosphere (f/F) are shown.

Water absorption from a 40% calcium nitrate solution was studied by Gukhman, Petrov and Yakovlev [120], who found that a nitrocellulose film immersed in such a solution was capable of absorbing up to 50% of water. After 5 min the water content reached 15–20%, and after 15 min it amounted to 25–30%.

From the practical point of view the absorption of acids by nitrocellulose is of major importance for the question of stabilizing nitrocellulose. It has been established (Wiggam [121]) that nitrocellulose absorbs dilute nitric acid and dilute sulphuric acid to the same extent, the absorption of hydrochloric acid being somewhat less.

The capacity of nitrocellulose to absorb vapours of organic solvents from the

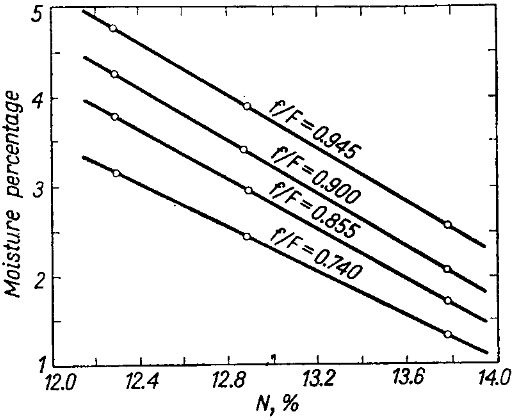

FIG. 109. Hygroscopicity of nitrocellulose as a function of nitrogen content (de Pauw [119]).

air has also been investigated. Here again the amount of substance absorbed depends on the nitrogen content of the nitrocellulose. According to Jenkins, Bennet and Rubenstein [122, 43]) there exists a certain maximum nitrogen content, characterized by the highest absorption capacity of nitrocellulose. Nitrogen values greater or less than this lower the absorption capacity. In the case of acetone, maximum absorption is attained at 12% N.

The absorption of vapours is accompanied by a positive thermal effect. Kargin and Papkov [123] measured the heat developed when acetone or pyridine were absorbed by nitrocellulose from petroleum ether or from a pure solvent, and found it was about 20 cal/g for acetone, and about 30 cal/g for pyridine.

The heat of absorption of acetone, ethanol, or ether by nitrocellulose was reported by Calvet [124]:

nitroramie 14% N:	ethanol	1.30 kcal/mole solvent
	ether	2.50 kcal/mole solvent
	acetone	3.88 kcal/mole solvent
nitroramie 11.5% N:	ethanol	1.80 kcal/mole solvent
	ether	3.37 kcal/mole solvent
	acetone	4.09 kcal/mole solvent

The heat of absorption of a mixed solvent: ethanol + ether, has been determined by the same author. The value varied according to the composition of the solvent reaching its maximum value at an ether: ethanol mole ratio of 1:1.3. The same solvent gave the maximum absorption heat both with high-nitrated and low-nitrated nitrocellulose. The thermal effect was appreciably larger for lower nitrated nitrocellulose. This seems to confirm Highfield's theory (see pp. 248, 256) that molecules of alcohol form bonds with the free hydroxyl groups of nitrocotton, thus producing a complex compound soluble in ether.

Other sources (Calvet and Izac [125]) report a value of 67.5 cal/g for the heat of absorption of acetone.

The investigations of Kargin and Stepanova [126] indicate that the heat of solution of nitrocellulose is slightly greater than the heat of absorption. The heat of solution was discussed on pp. 248–249.

OPTICAL PROPERTIES OF NITROCELLULOSE

Like cellulose, nitrocellulose demonstrates optical anisotropy (double refraction) which is regarded as one of the facts confirming the microcrystalline structure of the substance. A relationship between this property of nitrocellulose and the nitrogen content has been discovered by Ambronn [127] who studied the double refraction of cellulose. Differences in the refractive index for rays of different wave-lengths in two directions at right angle are of the order —0.50×10^{-3} to $+2.8 \times 10^{-3}$ (Table 60).

TABLE 60

DIFFERENCES OF REFRACTIVE INDICES ALONG TWO PERPENDICULAR DIRECTIONS FOR DIFFERENT WAVE-LENGTH

Nitrocellulose with nitrogen content, %	435 mμ	546 mμ	579 mμ	650 mμ
13.16	−0.50	−0.32	−0.31	−0.23
12.85	−0.32	−0.20	−0.17	−0.12
11.88	−0.12	−0.08	0	+0.02
10.55	+0.35	+0.32	+0.31	+0.30
cellulose	+2.8	+2.2	+2.07	+1.91

The data show that nitrocellulose containing 11.88% of nitrogen is isotropic for a wave-length of 579 mμ. Isotropic properties have also been established with nitrocellulose in a colloidal state, the phenomenon being attributed to the unoriented state of the micelles. However stretching a solid colloidal mass of nitrocellulose (celluloid) mechanically is sufficient to produce the anisotropic effect, since elongation of the micelles (and molecular chains bound by covalent bonds) causes them to orient and align themselves in the direction of the stretching force (Wächtler [128]).

These investigations agree well with experiments by Trillat [129] who found that the X-ray diagram of colloidal nitrocellulose showing a non-oriented structure of crystallites (interference rings), altered after being stretched to indicate a fibrous structure in which the crystallites were oriented along the axis in the direction in which the film was stretched.

Under the polarizing microscope nitrocellulose acquires different colours. According to Tissot [130] the different colours of nitrocellulose (11.6–12.55% N) seen through crossed nicols depended on the nitrogen content of nitrocellulose, but his conclusions were subjected to strong criticism in the later work of Phillips [131], who found that the colour of nitrocotton in polarized light does not depend on the nitrogen percentage, but it is related to the degree of aggregation of the nitrocellulose molecules. A red colour is seen when the degree of dispersion is high and blue when it is low.

Nitrocellulose fibres of different nitrogen content, suspended in glycerine, were investigated in a polarizing microscope by Miles [132]. He classified the samples into three groups:

(1) steel-grey to bluish-grey:	below 11.0% N
(2) yellow to brownish-yellow:	11.4 –11.8% N
(3) blue:	over 11.8% N

More recently the experiments with polarized light have been extended to gelatinized nitrocellulose.

A solvent containing 80% of nitroglycerine and 20% of nitroglycol to which 0.02% of crystal violet had been added was used by Fenson and Fordham [133]. The technique of adding a dyestuff to a solvent when investigating the process of dissolution of nitrocellulose was first described in a paper by Mangenot and Raison [134]. Using Sudan Red or Indophenol Blue, they succeeded in following the gradual progress of solution from the initial swelling of the nitrocellulose until the fibre ceased to be visible. The transformations taking place in the interior of fibres could be seen by following the absorption of the dyestuff.

Fenson and Fordham report observing in polarized light the colours listed in Table 61.

TABLE 61

THE COLOUR OF NITROCELLULOSE IN POLARIZED LIGHT

Nitrogen content of nitrocellulose %	Colour
11.4	pale red to grey
11.5–11.8	pale yellow, brown to red
11.9	neutral
12.0–12.6	pale blue to grey
12.6	light blue to greenish white

Both Mangenot and Raison, Fenson and Fordham have established from their microscopic studies on swelling and solution of nitrocellulose fibres that the surface of the fibres consists of a thin coating of a distinctively less soluble substance than the interior of fibres. Fenson and Fordham assumed that this was a superficial layer that had been partially denitrated in consequence of drastic stabilization processes. Therefore in the instance of a nitrocellulose of 11% N a solvent penetrates into the fibres through the damaged points of this layer.

Unpublished microscopic experiments of T. Urbański [29] on the dissolution of nitrocellulose fibres provide additional evidence that there exists a layer hindering the action of solvents, since the fibre starts to dissolve at the ends which have been torn and frayed by passage through the beaters.

The absorption spectrum of nitrocellulose solutions has been examined (Rassow and Aehnelt [135]). It has been established that the capacity to absorb light differs with the origin of the nitrated cellulose. Thus nitrocellulose made from wood pulp gives a slightly different absorption spectrum from that of nitrocotton.

G. G. Jones and Miles [136] examined the ultra-violet absorption spectra of nitrocelluloses having a range of nitrogen contents from 10.9 to 14.1%. The absorption curve shows a maximum close to 220 mμ, and an inflection below 300 mμ. The extinction is relatively small ($\varepsilon = 15.0$). This is typical of aliphatic compounds which lack a conjugated double bond system and give only the "R" spectrum.

Experiments by Ellis and Bath [137] on the infra-red absorption spectrum of cellulose have indicated the existence of hydrogen bonds between the hydroxyl groups of the cellulose molecules, probably following the —O—H···O— pattern (see p. 225).

An extensive analysis of infra-red absorption spectra has been carried out by Nikitin [138] who investigated native cellulose, mercerized cotton, cellulose esters (nitrates, acetates), and cellulose ethyl ether. Cellulose gave a number of the overtone absorption bands between 6711 and 4739 cm^{-1} that correspond to the overtone vibrations of hydroxyl groups bound by hydrogen linkages. These bands disappear as the hydrogen atoms of the hydroxyl radicals are substituted. In the spectrum of a cellulose dinitrate of 12.8% N, the band 3571 cm^{-1} appears caused by the hydroxyl groups freed from hydrogen bonds. A "trinitrate" containing 13.7% of nitrogen does not give any of those bands. Instead another band of 1639 cm^{-1} occurs, belonging to the O-nitro group. Well in line with these data are the results of Barchewitz, Henry and Chédin [139]. Two maxima in the infra-red absorption spectrum, charac-

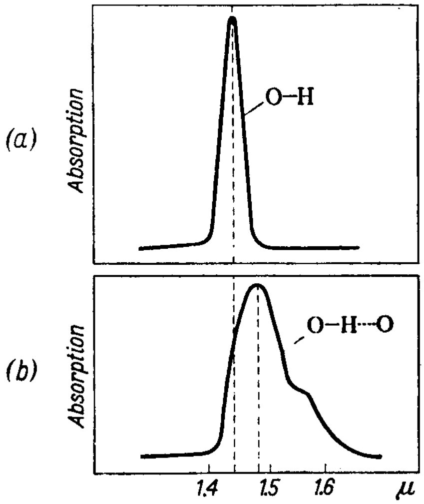

FIG. 110. Hydroxyl bands in infra-red spectrum of cellulose (Nikitin [138]).

terizing the O-nitro group, i.e. about 1667 and 1282 cm^{-1} have been found by Champetier and Clément [140]. Similar results have been reported by Zhbankov [141].

Nikitin has proved that in cellulose obtained by regeneration of nitrocellulose, the bands typical for hydrogen bonded OH group reappear. The curve in Fig. 110a represents the absorption band of cellulose dinitrate due to the presence of a OH group. After the regeneration of cellulose the absorption curve on Fig. 110b is obtained with the band shifted and widened owing to the hydrogen linkage.

ELECTRICAL PROPERTIES OF NITROCELLULOSE

It has been demonstrated experimentally on an industrial scale that nitrocellulose is readily charged with static electricity by friction, even by the air current during drying. Dry nitrocellulose charged with electricity may ignite on discharging.

Lee and Sakurada [142] have examined the dielectric constant of nitrocellulose dissolved in acetone and in acetone–hexanone mixtures. They found that the dielectric constant was only very slightly dependent on the viscosity, and completely independent of the concentration.

Among other electrical properties of nitrocellulose, attention should be paid to the experimental work on the electrical conductivity of solutions. Thus Dobry [143] found the conductivity of a nitrocellulose solution in acetone to be proportional to its concentration. Experiments on the electrophoresis of solutions made by Lantz and Pickett [144] demonstrated that the particles of nitrocellulose carry a negative charge. Electrolysis of the solution causes the nitrocellulose gel to collect at the anode. This gel may contain the metal of which the anode is constructed, as demonstrated by Apard [145].

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CHAPTER XI

CHEMICAL PROPERTIES OF NITROCELLULOSE

STABILITY

ONE of the most important problems in nitrocellulose technology concerns the purification process intended to increase as far as possible the stability of the product.

In the initial period of nitrocellulose manufacture numerous catastrophic explosions took place due to insufficient purification of the product. The purification method developed by Lenk [1] was then in use:

(1) washing nitrocellulose for at least two weeks with running water;

(2) boiling for several minutes in a 2% sodium carbonate solution and keeping in concentrated sodium silicate solution;

(3) rinsing with water and drying.

It became clear, however, that the methods introduced by Lenk were not sufficient to ensure a high enough chemical stability of the product. Also it became clear that a systematic study of stability and stabilization of nitrocellulose are needed.

The first study of the stability of nitrocellulose seems to be that of de Luca [2]. It is described below (p. 307).

A turning point in the field of stabilizing nitrocellulose was reached when Abel [3] discovered in 1865 that a certain amount of acid is retained within the channels extending along the fibres and this was causing the lack of stability of the nitrocellulose then produced. According to Abel stable nitrocellulose can be obtained by longer boiling of nitrocotton fibres cut in short pieces.

Later it was proved experimentally that the resistance of nitrocellulose to heating was dependent on the composition of the mixed acid, thus on the quantitative proportions of its three ingredients: sulphuric acid, nitric acid and water. With a high concentration of sulphuric acid in the nitrating mixture the nitrocellulose stability is reduced as established by Lunge's work mentioned below. Simultaneously it was suggested (Cross, Bevan and Jenks [4], Berl and Klaye [5]) that during nitration initially sulphuric acid esters are formed which are afterwards interchanged with nitric acid. The result is that cellulose nitrates or mixed sulphuric and nitric acid esters are produced, the latter if the chemical exchange is incomplete. These researches suggested that the mediocre stability of nitrocellulose might be due to the sulphuric acid esters or mixed cellulose sulphate–nitrates present in the product (Hake and Lewis [6]).

In point of fact it has been established by many workers that a nitrocotton freshly produced and washed from acid could contain up to 8% of sulphuric acid cellulose esters. Berl and Boltenstern [7] stated in later investigations that sulphuric acid always occurred in the stabilized nitrocotton in two forms: (a) as an inorganic salt, for the most part $CaSO_4$; (b) as sulpho groups chemically combined with cellulose. Their data are given in Table 62.

TABLE 62

SULPHURIC ACID CONTENT IN STABILIZED NITROCELLULOSE

Nitrogen content in nitrocellulose, %	Sulphuric acid content, %		The ratio of the total amount of acid to the part bonded as inorganic salts
	total amount	bonded as inorganic salts	
11.20	0.24	0.12	2:1
11.88	0.16	0.12	1.3:1
12.45	0.16	0.10	1.7:1
13.00	0.27	0.12	2.3:1
13.19	0.25	0.10	2.4:1
13.25	0.27	0.13	2.1:1

According to Hess, Trogus and Tomonari [8] mixed sulphuric and nitric esters of cellulose are soluble in methyl alcohol. Hence by boiling nitrocellulose in methyl alcohol it is possible to remove these substances up to a quantity corresponding to some 1% of the nitrocellulose mass. The extracted product contains three NO_2 and two SO_3H groups for every two $C_6H_{10}O_5$ units.

An appreciable advance towards explaining the essential basis of stabilizing nitrocellulose, and towards inventing an adequate stabilization process came from the studies of R. Robertson [9]. He has stated that the sulpho groups in cellulose sulphates and sulphate–nitrates undergo a quick and complete decomposition when boiled in the presence of dilute acids. Alkaline boiling on the other hand, causes the mixed ester to decompose very slowly and incompletely. This is why in practice prolonged boiling of at least 20 up to 100 hr in pure water is recommended as the first operation. The water becomes quickly acid during boiling due to the presence of acid absorbed or formed from the decomposition of unstable esters. According to Robertson this hydrolysis is most effective, when about 1% of sulphuric acid is present in the water. After changing the water and repeating the boiling in fresh water, a mild alkaline boiling (most preferably using calcium carbonate) can be carried out in order to neutralize the acid products formed during the previous treatment. If the alkali is added too soon to the water it may check the process of stabilization, since any incompletely hydrolysed sulphuric acid esters present are capable of forming salts in the alkaline stabilizing liquor, for instance calcium salts, difficult to dissolve in water, and to decompose.

Goujon [10] also found it necessary to begin the stabilization with an "acid boiling", and he confirmed the danger of too early an alkalization of the stabilizing bath. It has been found (Demougin and Landon [11]) that the stabilizing capacity of acids decreases in the following order: HNO_3, HCl, H_2SO_4.

Later experiments were carried out with a nitrocellulose stabilization process that consisted in treating a partially purified nitrocotton in an ammonia bath (e.g. Reeves and Giddens [12]). This was based on the supposition that ammonia was capable of neutralizing accurately acids contained in the interior of nitrocellulose fibres. However, this method has not been adopted in practice, since it was feared that the sulpho groups attached to cellulose in the form of mixed esters would undergo only partial hydrolysis in the presence of ammonia and later spontaneous hydrolysis of these substituents in the finished (stabilized) product might reduce its stability.

On the basis of his extensive works on the sulpho groups attached to cellulose in the form of neutral esters $R_{cel}OSO_2OR_{cel}$ and hydrogen sulphates $R_{cel}OSO_2OH$, Kullgren [13] concluded that stabilization should be begun immediately after the spent acids are removed from nitrocellulose.

Cellulose nitrated with nitric acid vapour or by means of $HNO_3+N_2O_5$ mixtures demonstrates a significantly higher stability than nitrocellulose nitrated in a mixture of nitric and sulphuric acid. This provides further evidence that the presence of sulphuric esters in nitrocellulose is responsible for its low stability.

Very extensive investigation made by A. C. Smith [14] showed that nitrocellulose with a low nitrogen percentage contained cellulose hydrogen sulphate, whereas in nitrocellulose with a high nitrogen content, sulphuric acid and oxidation products of cellulose were detected. For this reason, nitrocellulose with a relatively low degree of nitration approaching 12% N or slightly exceeding 12% is particularly easily stabilized.

Smith carried out his experiments by means of the following technique: nitrocotton removed from the nitrating acid was washed in running water until the water was no longer acid. The total acid content (by titrating its acetone solution), and the concentration of sulphuric acid esters were determined in the products. The results are shown in Table 63.

An interesting observation has been made while attempting to purify nitrocotton by dissolving it in acetone followed by precipitation with water. Guncotton (sample 1) was fairly well purified and stabilized by this method, but collodion cotton (sample 4) retained almost the whole amount of acid present in it before purification and it was just as unstable as before, because the sulphuric esters were dissolved and reprecipitated with the nitrocellulose. Incidentally this is convincing chemical evidence confirming the existence of sulphuric acid cellulose esters in lower nitrated cellulose.

Smith also stated that the sulphuric acid content in nitrocotton was dependent of the proportion of H_2SO_4 in the mixed acid. Thus if the sulphuric acid content

TABLE 63

SULPHURIC ACID AND ITS ESTERS IN NITROCELLULOSE (SMITH [14])

No.	Type of nitrocellulose	Nitrogen content %	H_2SO_4 as free acid %	H_2SO_4 as nitrocellulose hydrogen sulphate %
1	Guncotton	13.4	0.69	0.08
2	Pyrocollodion cotton	12.6	0.44	0.16
3	High-viscosity collodion cotton	12.1	0.17	0.30
4	Low-viscosity collodion cotton	10.7	0.00	0.52

of the nitrating mixtures was increased from 18 up to 64%, the product of 13.4% N included from 0.16 to 0.68% of sulphuric acid.

Similar observations were also published earlier by Tribot and Marsaudon [16]. Recently, however, Lhoste [17] has questioned the validity of the hypothesis of the formation of sulphuric acid esters during the nitration of cellulose. On the basis of analytical data the author has arrived at the idea that sulphuric acid is bound with nitrocellulose solely by occlusion. He found no evidence to confirm the existence of cellulose sulphates in nitrocotton.

The values reported by Lhoste comparing the total amount of sulphuric acid with the amount of sulphuric acid bound in nitrocellulose before stabilization, and then at the time of stabilization boiling in distilled water, are collected in Table 64.

TABLE 64

CONTENT OF SULPHURIC ACID IN NITROCELLULOSE (IN % OF THE H_2SO_4) (AFTER LHOSTE [17])

Nitrogen content %	Sulphuric acid	Stabilization boiling, hr						
		0	5	10	25	50	100	200
13.40	Total	0.753	0.332	0.270	0.143	0.110	0.054	0.020
	Free	0.760	0.279	0.251	0.120	0.080	0.077	0.039
12.52	Total	0.517	0.047	0.040				
	Free	0.481	0.056	0.034				
11.24	Total	0.401	0.019					
	Free	0.385	0.028					

The analytical results for total and free sulphuric acid figures do not differ within the limits of experimental error.

It follows from these figures that practically all the sulphuric acid is bonded.

Lhoste has also drawn attention to the fact that the rate of removal of sulphuric acid from nitrocellulose depends on its nitrogen content. The more highly nitrated the nitrocotton, the more slowly sulphuric acid is eliminated from it. Thus in the instance of nitrocellulose of 13.40% N, a 100 hours' boiling is necessary to attain the same sulphuric acid content as that of nitrocellulose with 12.19% N-content boiled for 10 hr.

Lhoste's views are rather unexpected for they are contrary to those of most of the other authors and particularly of A. C. Smith (p. 295).

Certain differences in numerical data reported in various publications can be justified to some extent by differences in the analytical methods used. On the other hand, the values given by Lhoste seem to show that the sulphuric acid in nitrocotton could be combined with nitrocellulose molecules less firmly than in an ester group. For instance, it is not out of the question that sulphuric acid may be bound with nitrocellulose as an inclusion (clathrate) compound. (Attention was also drawn to this point by Miles [15] in his monograph on cellulose nitrate.)

The content of sulphuric acid may also depend on the type of cellulose nitrated, according to Gagnon, Keirstead and Newbold [18].

Research into the course of partial nitrocellulose denitration occurring during stabilization boiling has provided material for a further inquiry into the question of removing both sulphuric acid, and sulpho groups contained in nitrocotton during the stabilization process.

This problem was first investigated by Vieille [19]. Later Chédin and Tribot [20] made a detailed study of the composition of the acids that passed into the water while nitrocellulose was boiled for long periods. Nitrocotton of 13.2% N was prepared by means of the usual mixed acid containing 22% of nitric acid. The results of the experiments are illustrated in Fig. 111. Up to 90 hr the concentration of both of acids in water increased rapidly. Thereafter it slowed down. The increase of nitric acid concentration in the water became less marked while the amount of sulphuric acid no longer increased. The ordinates between *I* and reference line *III* indicate the evolution of nitric acid which is constant (*ca.* 2.48) at any time of the second stage of the hydrolysis. The loss of nitric acid during 90 hr was 2.80% corresponding to a 0.62% nitrogen loss by the nitrocellulose. Such a strongly marked denitration demonstrates the difficulties of manufacturing high-nitrated nitrocellulose by the usual methods, even if the product obtained immediately after the nitration has a nitrogen content approaching that of cellulose trinitrate [15].

In order to explain the limited stability of not fully purified nitrocotton a theory has been developed that at the time of esterifying cellulose hypothetic nitrous acid esters are formed alongside nitric esters under the influence of nitrogen dioxide, present in the nitrating acid. This suggestion was apparently confirmed by Nicolardot and Chertier [21] who assumed they had prepared cellulose nitrites as they treated a suspension of cellulose in dilute nitric acid by means of nitrous acid. Cellulose nitrites were separated from the nitrates by dissolving the latter in acetone. These cellulose nitrites were described by the authors as a grey, hygroscopic powder, containing about 2.5% of nitrogen, immiscible with water and organic

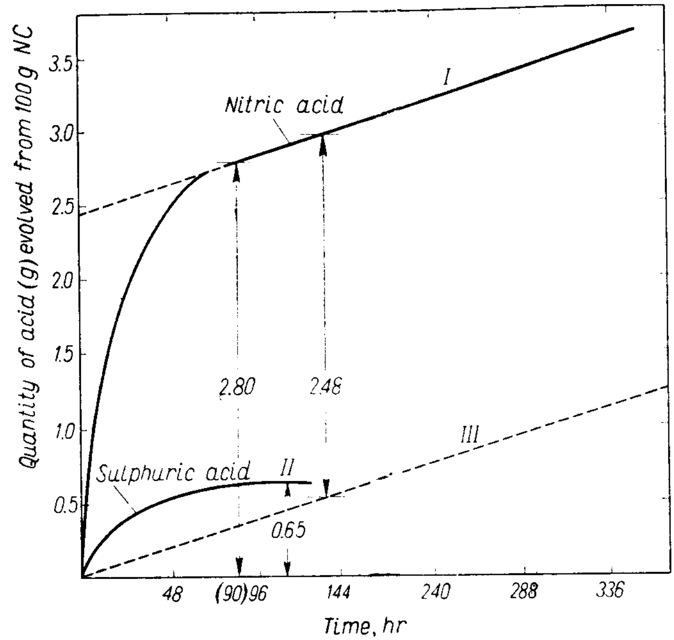


FIG. 111. Production of acids by boiling guncotton (13.2% N), according to Chédin and Tribot [20] and Miles [15].

solvents. There is some doubt however, whether the substance was not composed of cellulose oxidation and nitration products.

Furthermore, certain nitrocellulose degradation products, for example organic acids, exert an adverse influence on the stability of nitrocellulose. That the stability of nitrocellulose is raised by washing it with an alcohol can be quoted in support of this view. Thus as a quick laboratory stabilization method boiling nitrocotton with methyl alcohol (Tomonari [22]) or with ethyl alcohol (Muraour [23]) is recommended. In accordance with the investigations of Hess, Trogus and Tomonari [8] already cited, methyl alcohol is capable of removing not only the degradation products, but also mixed esters of sulphuric and nitric acids.

Following the changes in the properties of nitrocellulose during stabilization boiling, Will [24] has come to the conclusion that the higher the nitrogen content, the longer stabilization boiling is necessary. Thus for every nitration degree the substance should be boiled for a certain, determined interval of time in hours. According to Will a well stabilized nitrocotton can be recognized by the fact that on heating at 134.5°C in a stream of carbon dioxide, it breaks down to produce nitrogen at a steady rate:

$$\frac{\Delta n}{\Delta t} = \text{const.}$$

where Δn = the amount of nitrogen lost by the nitrocellulose at time Δt.

Insufficiently purified, non-stabilized nitrocotton demonstrates a variable value of $\Delta n/\Delta t$. The evolution of nitrogen as a function of time is illustrated in the diagram (Fig. 112). The curves *I–IV* relate to nitrocellulose of a high nitrogen content (13% N) boiled in water for different periods from 30 to 100 hr. The longer the time of boiling, the more the curve approaches a straight-line. Finally, after 100 hr a straight line is attained. Will therefore assumed that in order to stabilize such nitrocellulose at least 100 hr boiling is needed.

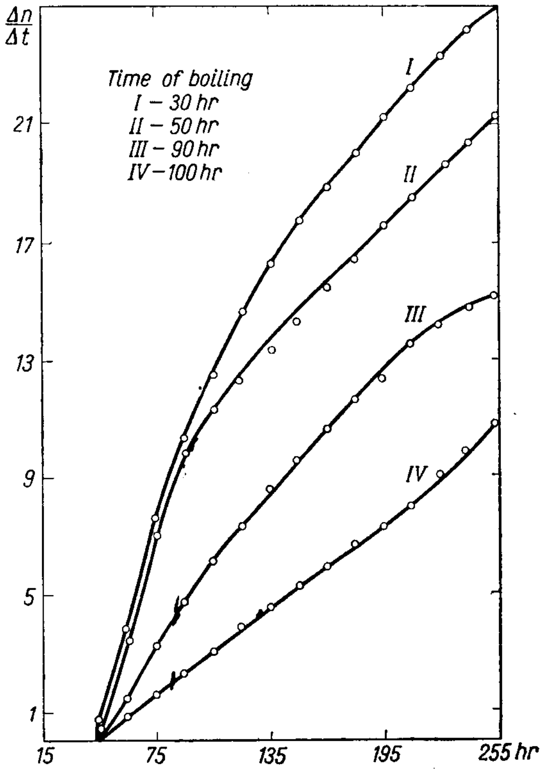


FIG. 112. Decomposition of nitrocellulose of different stability at 134.5°C, according to Will [24].

On the basis of his results already quoted, Goujon [10] also concluded that there exists a threshold stability of nitrocotton that can be achieved by sufficiently prolonged stabilization boiling. Using the Taliani test Goujon determined the pressure of the gases evolved on keeping nitrocellulose at the temperature of 135°C. He found the time necessary to attain the threshold stability to be nearly twice as long as that indicated by Will. Thus in the instance of guncotton No. 1, i.e. nitrocellulose of 13.3% N, Will considers 120-hours' boiling is indispensible, whereas Goujon recommends 240 hr. In the case of guncotton No. 2. with a nitrogen content of 12.0%, Goujon considers 24-hours' boiling followed by washing with water containing calcium carbonate, to be long enough.

When the threshold stability has been attained, further boiling does not improve the nitrocellulose any more and the gradient $\Delta n/\Delta t$ at any temperature is dependent on the nitrogen value of the nitrocellulose (Fig. 113).

The stabilization time may be considerably shortened if the product is boiled in water under pressure. Data from Goujon's paper reported below show to what extent the time of boiling was shortened by using autoclaves for the stabilization of high-nitrated cotton (CP_1, p. 373). Boiling at 100°C for 120 hr is equivalent to a boiling:

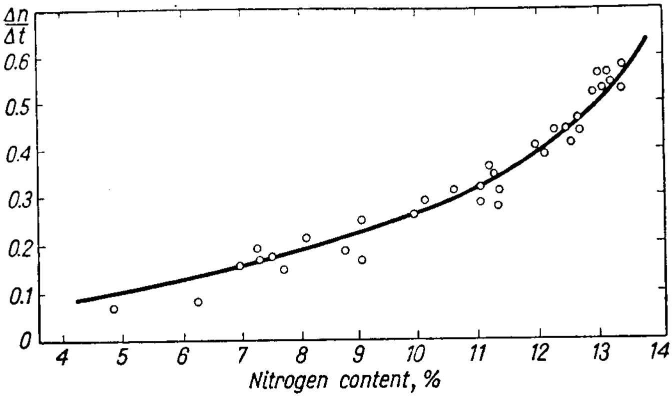


FIG. 113. Rate of decomposition of nitrocellulose (Δ_n/Δ_t) as a function of nitrogen content (Will [24]).

at 110°C for 30 hr
at 120°C for 16 hr
at 130°C for 6 hr

In practice the following principle of stabilization boiling is generally accepted. First prolonged boiling is carried out without changing the water. The water becomes more and more acid due to the acid substances released by the product. This fundamental stabilizing operation should be prolonged as long as possible. According to Goujon, for guncotton No. 2 (CP_2) it should last 15–20 hr, for guncotton No. 1 (CP_1) 72–96 hr, whereas for very high-nitrated guncotton 120–192 hr are necessary. The water is then filtered off, the nitrocotton may be rinsed, and then boiled again for a short time. Finally the fibres are pulped and given an alkaline boiling or washing in the presence of calcium carbonate.

In more up to date processes nitrocellulose a boiling under atmospheric pressure is first given and then heated for a short time in an autoclave, under pressure, at a temperature of 140°C. This results in an appreciable saving in the total time required for stabilization. Stabilization by acting with readily absorbed substances [97] and in solvents (p. 392) was also reported.

Hess *et al.* [25, 8] carried out X-ray investigations of nitrocellulose during the stabilization process. In the X-ray diagrams of the nitrocotton fibres immediately after nitration, almost no interference rings were visible. They appear only after acid is removed by thorough washing. As the result of prolonged stabilization in 50% acetic acid, or of boiling the substance in methyl or ethyl alcohol, sharp diagrams are obtained (Fig. 87, p. 241).

Since on stabilization the outlines of interference rings became more distinctive, new rings became visible, while simultaneously ones formerly perceptible disappeared, the authors suggested that owing to chemical processes during stabilization, nitrocellulose undergoes a certain transformation in crystalline structure. Further the changes in the X-ray diagrams also depend on the composition of the mixed acid. Thus if mixed acid poor in water is used to yield a product with a nitrogen content of about 14%, a substance giving the X-ray diagram characteristic of cellulose trinitrate is formed immediately on nitration with a mixture containing a large proportion of nitric acid. When nitration is carried out with an HNO_3 concentration between 18 and 46%, the change in the X-ray diagram mentioned above takes place during stabilization of the product.

Ropuszyński [26] recently reported that the action of a magnetic field during the boiling of nitrocellulose in water produces a beneficial effect on the stability of nitrocellulose.

For example, nitrocellulose of 13.0% N made from wood cellulose, boiled for 74 hr, was compared with a product subjected to the same treatment in conjunction with the action of a strong magnetic field.

The results of pH measurement of samples heated at 120°C were:

	pH after 2 hr	after 4 hr
nitrocellulose boiled, initial pH = 6.95	3.36	2.78
nitrocellulose subjected to the action of magnetic field and boiled, initial pH = 6.95	4.61	3.21

In spite of the most extensive investigations into the stabilization of nitrocotton, the essence of the process has not yet been made clear. It seems that the removal of unstable products present in the nitrocotton alone cannot explain sufficiently clearly the stabilization of nitrocellulose by stabilization boiling. It has also been suggested that cellulose nitrate directly after nitration has an unstable chemical structure, e.g. a peroxy structure. It was assumed that this structure proceeds to a stable system during boiling. As indicated by the X-ray investigations of nitrocotton at different stabilization stages, mentioned above, at the time of the stabilizing boil a change in the microcrystalline structure of the compound takes place. This structural change may well exert an influence upon the stability of the nitrocellulose.

COMPLEX COMPOUNDS

Apard [27] found that the addition of finely powdered plumbous oxide, calcium oxide or calcium hydroxide to a 1% nitrocellulose solution in acetone, ether–alcohol or amyl acetate initially brought about an increase of the viscosity. Further addition of these substances caused the nitrocellulose to coagulate, together with the added metals. Apard therefore considered that nitrocotton formed complex compounds with these oxides.

Rogovin and Shlakhover [28] report that nitrocellulose produces a complex compound with calcium hydroxide. If coagulation does not take place, then an increase in viscosity is observed in the presence of calcium hydroxide (Glikman [29]).

It has likewise been shown by Morozov [30] that it is possible to coagulate nitrocellulose under the influence of boric acid, in the presence of the following metal oxides: Mn, Fe, Ni, Cu, and Zn. This author noticed that the nitrocotton gel formed owing to the influence of the oxides redissolved in the course of time, probably as a result of a change in chemical composition. On the other hand, the precipitate obtained by treating nitrocellulose with plumbous oxide or aluminium oxide is insoluble. Papkov and Khveleva [31] have established that a similar coagulation takes place under the influence of such salts as: zinc sulphate, magnesium chloride and aluminium chloride.

It has long been known that nitrocotton may be precipitated from solution in the form of a gel on the addition of a metallic powder, e.g. copper, aluminium. Jenkins [32] examined the activity of different metals as coagulating agents, and found lead to be the strongest, and zinc the weakest coagulating agent. The metallic powders studied have been ranged with respect to this property to form a series as follows:

$$\mathrm{Pb} > \mathrm{Ca} > \mathrm{Ag} > \mathrm{Sn} > \mathrm{Fe} > \mathrm{Cu} > \mathrm{Zn}$$

The addition of different organic acids weakens the effect or prevents it altogether. The strongest anticoagulating activity is that of maleic acid.

Gloor and Spurlin [33] are of the opinion that compounds are formed between the nitrocellulose and the powdered metal by means of the secondary valencies. They have demonstrated that the higher the molecular weight of the nitrocotton, the smaller the quantity of metal powder necessary to cause the gel to coagulate.

It was further observed by Pamfilov, Shikher and Shikher [34] that the less the nitrocellulose had been stabilized the quicker the precipitation of gel. On this basis it was assumed that traces of acids accelerate the coagulation process. According to Vodiakov [35] the quantity of metal or metal oxide combined or absorbed in the gelatinized nitrocellulose is approximately proportional to its nitrogen content.

A hypothesis has been published by de Waele [36] that nitrocotton combines with metallic oxides (pigments) through the carboxylic groups. The latter are present in partially oxidized derivatives of cellulose that accompany nitrocellulose. More recently Campbell and Johnson [37] have come to conclusions similar to those of Vodiakov and of de Waele.

Taking into consideration the nature of the complex compounds between nitrocotton and metals or metal oxides, Miles [15] suggested that they approach in chemical character the cuprammonium complexes of cellulose.

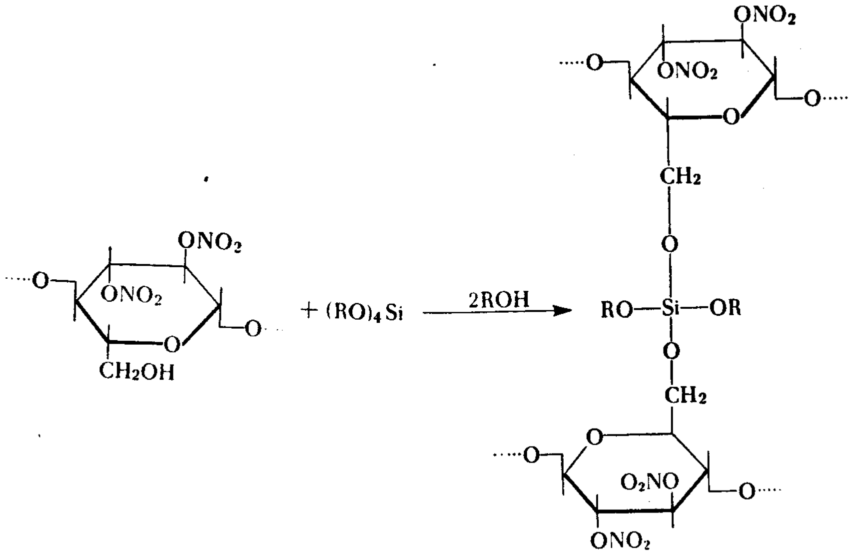
CROSS-LINKING

(INCREASING THE VISCOSITY BY MEANS OF CROSS-LINKING)

There exist instances where an increase in the viscosity of nitrocellulose solutions is recommended as in the product intended for manufacture of blasting gelatine, i.e. for the solution of nitrocellulose nitroglycerine. The solution must have the consistency of firm gelatine.

Jullander [38] has proposed reacting nitrocellulose 12.2% of N with inorganic acid polychlorides such as $SiCl_4$, PCl_5, $POCl_3$, or with chlorides of dicarboxylic acids, e.g. oxalyl chloride. T. Urbański and G. K. Jones [39] used thionyl chloride for the same purpose and Bouchez [94] sebacyl chloride. There is no doubt that these substances react with free hydroxylic groups to form cross-linkages. These methods do not appear to be of practical value, since during the reaction hydrogen chloride is evolved and in order to remove this acid the nitrocotton would have to be stabilized again. Besides, there exists the undesirable possibility of producing with great ease a substance so thoroughly cross-linked that it is insoluble in organic solvents. The processes also appear to be rather expensive as large enough quantities of cross-linking agents are required.

Another interesting cross-linking was obtained by Kreshkov, Guretskii and Andryanov [39a]. They reacted tetra-alkoxysilanes with nitrocellulose to obtain a reaction with free OH groups.



The product is highly resistant towards acids. It possesses high thermal resistance and good dielectric properties.

More important from the practical point of view is the discovery of Fordham, W. H. Marshall and Browne [40] that dihydroxydimethyl urea, commonly known under the name of dimethylol urea, and also its ethers, were suitable agents for producing cross-linkages. The action of those substances is very slow, however. Thus the addition of about 0.1% of dihydroxydimethyl urea dibutyl ether to a low-viscosity solution of nitrocellulose in nitroglycerine produces the desired viscosity increase only after a week if kept at 60°C (Fordham and Browne [41]).

Among other substances capable of cross-linking di-isocyanates, e.g. hexamethylene di-isocyanate, $OCN-(CH_2)_6-NCO$, should be mentioned. It also reacts with free HO groups to form carbamic esters.

HYDROLYSIS AND DENITRATION

The general aspect of the problem of hydrolysis has been discussed already (p. 7). Here some particular points on hydrolysis of nitrocellulose will be briefly described.

Nitrocellulose, treated with different hydrolysing agents such as aqueous solutions of alkalis, does not yield cellulose and the corresponding metal nitrate, but a range of highly variable decomposition products of cellulose as well as of inorganic substances.

Different authors have isolated definite compounds from the products of alkaline hydrolysis of nitrocotton. Wolfrom *et al.* [42] enumerate the compounds that are produced by hydrolysis of nitrocellulose in the presence of acids and bases:

inorganic nitrates and nitrites,
cyanides,
oxides of nitrogen (N_2O, NO, NO_2),
oxides of carbon (CO, CO_2),
ammonia,
organic acids: oxalic, malic, formic, glycolic, butyric, malonic, tartaric, trihydroxyglutaric, dihydroxybutyric, hydroxypyruvic, saccharic, tartronic.

Most of these products have been detected by the earliest investigators of nitrocellulose, such as Vohl [43], Béchamp [44], Hadow [45], Will [46] and M. Berthelot [47].

In the presence of solid sodium hydroxide the reaction can proceed so quickly and violently that it can bring about ignition of the nitrocotton.

The most extensive quantitative examination of the alkaline decomposition of nitrocellulose has been carried out by Kenyon and Gray [48].

Nitrocellulose can undergo hydrolysis by moisture at temperatures above room temperature, or even at room temperature as discussed in more detail below in the chapter on the decomposition of nitrocotton.

Nitrocellulose dissolves in concentrated sulphuric acid, at the same time decomposing slowly, losing nitric acid to form a sulphuric ester.

In concentrated nitric acid, sp. gr. 1.52, it dissolves on warming (80 to 90°C). As the result of the prolonged action of more dilute nitric acid, specific gravity 1.41, a partial denitration and formation of oxycellulose occurs.

In order to achieve complete hydrolysis of nitrocotton, and to recover cellulose as unimpaired as possible, nitrocellulose is subjected to the action of sodium or ammonium hydrosulphide according to the equation:

$$C_6H_8O_3(ONO_2)_2 + 2NaHS \longrightarrow C_6H_{10}O_5 + 2NaNO_2 + 2S$$

$$2NaHS + 2S \longrightarrow Na_2S_3 + H_2S$$

The nitrate groups are removed and reduced to sodium nitrite. The reaction is of the first order.

This method of denitrating cellulose nitrate was widely used industrially to regenerate cellulose from the first (nitrocellulose) artificial fibre (Chardonnet [49]).

Rassow and Dörr [50] examined the influence of different denitrating agents and concluded that a denitration performed with the aid of KHS or NH_4HS proceeded more rapidly in an alcoholic solution that in an aqueous one. According to these investigators the denitration is never complete, some nitrate groups remaining unchanged. These may be detected by treating the substance with diphenylamine dissolved in concentrated sulphuric acid. A blue colour demonstrates that owing to the presence of nitrate groups nitric acid and nitrogen oxides are evolved under the influence of sulphuric acid.

To explain the mechanism of denitrating nitrocotton by means of hydrosulphides the reactions (17) and (18) have been proposed by Nadai [51] (see p. 9). The reaction was also studied by Merrow, Cristol and Van Dolah [52] (see p. 9, reactions (15) and (16)).

During the reduction, nitrite ions and polysulphides are produced. The hydrolysis reaction (17) is rather slow, if performed in a medium of alkaline hydroxides alone. It can proceed considerably more rapidly if carried out in the presence of HS ions (18).

According to a statement of Oldham [53] nitrocellulose can be denitrated by reduction with iron or an iron–zinc mixture in an acetic acid solution.

It has been demonstrated by the work of numerous investigations that regenerated cellulose may contain 0.5–2.0% of nitrogen. Yield of the denitration reaction amounts to 90–96%.

During denitration cellulose is also degraded to some extent. This is probably the result of oxidation–reduction processes. Rogovin and Shlakhover [54] and Staudinger *et al.* [55] have established the average length of a regenerated cellulose chain-molecule to be appreciably shorter than the length of a nitrocellulose chain.

Cellulose trinitrate, 13.8% N, undergoes rapid denitration at room temperature when treated with dry pyridine. Segall and Purves [55a] have stated that in the presence of hydroxylamine the course of the reaction is changed: one molecule of N_2 is produced and a highly polymerized fibre-like dinitrate with a number of nitro groups 1.7 is formed. During this reaction denitration without degradation takes place.

The dinitrate produced is characterized by its solubility in organic solvents as well as by a relatively high resistance to alkalis. The NO_2 groups of this compound are attached in the positions 3 and 6. This has been determined by the following series of reactions:

$$\text{Dinitrate} \xrightarrow[\text{NaOH } 30\%]{(CH_3)_2SO_4} \text{Mono-O-methylcellulose dinitrate} \xrightarrow[NH_4HS]{\text{denitration}}$$

$$\longrightarrow \text{Mono-O-methylcellulose} \xrightarrow[5°C(16 \text{ hr})]{H_2SO_4\ 72\%} \text{2-O-methylglucose} \qquad (5)$$

Hence the O-substituents (NO_2 groups) are placed in positions 3 and 6, so that the substance is a 3,6-cellulose dinitrate.

Nitrocellulose with a nitrogen content of 13.0 up to 13.9% has been reduced by Soffer, Parrotta and di Domenico [56] by means of lithium-aluminium hydride in a tetrahydrofuran medium. A yield 90–95% of considerably degraded cellulose was obtained.

X-Ray investigations on regenerated cellulose have shown that its structure approximates to the constitution of hydrated cellulose, i.e. mercerized cotton.

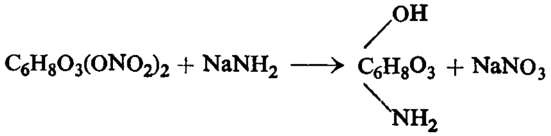
An interesting chemical exchange process occurs when nitrocellulose is boiled with sodium iodide: the primary nitrate groups ($-CH_2ONO_2$) are substituted by iodomethyl groups ($-CH_2I$). On treating high-nitrated cellulose (13.2% N) oxidation processes accompany this reaction, but these side reactions do not occur with low-nitrated cellulose. Murray and Purves [57] have studied these chemical reactions using nitrocellulose containing 2.5–9% N and established that at least half the O-nitro groups are bonded to primary alcoholic groups.

OTHER REACTIONS

Among other characteristic reactions of nitrocellulose worthy of notice is the transesterification of cellulose nitrate performed by means of acetic anhydride. In this way cellulose mononitro-diacetate was obtained (Berl and Smith [58]).

Clément and Rivière [59] also reported that cellulose acetate or a mixed ester — a nitrate–acetate — can be obtained by reacting cellulose nitrate with acetic anhydride, acetic acid, and sulphuric acid. According to more recent contributions, e.g. Wolfrom, Bower and Maker [60], the reaction should be performed as follows: Cellulose nitrate is dissolved in the cold in a little sulphuric acid and acetic anhydride, the surplus of acetic anhydride is then hydrolysed also in the cold, and cellulose acetate is extracted with a suitable solvent, such as chloroform. Other methods of acetylating nitrocellulose consist in reduction, for instance with zinc and hydrogen chloride, which entails denitration of the ester, followed by acetylation with acetic anhydride. All these reactions are carried out in the same vessel. Further, it is possible to synthesize mixed esters, cellulose nitrate–acetates, by subjecting cellulose to the action of a mixture that includes nitric acid, acetic acid and acetic anhydride in the presence of sulphuric acid (Krüger [61]). The use of a large amount of nitric acid favours the formation of nitrocellulose only. Mixed esters are formed when the concentration of nitric acid in the mixed acid is low. Danilov *et al.* [62] have reached a similar conclusion.

Amination of cellulose is a relatively new reaction (Scherer and Feildt [63]). It occurs if nitrocellulose in liquid ammonia is exposed to the action of sodium or potassium amide, according to the equation:



$$C_6H_8O_3(ONO_2)_2 + NaNH_2 \longrightarrow C_6H_8O_3\begin{matrix}\diagup OH\\ \diagdown NH_2\end{matrix} + NaNO_3 \qquad (6)$$

Only half the nitrate groups present in cellulose dinitrate is substituted by amine groups, the other half undergoing hydrolysis.

Aminocellulose is a reddish-yellow hygroscopic powder that dissolves readily in water. It can be diazotized and coupled with phenols to yield reddish dyes.

However, aminocellulose should be considered as a derivative of highly degraded cellulose, and could hardly be called a cellulose derivative.

The same objection should be raised to aminocellulose acetylide of Scherer and Saul [64].

DECOMPOSITION OF NITROCELLULOSE

Early experiments (1861–67) devoted to the decomposition of nitrocellulose were carried out by de Luca [2], who was the first to perceive that the decomposition rate of unstable guncotton increased more rapidly in moist air. He also found that decomposition was accelerated under the influence of the sunshine. Unstable guncotton stored in a dark room and at a low temperature, decomposed more slowly.

According to the classical work of Abel [3] the instability of nitrocotton samples is caused not so much by the tendency of nitrocellulose to decompose, as by the presence of certain impurities. Abel showed that the purest nitrocellulose was so resistant to decomposition by heating that it could withstand the action of a temperature between 65 and 100°C even for several months. He also demonstrated that low-nitrated cellulose added to guncotton does not exert an adverse effect on the latter's stability and its capacity to withstand the heat test.

Vieille [65] supposed a lower nitrated cellulose to be less stable than a higher nitrated one. This suggestion arose from considering the behaviour of differently nitrated cellulose towards hydrochloric acid. According to Vieille a low-nitrated cellulose is attacked by hydrochloric acid even in the cold, collodion cotton undergoes decomposition by hydrochloric acid only on boiling, whilst prolonged boiling is necessary to remove all the nitrogen from a guncotton containing 13% of nitrogen, and to convert it into nitrogen oxides.

The phenomenon described by Vieille seems to have no direct connection with the chemical stability of nitrocellulose, in the usual sense of this term, meaning the capacity of a substance to endure long storage, but appears to be limited to the capacity of being hydrolysed under exactly determined conditions, i.e. in hydrochloric acid. However, under these conditions cellulose itself does not manifest any chemical stability: it is readily dissolved in hydrochloric acid, being simultaneously hydrolysed to yield glucose. In respect of this property, an incompletely nitrated cellulose differs from cellulose less than a high nitrated product, hence it also retains a high sensitivity to the hydrolytic action of hydrochloric acid.

If the temperature of nitrocellulose is raised steadily, e.g. at the rate of 5°C/min, an explosive decomposition takes place at a temperature of 180–185°C. With a lower rate of heating the temperature of decomposition is lower: about 165°C.

The decomposition reaction of cellulose nitrate brought about by heating is an autocatalytic process. According to the investigations of Will (p. 299) completely pure nitrocellulose undergoes decomposition at a constant rate, if the decomposition products are removed, otherwise the reaction accelerates owing to the activity of acid products ($N_2O_4+H_2O$). Below the temperature of initiation decomposition is relatively slow. In the case of well stabilized nitrocotton it ceases at room temperature or a slightly higher one (30–35°C). An insufficiently stabilized nitrocellulose, that contains unstable cellulose esters or traces of acids, can decompose at normal storage temperature, finally producing an explosive decomposition in the same way as that resulting from heating.

From experiments on the decomposition of nitrocotton (13.1% N) within the temperature range 126.5–157°C, Will formulated an equation from which the decomposition of nitrocellulose can be estimated:

$$\log_{10} N = a+b\times 0.9932 t$$

where: N — milligrams of nitrogen evolved from 2.5 g of nitrocellulose in period of 15 min, t — temperature (°C), a, b — coefficients: $a = 8.84$, $b = -22.86$.

Miles [15] has applied the Arrhenius equation to the numerical data of Will and calculated the following values:

activation energy $E = 46.2$ kcal/mole
the constant $\log_{10}B = 24.68$

It is noteworthy that in more recent studies on nitrocellulose decomposition (Wilfong, Penner, Daniels [66]) similar results and values for the activation energy have been obtained, namely $E = 46.67$ kcal/mole in the temperature range 84 to 162°C. R. D. Smith [67] has examined the thermal decomposition of nitrocotton of 11.8% N in such high-boiling substances as chlorodinitrobenzene, nitronaphthalene, benzophenone, within the temperature range 165–200°C and determined the values:

$$E = 43.0 \text{ kcal/mole}, \log_{10}B = 18.0$$

Will and other contemporary workers assumed that nitrogen evolved during the thermal decomposition of nitrocotton occurred chiefly as nitrogen oxide. On the contrary nitrogen dioxide is produced in relatively inappreciable quantities. R. Robertson and Napper [68] used Will's apparatus to decompose nitrocotton in an atmosphere of carbon dioxide. They examined the decomposition products spectrographically and established that over 50% of the nitrogen evolved from nitrocellulose is produced in the form of nitrogen dioxide.

The proportion of nitrogen dioxide among the decomposition products varies according to the experimental conditions. Thus on maintaining a temperature of 135°C for 60 hr the nitrogen content was decreased from 13 to 8.7% N. The evolution of nitrogen was more or less constant at *ca.* 0.72 mg per hour per 1 g of nitrocellulose. At the beginning nitrogen dioxide represented as much as 54% of the total quantity of nitrogen, while near the end it was scarcely 8%.

In view of those experiments some results reported by later authors who did not find NO_2 among the thermal decomposition products of nitrocellulose should be subjected to revision. There is in fact, a serious controversy concerning this question as shown in the following paragraphs.

Koehler and Marqueyrol [69] investigated the products of nitrocellulose decomposed under pressure. The decomposition products were removed in order to avoid the possibility of starting side reactions and to preclude any catalytic action by the decomposition products on the nitrocellulose. It has been stated that the composition of the gases evolved during decomposition is almost independent of the temperature and this is compatible with the data reported by Robertson. However, the composition of the products differs from that found by Robertson. These are as follows (omitting the water formed):

NO	62.0%
CO_2	20.0%
CO	8.5%
N_2O	3.8%
N_2	6.0%

According to Goujon [10] heating nitrocotton in a carbon dioxide medium causes the nitrogen to evolve chiefly in the form of NO_2 and NO. In addition some N_2 and N_2O are produced. Hydrogen is evolved mainly as H_2O, carbon as CO_2 and to a smaller extent as CO. Traces of hydrocarbons are also formed.

If decomposition takes place with access to air, nitrogen oxide is, of course, converted to nitrogen dioxide. A large proportion of the latter is re-absorbed by nitrocellulose and hastens its decomposition, particularly in the presence of moisture, as it reacts as nitrous and nitric acids.

The researches of A. Sapozhnikov and Borisov [70] and of A. Sapozhnikov and Yagellovich [71] were devoted to a study of the evolution of gases during thermal decomposition of guncotton in air. As shown in the graph (Fig. 114) the quantity of gaseous products evolved is dependent on the temperature of heating.

The loss of weight and the volume of gases evolved from 1 g of guncotton are listed in Table 65.

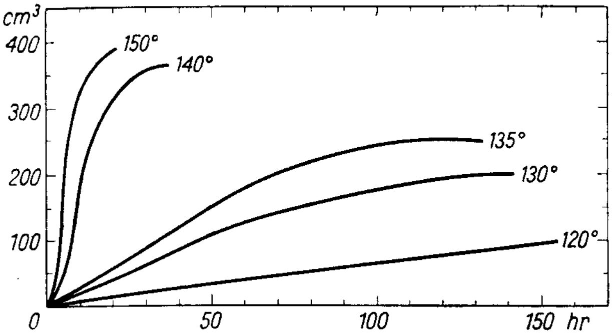


FIG. 114. Gas evolution from nitrocellulose at different temperatures (Sapozhnikov *et al.* [70]).

TABLE 65

THE EFFECT OF HEATING ON NITROCELLULOSE DECOMPOSITION

Temperature of heating °C	Time of heating hr	Volume of developed gases cm³	Loss of weight %	Loss of nitrogen %
125	150	162	49.7	64
135	150	236	61.8	83
140	40	310	66.5	91
150	20	325	70.2	98

On the basis of gas analyses the following gaseous decomposition products were calculated by Sapozhnikov and Borisov:

for a temperature of 125°C:

$$C_{24}H_{29}O_9(NO_3)_{11} \longrightarrow 2.5CO_2 + 1.60CO + 1.98NO + 2.52N_2 + 14.5H_2O \quad (7)$$

for a temperature of 135°C:

$$C_{24}H_{29}O_9(NO_3)_{11} \longrightarrow 5.03CO_2 + 2.10CO + 2.93NO + 3.04N_2 + 14.2H_2O \quad (8)$$

for a temperature of 140°C:

$$C_{24}H_{29}O_9(NO_3)_{11} \longrightarrow 6.22CO_2 + 3.20CO + 5.18NO + 2.70N_2 + 9.6H_2O \quad (9)$$

for a temperature of 150°C:

$$C_{24}H_{29}O_9(NO_3)_{11} \longrightarrow 6.27CO_2 + 3.58CO + 5.37NO + 2.70N_2 + 8.0H_2O \quad (10)$$

Hence at higher temperatures nitrogen is removed from the nitrocellulose almost completely.

Vandoni [72] has reported that at 108.5°C guncotton nitrogen is evolved into the atmosphere mainly as nitrous oxide. He has determined the percentage proportion of nitrogen compounds in the decomposition products as follows:

NO	1.89%
N_2O	13.79%
N_2	9.03%

plus: 63.61% of CO_2, 10.16% of CO, 1.52% of CH_4.

Vandoni has also examined the decomposition produced by treatment with water at 130°C of high-nitrated guncotton, 14% N, and the decomposition products of nitrocellulose of 12% N evolved when treated at 50°C with dilute (25% HNO_3) nitric acid.

The composition of the gases in both experiments was:

temperature	N_2O	NO	N_2	CO_2	CO	CH_4
130°C	26.57	1.05	3.96	64.43	2.70	1.29
50°C (with HNO_3)	15.39	32.33	5.01	42.13	5.24	0.0

A probable mechanism for the thermal decomposition of nitrocellulose has been suggested by Desmaroux [73] who assumed the occurrence of three types of decomposition reaction:

(1) hydrolysis of ester (—ONO_2) groups;

(2) hydrolysis of linkages between particular glucose units;

(3) intermolecular oxidation of particular anhydroglucose rings, while during the oxidation of one ring the neighbouring units may remain intact.

Desmaroux [73a] followed the decomposition of nitrocotton kept at a temperature of 132°C and established that the reaction types (1) and (3) predominated. Only $\frac{1}{3}$–$\frac{1}{2}$ of the substance broke down by the hydrolysis of ester groups. Desmaroux also determined the loss of weight of the sample so as to compare it with the loss of nitrogen. The weight loss of the nitrocellulose calculated on the basis of the nitrogen lost is 3–12 times smaller than the total weight loss, as seen from the data in Table 66.

TABLE 66

THERMAL DECOMPOSITION OF NITROCELLULOSE (ACCORDING TO DESMAROUX [73a])

Nitrogen content of nitrocellulose %	Sample heated for 24 hr (at 132°C)			Sample heated for 32 hr (at 132°C)		
	P	*N*	*R*	*P*	*N*	*R*
13.38	0.131	12.94	5.4	0.093	12.86	3.3
12.32	0.154	11.77	5.4	0.269	11.61	7.4
12.13	0.254	11.58	8.6	0.372	11.40	10.0
11.71	0.325	11.07	7.9	0.512	10.86	12.2

The symbols used in Tables 66 and 67 indicate:

P — the loss in weight of 1 g of nitrocotton, N — the nitrogen content (in per cent). R — the $P/(N_0—N)$ ratio, where $N_0—N$ is the loss in weight of 1 g substance calculated from the loss of nitrogen.

Lower nitrated types of nitrocotton lose their nitrogen to a smaller degree than higher nitrated types, as would be expected.

In addition to the three main types of reaction involved in nitrocellulose decomposition, the author assumes that secondary reactions also occur originating in the chemical combination between oxides of nitrogen and water vapour to produce nitric and nitrous acids, which in turn react with the nitrocellulose. By heating nitrocotton with dilute nitric acid at 40°C, Desmaroux found in this instance that hydrolytic and oxidation reactions predominate, causing a weight loss of $\frac{1}{2}$–$\frac{1}{4}$ of the total loss (see Table 67).

TABLE 67

THERMAL DECOMPOSITION OF NITROCELLULOSE (ACCORDING TO DESMAROUX [73a])

Nitrogen content of nitrocellulose	HNO_3 %	Sample heated for 24 hr (at 40°C)			Sample heated for 72 hr (at 40°C)		
		P	*N*	*R*	*P*	*N*	*R*
13.38	25	0.012	13.25	1.63	0.014	13.12	0.97
	45	0.058	12.60	1.39			
12.13	25	0.00	11.93	—	0.029	11.72	1.42
	45	0.265	10.09	2.76			

In one of the experiments, a denitration of the nitrocotton without any perceptible loss of weight was observed. This showed that nitrocellulose of low nitrogen content (12.13%), was denitrated with ease, and is in good agreement with Vieille's observation (mentioned above), that lower nitrated nitrocellulose was more easily decomposed when boiled with an acid. Gelernter *et al.* [96] examined the decomposition of nitrocellulose (10.8–11.8% N) labelled with ^{15}N at 157°C and found the secondary ONO_2 groups less stable than those of C_6.

Decomposition of nitrocellulose by light. The effect of sunlight and of ultra-violet light on the viscosity of nitrocellulose solutions has already been discussed (see p. 275). However, the irradiation of nitrocellulose causes not only a decrease in the degree of polymerization but also a decomposition involving denitration. D. Berthelot and Gaudechon [74] followed the effect of irradiating nitrocotton by ultra-violet light, and found among the decomposition products CO, CO_2, N_2 and oxides of nitrogen. A. Kraus [75] reported that nitrocellulose containing 11.74% of nitrogen was denitrated to 10.81% by irradiation for 48 hr.

T. Urbański and Malendowicz [76] have examined the rate of decomposition of nitrocellulose by ultra-violet light. The results showed (T. Urbański [77]) that nitrocellulose of 13.3% N undergoes decomposition expressed by an exponential equation, whereas lower nitrated nitrocotton, 11.9% of N, decomposes approximately in accordance with a linear function. Somewhat discordant results were published by Oguri, Takei and Fujita [78] who reported the fall in nitrogen content of nitrocellulose to be 1.0% N, after 3 hours irradiation, and 1.95% N after 8 hr.

G. G. Jones examined the effect of ultra-violet light of different, selected wave-lengths on nitrocellulose, containing 12.2% N, dissolved in methanol or in ethyl acetate.

Radiation of 253.6 mμ wave-length especially is capable of reducing the viscosity of nitrocellulose solutions. Radiation of 366 mμ wave-length has practically no influence on the viscosity. Nitrogen content was decreased in both cases. With 366 mμ radiation applied under specific experimental conditions, the nitrogen content was reduced after 48 hr from 11.85 to 11.68%.

It is also known that nitrocellulose or nitrocellulose film grows yellow as a result of prolonged exposure to sunshine.

Nitrocellulose (11.8%N) has been decomposed by the action of intense γ-radiation and its microstructure (as shown by X-rays) was entirely disrupted [95].

Other factors. It has been stated many times that some kinds of moulds, e.g. *Aspergillus*, can grow on wet nitrocotton. The first systematic enquiries in this field were made by Bokorny [79]. He found that moulds could grow in a medium comprising an aqueous solution of mineral salts, in which nitrocellulose was suspended. Bokorny suggested that nitrocellulose provided the mould with essential carbon, and perhaps nitrogen. Hence, anxiety was aroused (e.g. Sy [80]) concerning the possibility that denitrifying bacteria might bring about the decomposition of nitrocotton. It was established however by further investigations (Malenković [81], Jacqué [82]), that only the mineral salts dissolved in the water were being utilized by the moulds and by the micro-organisms, which cannot bring about the decomposition of nitrocellulose. However they can produce various organic substances, e.g. acids, which in turn may have an adverse effect on the stability of nitrocellulose and other nitric esters. It has been established that nitrocellulose can be protected against moulds by the addition of a small amount of corrosive sublimate. This technique was used for a time at the beginning of the current century, particularly for nitrocotton exported to tropical countries. Later the method was abandoned for the corrosive sublimate interfered with the heat test with potassium iodide–starch making it difficult to detect inadequate stabilization of the nitrocellulose (the question will be discussed in detail in Vol. III).

EXPLOSIVE PROPERTIES OF NITROCELLULOSE

The equation of decomposition and the physical constants reported by Kast [83] are quoted below. They refer to guncotton of 13.1% N:

$$2\left\{\begin{array}{l} C_{24}H_{29}O_9(ONO_2)_{11} \\ \\ C_{24}H_{30}O_{10}(ONO_2)_{10} \end{array}\right. = 36CO_2 + 47CO + 4CH_4 + 39H_2O + 2C_2H_2 + 3HCN + 3.5H_2 + 18.5N_2 + 2NH_4HCO_3$$

Heat of explosion	1025 kcal/kg
Volume of gases evolved	$V_0 =$ 765 l./kg
Temperature	$t = 3100$°C

The decomposition equation for the same guncotton containing 16% of water, has the following values:

$$2\left\{\begin{array}{l} C_{24}H_{29}O_9(ONO_2)_{11} \\ \\ C_{24}H_{30}O_{20}(ONO_2)_{10} \end{array}\right. + 48H_2O = 41CO_2 + 37CO + 5CH_4 + 63H_2O + C_2H_2 + HCN + $$

$$+ 7.5H_2 + 15.5N_2 + 10NH_4HCO_3 + 875 \text{ kcal/kg}$$

$$V_0 = 720 \text{ l./kg}$$

$$t = 2260°\text{C}$$

Guncotton such as the above, in a dry state, compressed to a density of 1.30 g/cm^3 demonstrated a detonation rate of 6300 m/sec, and an expansion in the lead block of 375 cm^3, while guncotton with 16% of water content detonated with a rate of 6800 m/sec, and produced an expansion in the lead block of 280 cm^3.

Milus [84] investigated the explosive decomposition of nitrocotton with different nitrogen content and obtained experimental data which he used to calculate the values tabulated below (Table 68).

Taking into account earlier experiments, Roux and Sarrau [85] have estimated the heat of explosion of guncotton to be 1056 kcal/kg, a value compatible with those

TABLE 68

EXPLOSIVE DECOMPOSITION OF NITROCELLULOSE (AFTER MILUS [84])

	Nitrogen content of nitrocellulose, %				
	12.62	13.0	13.15	13.2	13.45
Heat of explosion					
cal/g (H_2O liquid)	973	1025	1046	1055	1096
cal/g (H_2O vapour)	865	925	946	955	955
Volume of gases:					
V_0 cm^3/g (H_2O liquid)	900	880	874	868	857
Composition of the gas:					
(H_2O liquid)					
CO_2	21.2	23.8	24.3	24.4	27.0
CO	45.9	43.9	43.7	43.5	41.0
H_2	18.7	17.3	16.7	16.5	16.1
CH_4	0.4	0.4	0.4	0.4	0.3
N_2	13.8	14.6	14.9	15.1	15.6
Temperature of explosion:					
t, °C	2840	3025	3095	3130	3245
Composition of gases calculated for respective temperature of explosion:					
CO_2	10.5	13.9	14.3	14.4	16.0
CO	43.8	40.8	40.5	40.2	38.6
H_2	9.5	9.6	9.2	9.0	7.9
N_2	11.1	11.7	11.9	12.1	12.5
H_2O	25.1	24.0	24.1	24.3	25.0

quoted above. According to Taylor and Hall [86] the heat of explosion for nitrocelluloses containing 12.1–12.3% N varies from 883.5 to 929.5 kcal/kg. The discrepancies are undoubtedly attributable to differences in the conditions of experiments, i.e. by the formation of different explosion products. Taylor and Hall report that the heat of explosion of nitrocotton in calories per gramme (Q) for constant volume and liquid water at 0°C, may be expressed as a linear function of the nitrogen content:

$$Q = 144.9\,N - 850.3$$

The heat of combustion (experimental values) and the heat of formation (calculated) by Tomioka [87] and Lenze *et al.* [88] for nitrocelluloses of different nitrogen content are listed in Table 69.

TABLE 69

HEAT OF COMBUSTION AND HEAT OF FORMATION OF NITROCELLULOSE

Nitrogen content %	Heat of combustion kcal/kg	Heat of formation kcal/kg	Author
7.66	3071	958.9	Tomioka [87]
10.14	2717	804.1	Tomioka [87]
11.06	2612	742.3	Tomioka [87]
12.45	2434	645.2	Tomioka [87]
12.88	2390	616.5	Tomioka [87]
13.53	2236	594	Lenze, Metz and Rubens [88]
13.58	2286	568.7	Tomioka [87]
13.92	2239	513	Lenze, Metz and Rubens [88]
14.12	2208	504	Lenze, Metz and Rubens [88]

Values found for the heat of formation of nitrocellulose by Taylor and Hall are lower than those given in Table 69.

Recently, Jessup and Prosen [89] have examined the heat of combustion of cotton cellulose and wood pulp cellulose, and of their nitrates. The data for di- and trinitrate are higher than those of Taylor and Hall, and approximate to the

TABLE 70

HEAT OF FORMATION OF NITROCELLULOSE (AFTER TAYLOR AND HALL [86])

Nitrogen content %	Number of nitro groups in relation to C_6	Molecular weight of a C_6 unit	Heat of formation	
			$-\Delta H_f$ kcal/mole	kcal/kg
10	1.71	238.8	181.4	759.6
11	1.97	250.6	174.0	694.3
12	2.26	263.8	165.7	628.1
13	2.58	278.3	156.5	562.3
14	2.94	294.6	146.3	496.6

values published by earlier authors (Tomioka [87], Lenze, Metz and Rubens [88]). No essential difference has been found between the values for cotton and wood pulp cellulose.

Jessup and Prosen deduced for nitrocotton an equation that expresses the heat of combustion and the heat of formation as functions of the nitrogen content:

$$-4176.70+14.126\, f' \text{ cal/g of nitrocellulose and}$$

$$-5896.88+21.178\, f' \text{ cal/g of nitrocellulose, respectively,}$$

where f' — the mass of nitrogen in nitrocellulose calculated for the mass of nitrocotton $= 1.0$. The formula is valid for f' values from 0.115 to 0.135

Nitrocellulose is very inflammable. It burns extraordinary readily though without detonating. Explosion can occur on burning large amounts of guncotton particularly in a confined space. The rate of burning depends on the type of guncotton, i.e. on the degree of nitration, the degree of fineness etc. as well as on the moisture content. Dry nitrocellulose is extremely inflammable and very dangerous. A higher fineness reduces the inflammability by increasing the loading density under given pressure. Increase in nitrogen content on the other hand increases the inflammability.

Andreyev [90] has established the linear rate of burning for guncotton and collodion cotton under different pressures:

For guncotton No. 1

density 0.56–0.68 g/cm^3, under pressures (p) of 3–12 kg/cm^2 the rate of burning is defined by the equation

$$U = 0.0907+0.0405p$$

For collodion cotton

density 0.47–0.54 g/cm^3, under pressures in the range 4–30 kg/cm^2

$$U = 0.0710+0.0162\,p$$

According to Andreyev and Polyakov the rate of burning under higher pressures, e.g. over a few kg/cm^2, increases more slowly and follows a nearly straight-line law (Fig. 115).

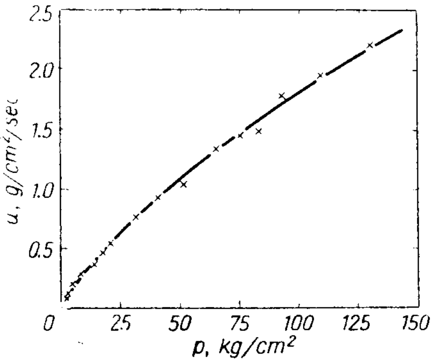


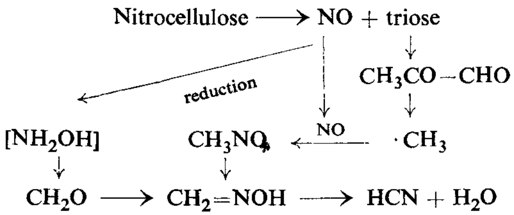
FIG. 115. Rate of burning of nitrocellulose under different pressures according to Andreyev [90].

Experiments on burning nitrocellulose (deflagration and explosion) were carried out in World War II by Rideal and A. J. B. Robertson [91]. One interesting observation they made was that nitrocotton heated for a long time at 200°C under a pressure of 50 mm Hg liquefied shortly before the explosion. Nitrocellulose has been known to melt while being stabilized in an autoclave at an elevated temperature, since it overheats if there is too little water in the autoclave (on melting nitrocellulose, see p. 242).

Recently extensive investigations on burning nitrocellulose under reduced pressures have been carried out by Wolfrom *et al.* [42, 92] who have described their results in a series of papers. Nitrocellulose of 12.6–13.2% N was examined. It was ignited under pressures of 2–3 mm Hg or 200 mm Hg.

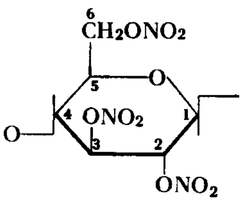
At the lowest pressures investigated, a white fragmented oxycellulose nitrate (9% N) was isolated in good yield (*ca.* 40% by weight). The yield of this material decreased rapidly with increasing pressure, and a liquid mixture containing formic acid, formaldehyde, glyoxal and HCN was obtained. The cyanide ion is detectable immediately following ignition, and disappears soon after, simultaneously with the disappearance of compounds with a carbonyl group, such as formaldehyde and glyoxal. This is probably due to the formation of cyanhydrins which have been found in the decomposition products.

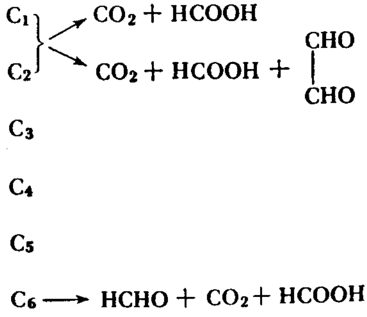
Intermediate formation of a triose (identified as phenylosazone) was also proved by the authors and the following sequence of reactions is suggested:



(11)

In the last paper of Wolfrom, Shafizadeh *et al.* [93] nitrocellulose labelled at C_1 and C_2 with ^{14}C was used for the experiments. This led to the conclusion that C_1 gives mainly CO_2 and lesser amounts of formic acid and glyoxal (the latter from C_1 and C_2) and that the major product from C_6 is formaldehyde with lesser amounts of formic acid and CO_2:





As a safety precaution nitrocellulose intended to be transported should always contain 25–30% of water. Guncotton rich in nitrogen will, however, ignite even if the water content exceeds 40%, but it is difficult to raise the moisture content above 30%, since nitrocellulose is not capable of absorbing more water.

Collodion cotton used industrially for lacquers, celluloid and such like, can be transported after being wetted with ethyl, propyl or butyl alcohol the choice depending on which alcohol is to be used as a component of the solvent for the nitrocellulose in question.

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CHAPTER XII

NITRATION OF CELLULOSE

NITRATION WITH NITRIC ACID

THE first attempts to esterify cellulose by means of nitric acid consisted in treating cellulose with the acid without any dehydrating agents. Vieille [1] discovered in 1882 that on nitration with nitric acid alone the rate of reaction and the nitrogen content of the nitrocellulose increased as the concentration of HNO_3 was increased:

concentration of HNO_3, %:	77.3	80.8	83.5	87.0	89.6	92.1	95.1
% N in nitrocellulose:	6.85	8.07	8.78	10.33	11.53	12.23	12.68

Attempts to obtain nitrocellulose containing more than 12.7% of nitrogen failed. When acid diluted below 77% was used partial dissolution of the product occurred. As an explanation for this, Vieille suggested that the soluble substances represented products which were hydrolysed or oxidized under the influence of the relatively dilute nitric acid. The reactions of hydrolysis and oxidation occur less readily the more concentrated the nitric acid, and the more hydroxyl groups are esterified. It also seems that nitrate groups counteract the side processes (such as oxidation).

A number of authors have shown that esterification can be carried out with nitric acid of over 65% concentration. Sixty five per cent acid, of specific gravity 1.14, yields addition products with cellulose, as obtained by Knecht [2]. After removing the acid retained mechanically Knecht established that the addition compound contained nitric acid corresponding to 7.7% N. This is approximately equivalent to one NO_2 group for every anhydroglucose unit. Drowning the addition product in water causes nitric acid to split off. Knecht thought that it was an exceptionally labile nitrate. Häussermann [3] found it to be a rather unstable addition product. Champetier and Marton [3a] examined the ultra-violet reflexion spectrum of the Knecht compound. They found it contains a band 270–305 mμ which is not present in the spectrum of nitrocellulose. The authors considered that this supports the view that the Knecht compound is an individual substance differing from nitrocellulose.

Cellulose regenerated from the addition compound may demonstrate a certain degree of nitration, say 0.5–2.2% N. The properties of the compound are similar to those of hydrocellulose: glittering fibres, increased hygroscopicity, higher reactivity.

X-Ray investigations by Hess and Katz [4] suggest that the addition product is probably compatible with the formula $C_6H_{10}O_5 \cdot HNO_3$. The X-ray diagram of the compound is a characteristic one differing from that of cellulose. On the basis of their research these workers concluded that the addition compound was produced by the action of 86% nitric acid. According to Trogus [5] it is not out of question, that besides the product of composition mentioned above, another compound is formed consisting of cellulose and nitric acid hydrate: $C_6H_{10}O_5 \cdot HNO_3 \cdot H_2O$ (see below).

Moreover, there is some evidence that the addition compound is also formed as a transient product in the first stage of nitrating cellulose by means of a mixed nitric and sulphuric acid.

According to the experiments of Andress [6] the composition of the "Knecht compound" after being kept under reduced pressure for some time should be denoted by the formula $2C_6H_{10}O_5 \cdot HNO_3$. Andress has demonstrated that the compound produces a characteristic X-ray fibre diagram.

Later, Wilson [7] established that the composition of the compound after drying under a "high vacuum" is:

$$2C_6H_{10}O_5 \cdot HNO_3 \cdot H_2O$$

The product of absorption of nitric acid vapours by cellulose is according to Wilson not a Knecht compound, since it did not give the characteristic X-ray diagram although its chemical composition is approximately that of the Knecht compound.

Trogus [5] collected numerical data (Fig. 116) concerning the concentration of nitric acid to produce Knecht compound (*I*), nitration of cellulose expressed in terms of nitrogen content (% N) (*II*), freezing points of nitric acid–water solutions (*III*), and HNO_3 partial vapour pressure in nitric acid–water solutions (*IV*). The concentrations of HNO_3 in aqueous nitric acid that produce strong swelling or solution (*ca.* 80% HNO_3) of cellulose are also included. The diagram shows which factors play an important part in the formation of the Knecht compound and in the nitration of cellulose. It seems that the Knecht compound is formed when a mixture of almost equivalent quantities of the hydrates $HNO_3 \cdot H_2O$ and $HNO_3 \cdot 3H_2O$ acts on cellulose. The curve of nitration (*II*) follows a similar trend to the curve for the vapour pressure of HNO_3 (*IV*).

Andress and Rheinhardt [9] have discovered that cellulose swells in an aqueous solution of perchloric acid to produce the compound $2C_6H_{10}O_5 \cdot . HClO_4$ which also gives a characteristic X-ray diagram. Miles [8] has suggested that the composition of this substance is:

$$2C_6H_{10}O_5 \cdot HClO_4 \cdot H_2O$$

It is impossible to obtain nitrocellulose containing a high percentage of nitrogen by nitration with nitric acid alone. This is explicable by the fact that every concentration, even the strongest nitric acid, causes the cellulose fibres to swell, and thus hinders the diffusion of acid into the fibre mass. Attempts to nitrate cellulose by means of a mixture consisting of nitric acid and sulphuric acid have demon-

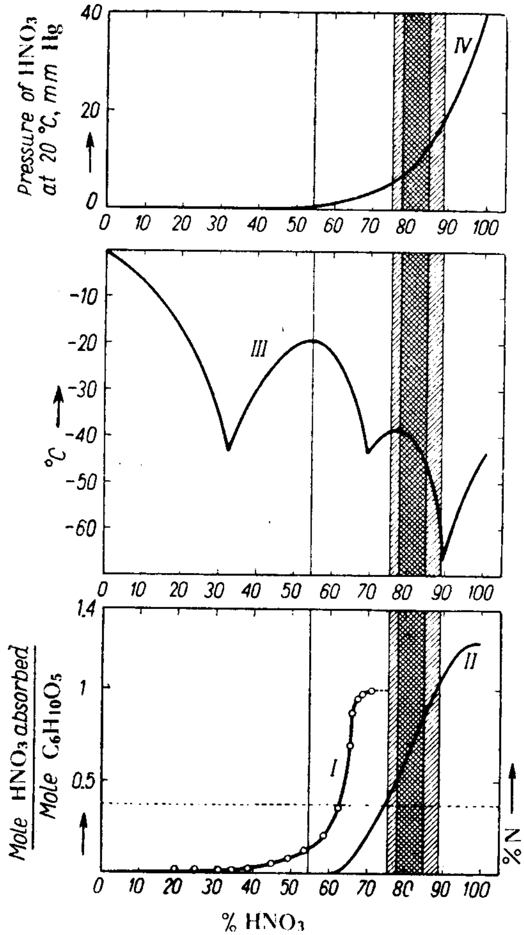


FIG. 116. Diagram by Trogus [5]: *I*—Formation of the addition (Knecht) compounds, *II*—Nitration of cellulose (in % N), *III*—Freezing temperature of HNO_3–H_2O solutions, *IV*—Partial vapour pressure of HNO_3 in aqueous nitric acid. Hatched area — strong swelling of cellulose fibre. Cross hatched area — solution of cellulose fibre in the acid.

strated, however, that the presence of sulphuric acid counteracts the swelling, and hence nitration can proceed more evenly.

On the other hand, attention should be drawn to the contribution of Miles and Wilson [10] who reported that nitric acid of 85% concentration causes the highest rate of nitration of all nitrating mixtures. An acid of this concentration produced a product containing 8.0% of nitrogen. Such an acid exerts a strong denitrifying effect on a higher nitrated nitrocellulose, as shown by the reversibility of the reaction of nitrating cellulose. Thus nitrocotton of 12.1% N is denitrated at a rate of 1.41% of N per hour at 20°C. Moreover, concentrated nitric acid of about 85% has been found to be most efficiently absorbed by nitrocellulose.

It is also possible to nitrate nitrocellulose which has already been partly prenitrated. This principle has been used in the manufacturing process for nitrating nitrocellulose of 13.5% N by means of 100% nitric acid to obtain a product with 14.09% N (de Bruin and Witte [28a]). Another method consists in nitrating nitrocellulose by means of nitric acid vapours. A detailed description of such a process as applied in Germany will follow later (see p. 353).

Chédin and Tribot [11] have demonstrated that a 100% nitric acid which is capable of nitrating cotton linters up to 13.2% N can produce a higher nitrated product, if the gelatinized nitrocellulose after being converted into an amorphous mass by dissolving the product in acetone, precipitating by addition of water and drying, is further nitrated be means of nitric acid. This proceedure repeated several times makes it possible to increase the nitrogen percentage to as much as 13.7 to 13.8% N.

ABSORPTION OF NITRIC ACID BY CELLULOSE AND NITROCELLULOSE

The absorption of nitric acid is a phenomenon preceding nitration. Afterwards nitric acid is also absorbed by the nitrocellulose formed. This phenomenon has been examined under various conditions: e.g. the absorption of nitric acid in vapour form and the absorption of HNO_3 from pure nitric acid and from its solution respectively.

Wilson and Miles [12] have measured the absorption of nitric acid by treating with it nitrocotton of 13.8% N. Under a pressure of 4 mm Hg as much as 15% of HNO_3, was absorbed by this nitrocotton. Nitric acid is absorbed better by a lower-nitrated substance, just as the absorption of water vapour is easier in the case of lower-nitrated nitrocellulose. The maximum absorption has been established with nitrocellulose of 7% N. The amount of nitric acid absorbed by cellulose depends on its type. For native cellulose it amounts to about 25% by weight of the cellulose, and approaches 50% for mercerized cellulose. Such differences in the behaviour of different kinds of nitrocellulose indicates that swelling has an appreciable influence on absorption. Mercerized cotton which is more liable to swell simultaneously shows stronger absorption.

In another investigation by the same authors [13] the absorption of HNO_3 from aqueous solutions of nitric acid has been investigated. The absorption proceed most effectively, attaining about 50% with nitrocellulose of 13% N, if the latter is immersed in acid containing 80% of HNO_3, which has approximately the composition $HNO_3 \cdot H_2O$.

The relevent data are shown in the chart (Fig. 117) which depicts the absorption of HNO_3 and of water in the presence of vapours produced from nitric acid, 78 to 80% of HNO_3

The absorption of nitric acid from the nitrating mixtures is exceptionally interesting and important from the theoretical and practical point of view. It has long been known that nitric acid absorbed from a mixed acid is richer in HNO_3 than the nitrating acid itself.

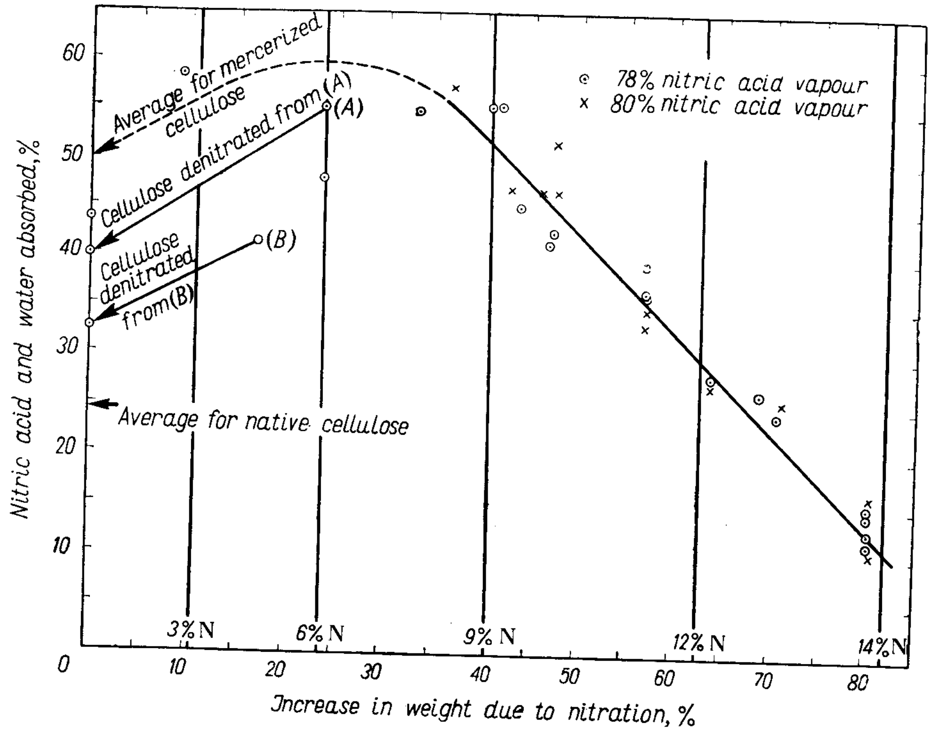


FIG. 117. Absorption of HNO_3 and water by nitrocellulose of 13.8% N (Wilson and Miles [13]).

The question of absorption of acids from their mixtures has been studied experimentally by Demougin and Bonnet [28], by Wilson and Miles [13] and more recently by Chédin [11]. The last author has provided clear experimental evidence that the nitric acid remaining in nitrocellulose after nitration has ended is present in two forms: as spent acid (after-nitration acid) of the same composition as the waste acid, and as nitric acid diluted to varying concentration by the water absorbed by the nitrocellulose fibres. The spent acid can be removed to some extent from the nitrocotton by squeezing it between rollers. By increasing the pressure from 150 to 550 kg/cm^2 the residue of this acid can be reduced from 121 to 45%. The chemical composition of the acid removed does not change appreciably with the wringing pressure. Nitric acid absorbed by nitrocellulose cannot be removed by mechanical operations such as, for instance, hydro-extraction.

Taking into consideration these experiments as well as later contributions (Chédin and Tribot [11]) Chédin has constructed a diagram (Fig. 118), the curves of which show:

(*1*) the chemical composition of mixed acids, from which a constant percentage of HNO_3+H_2O is absorbed;

(*2*) constant values of effective concentrations of nitric acid in the nitrating mixtures, expressed by the ratio

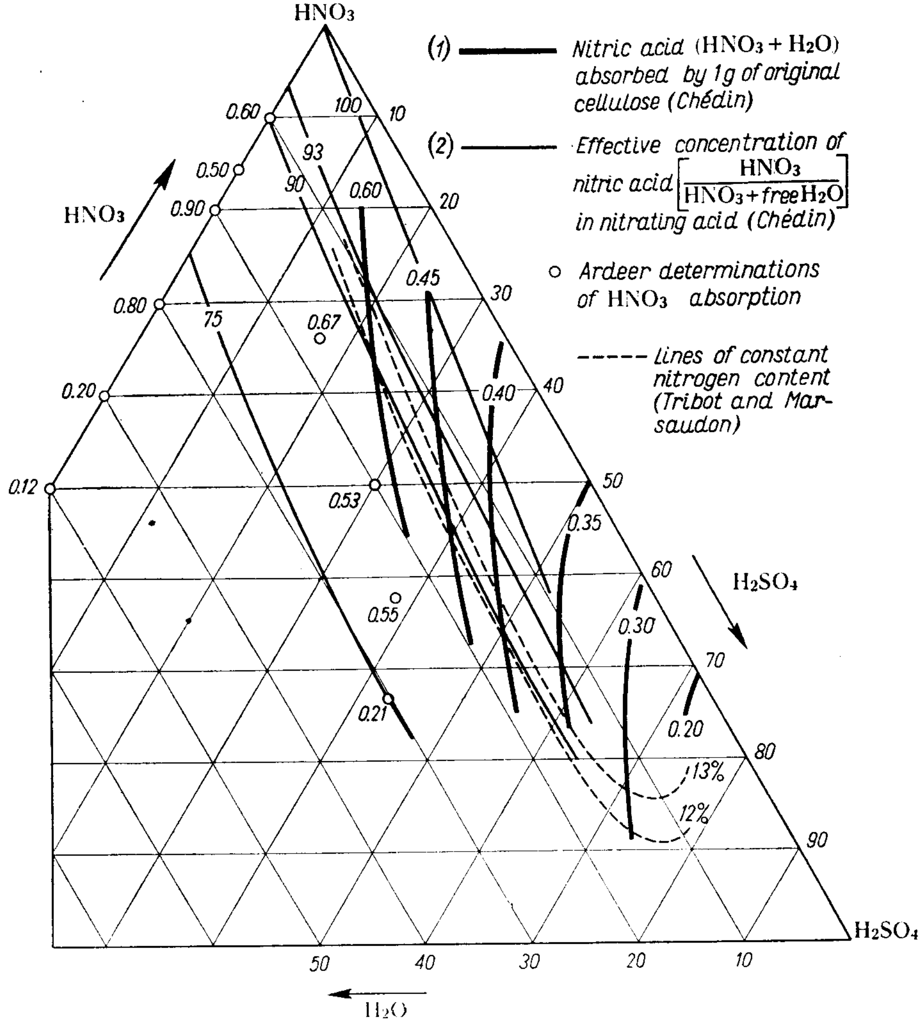


FIG. 118. Nitric acid absorption and effective concentration in mixed acid, according to Chédin and Tribot [11].

$$100\frac{HNO_3}{HNO_3 + H_2O}$$

The values (*1*) and (*2*) refer to absorbed nitric acid, the mixed acid retained in the nitrocellulose without being absorbed is neglected.

Thus the curves (*1*) and (*2*) give an idea of the absorption percentage (HNO_3+H_2O), whereas the curves of series (*2*) are intended to illustrate the concentration of the absorbed acid.

For example nitrocellulose of 12% N prepared by nitration with a mixed acid containing 17% of H_2O and 25% of HNO_3 absorbed about 37% of nitric acid of *ca.* 90% concentration.

These observations are of importance in practice as they indicate that on separation of acid from the nitrocellulose, e.g. in centrifuges, the composition of the nitrating mixture retained in the product changes so that the concentration of the nitric acid is increased. As a result an additional "after-nitration" process can occur. Due to the small amounts of acids present in the product, the heat developed during after-nitration can raise the temperature of acid nitrocotton sufficiently high to bring about inflammation or even explosion.

The tendency of nitrocellulose to absorb nitric acid that cannot be removed except by washing with water or by means of sulphuric acid insufficiently strong to dissolve the nitrocellulose (e.g. containing 50% of H_2SO_4) would seem to justify the supposition that nitrocotton is capable of forming complex compounds with nitric acid. There is however no other evidence in favour of this suggestion, although the formation of such complex compounds would appear possible.

NITRATION WITH MIXTURES OF NITRIC AND SULPHURIC ACIDS

The first attempts to nitrate cellulose by means of mixtures made up from nitric and sulphuric acids were made as early as by Vieille who in 1884 [1] also found that increasing the concentration of sulphuric acid in the mixture diminished the rate of the nitration reaction.

The rate of nitration of cellulose is dependent both on the rate of the chemical reaction of esterification itself, and on the rate of diffusion of the nitrating acid into the cellulose fibres. This is discussed later (p. 356).

The first extensive investigations into the relation between the nitrogen content of nitrocellulose and the composition of the mixed acid were carried out by Bruley [14]. They are summarized graphically in Fig. 119.

Lunge *et al.* [15] examined the effect of the composition of mixed acid, and the influence of the nitration temperature within the range from 0 to 80°C on the nitrogen content of nitrocellulose, the content of non-nitrated cellulose, the yield, the solubility of the products in ether–alcohol mixture and the viscosity of the acetone solution. Cotton linters were used. From these experiments it has been established that nitrocellulose containing more than 13.5% N is unstable and decomposed readily, as mentioned before.

Nitrocellulose containing 13.5% N can be obtained by nitrating with mixtures that are composed of sulphuric and nitric acid in various proportions, the water content being limited within 1 and 13%. Hence it can be concluded that in practice, the application of the most concentrated nitrating acids is not indispensable for producing nitrocellulose with the maximum nitrogen content (Table 71).

For mixed acids with a constant sulphuric to nitric acid ratio, the nitrogen content of the nitrocellulose falls as the proportion of water increases (Fig. 120).

After the water content in the mixed acid exceeds 13% the reaction proceeds more and more slowly. At the same time the solubility of the product increases up to a certain limit (Table 72).

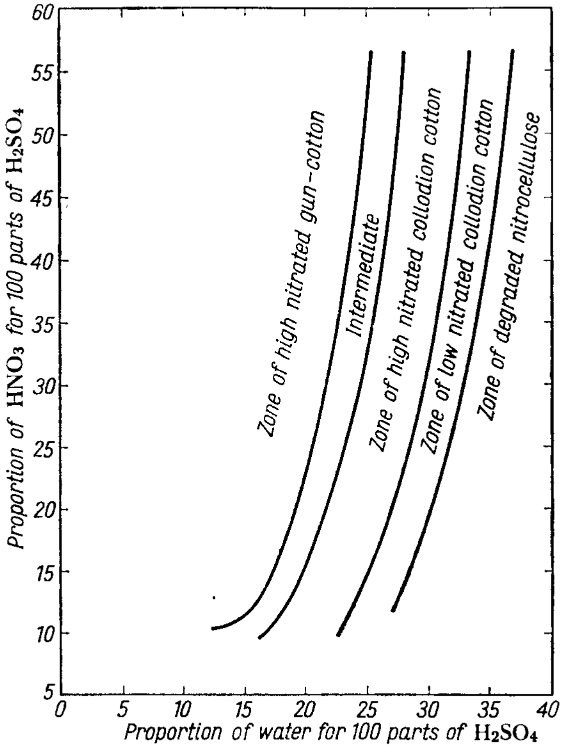


FIG. 119. Relation between the nitrogen content of nitrocellulose and composition of mixed acids, according to Bruley [14].

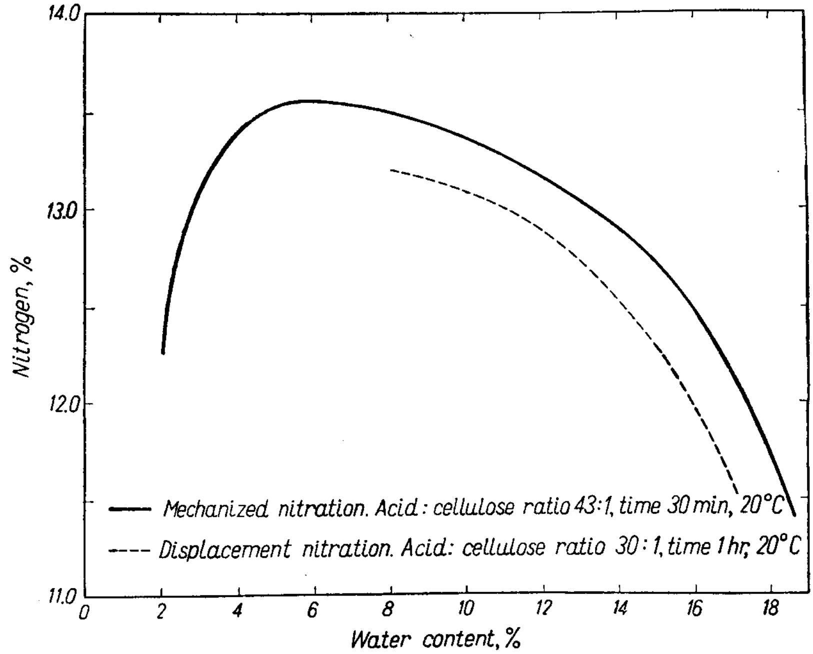


FIG. 120. Change of nitrogen content in nitrocellulose as a function of water con-

TABLE 71

THE EFFECT OF NITRATING CELLULOSE WITH MIXED ACIDS OF DIFFERENT COMPOSITION (AFTER LUNGE [15])

No.	Composition of mixed acid, %			Nitrogen content of nitrocellulose %	Yield %
	H_2SO_4	HNO_3	H_2O		
1	60.00	27.43	12.57	13.62	173
2	62.10	25.79	12.11	13.75	174
3	62.95	24.95	12.10	13.83	175
4	63.72	25.31	10.97	13.75	175
5	64.56	24.65	10.79	13.71	175
6	68.02	25.28	5.70	13.76	—
7	64.55	26.55	8.88	13.72	173
8	63.35	25.31	11.34	13.92	173
9	75.33	22.80	1.87	13.53	176
10	74.16	22.12	3.72	13.51	175
11	72.97	21.63	5.40	13.57	—
12	69.90	20.45	9.65	13.64	177
13	68.31	20.49	11.20	13.61	176
14	67.43	19.37	13.20	13.25	172
15	67.32	32.53	0.15	13.62	176
16	65.41	31.34	3.25	13.57	175
17	63.75	30.80	5.45	13.63	176
18	60.68	29.31	10.01	13.68	176

At a water percentage of 25–27%, hydrocellulose and oxycellulose are formed to an extent large enough to bring about a decrease in yield, and to diminish the nitrogen value of the product below the limit required for commercial application.

Numerous investigators have drawn attention to the above mentioned fact that an anhydrous mixture produces nitrocellulose of a lower nitrogen content than a mixed acid slightly diluted with water. Rassow and Bongé [16] attained the highest nitrogen content of nitrocellulose by using a nitrating mixture containing 9–10% of water, and further reduction in the water content did not result in any increase in the nitrogen content of the nitrocellulose, as the reaction rate is slowed down. Thus an anhydrous mixture containing sulphuric and nitric acid in a 1:1 ratio results in a nitrogen content of 13.2–13.5% only after an interval of 12 hr, whereas adding 10% of H_2O to the same mixed acid makes it possible to shorten the time of nitration to only 45–60 min.

It has been confirmed by Schiemann and Kühne [17] that increasing the water content in the nitrating acid favours nitration. They reported that an almost anhydrous mixture, e.g. composed of 22.6% HNO_3, 76.6% H_2SO_4, 0.8% H_2O, gave a product of 12.9% N content, whereas increasing the proportion of water in this acid to 9.5% caused the nitrogen content to rise to 13.5%.

The origin of this phenomenon has not yet been made clear. Anhydrous acids seem likely to cause too rapid swelling on the surface of the cellulose fibres, so that the nitrating acid penetrates only with difficulty into the fibres.

Schiemann and Kühne also stated that changes in the water content of the mixed acid, maintained within the limits from 3.5 to 13.5%, do not, in fact, cause appreciable variations in the nitrogen content of nitrocellulose.

Lunge *et al.* [15] has examined the influence of the $H_2SO_4:HNO_3$ ratio on the rate of reaction, confirming the earlier observations of Vieille that increasing the amount of sulphuric acid decreases the rate of the chemical reaction. Thus the maximum degree of nitration is reached:

for a ratio of $H_2SO_4:HNO_3 = 1$ after 0.5 hr
$H_2SO_4:HNO_3 = 3$ after 3 hr
$H_2SO_4:HNO_3 = 8$ after 30 days

The highest nitrogen content is achieved by keeping the proportion of $H_2SO_4:HNO_3$ within the limits $\frac{1}{4}$–$\frac{3}{4}$.

Further increase in the value of the $H_2SO_4:HNO_3$ ratio reduces the nitrogen percentage of the nitrocellulose until at $H_2SO_4:HNO_3 = 8$, a considerable part of the cellulose remains un-nitrated. (Table 73).

TABLE 72 (LUNGE [15])

SOLUBILITY OF NITROCELLULOSE AS A FUNCTION OF COMPOSITION OF MIXED ACID AND OF NITROGEN CONTENT

Composition of the mixed acid, %			Nitrogen content %	Solubility in ether–alcohol %	Yield %
H_2SO_4	HNO_3	H_2O			
45.31	49.07	5.62	13.65	1.50	177.5
42.61	46.01	11.38	13.21	5.40	176.2
41.03	44.45	14.52	12.76	22.00	—
40.66	43.85	15.49	12.58	60.00	167.0
40.14	43.25	16.61	12.31	99.14	159.0
39.45	42.73	17.82	12.05	99.84	153.0
38.95	42.15	18.90	11.59	100.02	156.5
38.43	41.31	20.26	10.93	99.82	144.2
37.20	40.30	22.50	9.76	74.22	146.0
33.72	39.78	23.50	9.31	1.15	138.9
35.87	38.83	25.30	8.40	0.61	131.2
34.41	37.17	28.42	6.50	1.73	—

The problem of the rate of nitration of cellulose is discussed in a more detailed way in a special section — p. 355.

It should be borne in mind that laboratory experiments on the nitration of cellulose on a gramme scale usually using a large excess of acid, do not portray plant conditions in an exact manner. Under laboratory conditions a two hours' nitra-

TABLE 73

THE EFFECT OF $HNO_3:H_2SO_4$ RATIO (LUNGE [15])

$HNO_3:H_2SO_4$ ratio	After 1/2 hr		After 24 hr		After 15 days
	nitrogen content %	yield %	nitrogen content %	yield %	
1:1	12.58	162.75			
1:2	13.25	174.14			
1:3	12.72	166.14	13.40	176.44	
1:5	8.14	130.88	13.10	166.6	12.74% N
			After 3 days		After 30 days
1:8	24.44% unnitrated cellulose		10.86	151.6	11.70% N, 152% of yield, 4.48% unnitrated cellulose

tion is frequently carried out, whilst in commercial manufacture, the nitration time is considerably shorter. It might therefore be concluded that commercial techniques would produce a lower nitrogen content than reported for laboratory conditions. On the other hand industrial equipment permits a more effective stirring so as to obtain more uniform product, thus compensating for the short time of reaction.

When nitrating to a nitrogen content of 12% and more the nitration rate is higher, hence no significant divergence exists between nitration on the industrial scale and laboratory experiments.

Increase in the proportion of sulphuric acid in the mixture tends to reduce the chemical stability of the product, probably in consequence of the formation of unstable sulphuric esters of cellulose.

On varying the temperature of nitration from 0 to 80°C, Lunge observed that:

(1) the reaction rate increases appreciably with temperature increase;

(2) at a temperature above 40°C the nitrogen content of the nitrocellulose is decreased, remaining unchanged at temperatures between 60 and 80°C;

(3) elevation of the temperature causes a decrease in yield due to decomposition of the product;

(4) at a higher temperature, the solubility increases and the viscosity of the solutions falls lower and lower.

The first effort to formulate a theory explaining the nitration of nitrocellulose is to be found in a paper by Sapozhnikov [18]. This author paid special attention to the role of sulphuric acid in the nitration process. Sapozhnikov's theory has already been outlined (Vol. I, p. 9) so only certain assumptions he made as the basis for his speculation will be mentioned here.

Sulphuric acid acts as a dehydrating agent in the mixed acid. In this way a hydrate,

$H_2SO_4 \cdot H_2O$, is produced, accompanied by higher hydrated compounds defined by the formula $H_2SO_4 \cdot xH_2O$. Likewise nitric acid is capable of forming hydrates. Thus in the nitrating mixture an equilibrium corresponding to the eqn. (1) is postulated:

$$HNO_3 \cdot nH_2O + xH_2SO_4 \rightleftarrows HNO_3 + (n-x)H_2SO_4 \cdot H_2O \qquad (1)$$

As the proportion of sulphuric acid in the mixture increases nitric acid loses water, because the affinity of H_2SO_4 for water is greater than that of HNO_3.

When the mole quantity of sulphuric acid balances the number of moles of water, i.e. when $n = x$, nitric acid loses all its water. Equation (1) is then converted to the form (2):

$$HNO_3 \cdot nH_2O + nH_2SO_4 \rightleftarrows HNO_3 + nH_2SO_4 \cdot H_2O \qquad (2)$$

According to Sapozhnikov, the esterification proceeds most intensively in the presence of anhydrous nitric acid HNO_3, as in eqn. (2). In the presence of smaller amounts of sulphuric acid, nitric acid hydrates are formed; in practice they are not capable of esterifying cellulose.

Research on the nitric acid vapour pressure in the ternary system

$$H_2SO_4\text{–}HNO_3\text{–}H_2O$$

allowed Sapozhnikov suggest a hypothesis explaining the relationship existing between the HNO_3 vapour pressure and the form in which nitric acid is present in the nitrating mixture. Thus a maximum vapour pressure is correlated with anhydrous nitric acid, a lower pressure being shown by nitric acid in the form of the hydrate, $HNO_3 \cdot H_2O$, while an even lower value is shown by the hydrate $HNO_3 \cdot 3H_2O$.

On expressing the relationship between the nitric acid vapour pressure and the composition of the mixed acid, and on its capacity to nitrating cellulose, by means of graphs, Sapozhnikov saw that the curves showing the nitric acid vapour pressure and of those indicating the degree of cellulose nitration were very similar in appearance. He therefore deduced that the nitrating effectiveness of mixed acids was dependent on the nitric acid vapour pressures of the mixture (Vol. I., Fig. 3). Figures 121 and 122 give the nitration and HNO_3 partial pressure curves for nitrating mixtures in weight %.

As mentioned in Vol. I, Sapozhnikov's theory was abandoned for some time, but latterly it has been revived, mainly due to work byVandoni [19] and Miles [8] — see Vol. I.

From a study of the vapour pressures of the mixed acids, Miles has concluded that the highest nitrogen content is to be achieved by nitrating with a mixed acid consisting of:

HNO_3	24.3%
H_2SO_4	65.8%
H_2O	9.9%

This is closely in line with experimental data published by Lunge, quoted in

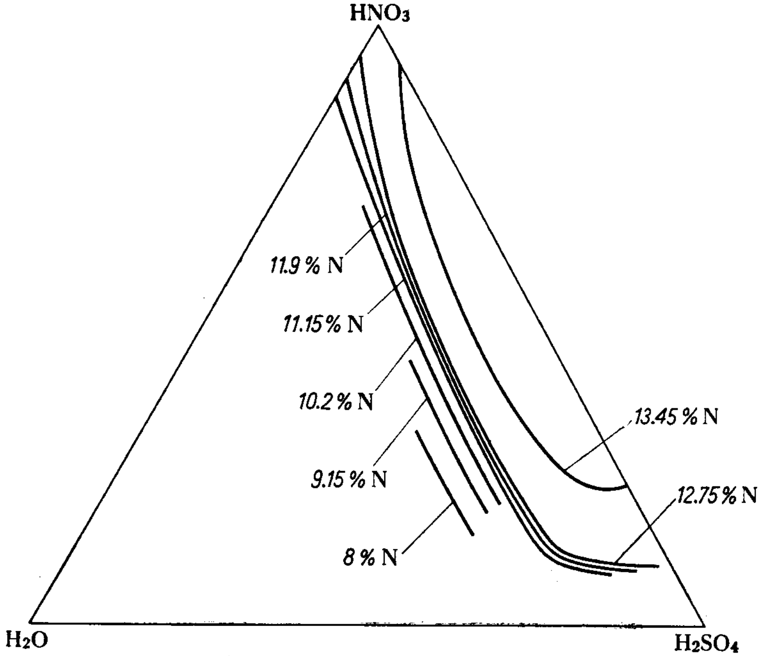


FIG. 121. Nitration of cellulose. A modified Sapozhnikov diagram with curves of equal nitrogen content in nitrocellulose. Composition of acid mixtures in weight %.

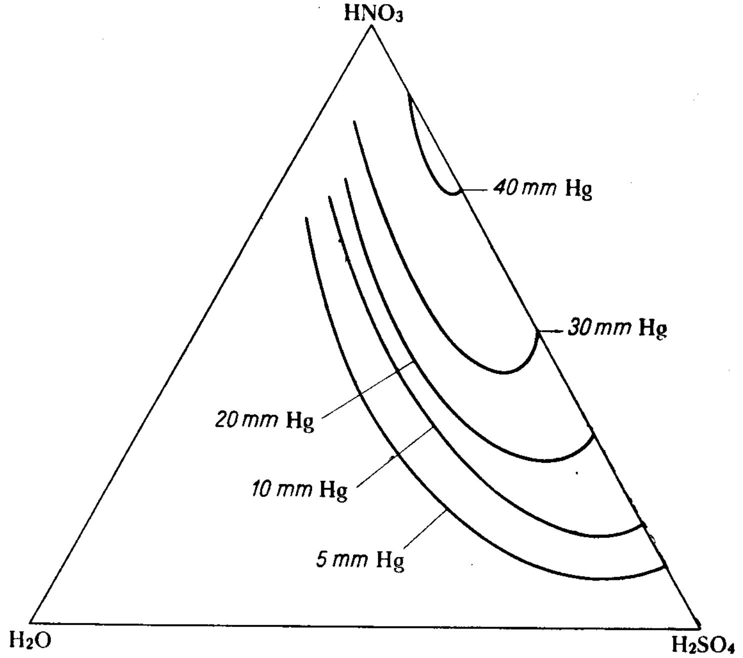


FIG. 122. Isobars of HNO_3 vapour pressure in nitrating mixtures. A modified Sapozhnikov diagram. Composition of acid mixtures in weight %.

Table 63 of this volume, which show that a nitrogen percentage of 13.92% may be attained, by using an acid composed of:

HNO_3	25.3%
H_2SO_4	63.4%
H_2O	11.3%

Miles and Milbourn [20] and Trogus [5] have revised Sapozhnikov's chart so as to indicate areas rich in water and most abundant in sulphuric acid, in which cellulose undergoes swelling at the time of nitration, the area richest in sulphuric acid where dissolution of cellulose prior to nitration proceeds and the zone defining mixtures being used in practice (Figs. 123 and 124).

Basing his view mainly on the theory of Hantzsch, that suggests that nitric acid at high concentrations exists in the form of the pseudo-acid $O_2N \cdot OH$, Farmer [21]

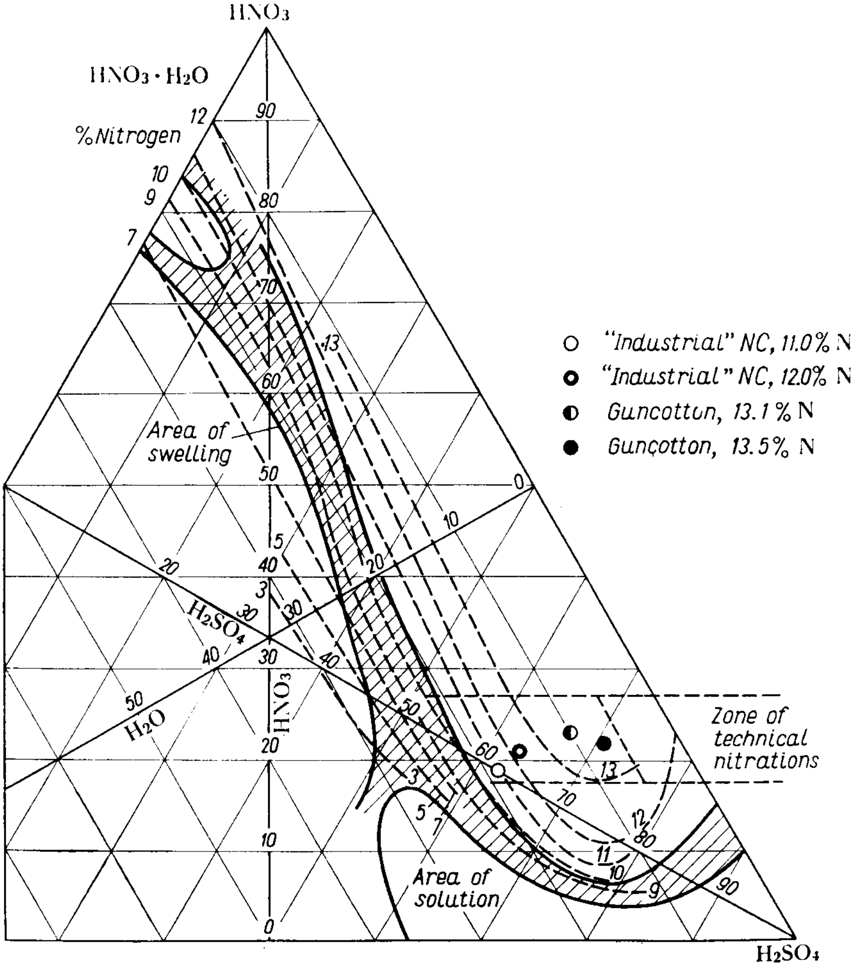


FIG. 123. Sapozhnikov diagram modified by Miles and Milbourn [20]. Composition of acid mixtures in weight %.

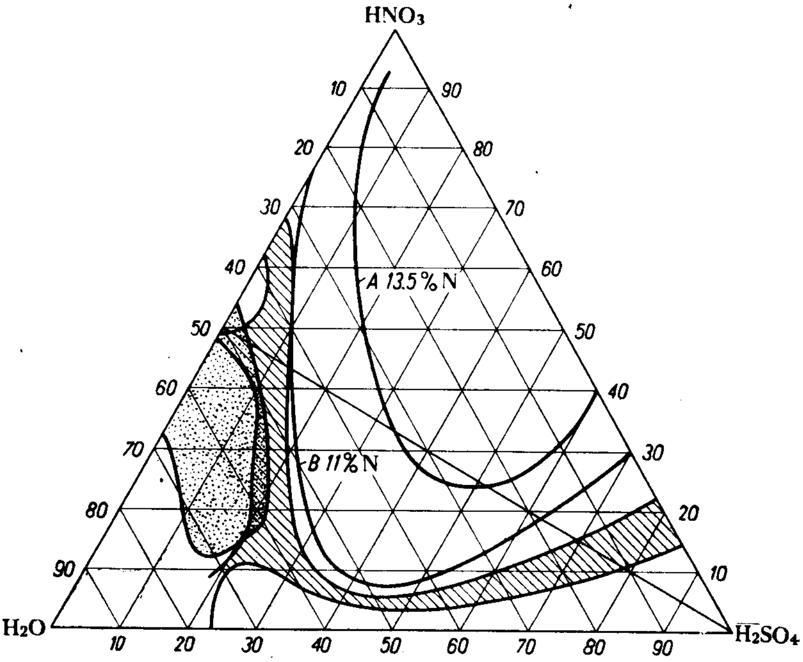


FIG. 124. Sapozhnikov diagram modified by Trogus [5]. Composition of acid mixtures in mole %.

suggested that nitric pseudo-acid is the active factor in the process of esterifying cellulose, similarly in the process of C-nitration. Sulphuric acid esterifies cellulose with difficulty, since it does not readily assume its pseudo-form. In a concentrated mixture of nitric and sulphuric acid, a nitronium sulphate is formed thus decreasing the concentration of the pseudo-acid form of nitric acid. In anhydrous nitric acid nitronium nitrate, which is also a salt inactive as an esterifying agent, should be present. Farmer thus explained the well-known observation that the esterifying capacity of a concentrated nitric acid and that of concentrated mixed acid is lower than that of acid containing a small proportion of water. The concentration of nitric pseudo-acid is highest in mixtures containing about 10% of water.

Berl *et al.* [22] established that the upper limit of cellulose nitration is reached when the composition of the nitrating mixed acid has the mole ratio

$$\frac{HNO_3}{H_2SO_4 \cdot H_2O} = \frac{1}{2}$$

Such a mixed acid corresponds with the following weight percentage of ingredients:

HNO_3	21.8%
H_2SO_4	66.0%
H_2O	12.2%

and is thus well in line with experimental values.

According to Chédin *et al.*, the higher the concentration of nitronium ions $NO_2^{\oplus}$ in the nitrating acid the more complete the nitration of nitrocellulose. Chédin [23] has produced a graph (Fig. 125) depicting the composition of mixed acids and their effect on cellulose. Thus, in the area *II*, rich in sulphuric acid but poor in nitric acid and water, a rather low concentration of $NO_2^{\oplus}$ is found, though

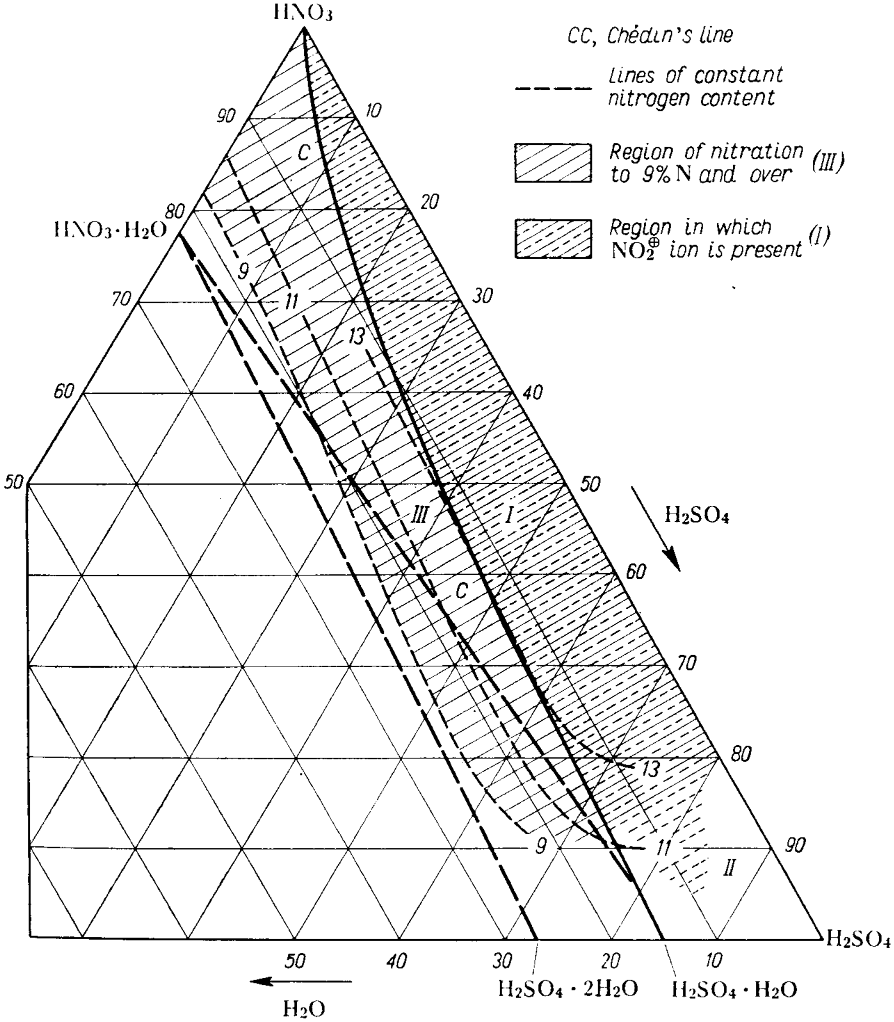


FIG. 125. Diagram of Chédin [23]: limits of compositions, nitrating cellulose, according to Miles [8].

almost the whole of the nitric acid is dissociated into $NO_2^{\oplus}$ and $OH^{\ominus}$ ions. This is why the degradation of cellulose predominates here, while nitration occurs only to an unimportant extent. Within the region *I*, cellulose is nitrated to a nitrogen value as high as 13.75% N. Nitric acid is only partially dissociated here, while sulphuric acid can be hydrated. In the area *III*, the $NO_2^{\oplus}$ ions are not detectable by spectrographic measurements. The nitrogen content of nitrocellulose is lower under these conditions. It falls considerably as the mixed acid is diluted with water.

The role of sulphuric acid during nitration is not limited to participation in the creation of the $NO_2^{\oplus}$ ions nor to binding water, however. Increase in the amount of sulphuric acid causes the ester produced, i.e. cellulose nitrate, to hydrolyse since the reaction is reversible.

The hydrolytic activity of sulphuric acid is one of reasons why efforts to obtain cellulose trinitrate by treatment with mixtures composed of nitric acid and sulphuric acid were a failure. The maximum percentage of nitrogen combined in ester form was not higher than 13.96%.

Berl and Klaye [24] pointed out the reversibility of the esterification reaction, and stated that the degree of cellulose nitration was dependent primarily on the final composition of the mixed acid.

Japanese authors [25, 26] were the first to formulate the nitration equilibrium in terms of the activities of nitric acid and water in the nitrating mixtures (see p. 357). It is self-evident that the final composition of the mixed acid differs from the initial one, as nitric acid is consumed and water is produced during the course of the reaction. Therefore the content of nitro groups in the nitrocellulose does not depend solely on the composition of the mixed acid, but also on the excess of acid, and thus it depends on the cellulose to acid ratio. If the excess of mixed acid is large enough, its dilution by water formed during nitration, and the consumption of nitric acid, is relatively unimportant. Hence the nitrogen content of nitrocellulose is higher.

If it is desired that the composition of the nitrating mixture should change as little as possible during the nitration, a large excess of acid must be used. In commercial practice a cellulose to acid ratio of 1:50 is usually used. This is 10–15 times as much acid as needed in relation to the amount of nitric acid calculated from theory.

To designate the change in composition of mixed acid brought about by nitration, Schiemann and Kühne [17] reported the data given in Table 74.

TABLE 74

CHANGE IN THE MIXED ACID RATIO AFTER NITRATION

Composition of the nitrating mixture, %			Composition of the spent acid, %			Cellulose to acid ratio	Nitrogen content of nitrocellulose, %
HNO_3	H_2SO_4	H_2O	HNO_3	H_2SO_4	H_2O		
24.78	70.82	5.40	20.69	71.29	8.02	1:50	13.0–13.5
23.05	68.07	8.88	18.20	69.56	12.24		
21.09	68.52	10.19	16.91	69.10	13.99		
22.65	76.50	0.85	21.80	76.71	1.49	1:80	12.9–13.5
21.73	73.15	5.12	20.29	74.37	5.34		
20.70	69.45	9.78	19.58	70.12	10.30		

Treating nitrocellulose with a mixed acid capable of producing cellulose nitrate with a lower nitrogen value results in a partial denitration of the cellulose. On the other hand nitrocellulose immersed in a mixture of concentrated acids undergoes further nitration. Berl *et al.* [24, 27] have reported unquestionable examples. For instance three samples of nitrocellulose of different nitrogen content: 10.9, 12.7, and 13.5% respectively, were drowned in two nitrating acids. After a sufficiently long time each of the three samples of nitrocellulose immersed in any one of the mixed acids showed the same percentage of nitrogen.

Cotton and guncotton No. 1 (high nitrated guncotton) were treated with a nitrating mixture consisting of

H_2SO_4	60.0%
HNO_3	22.5%
H_2O	17.5%

by Demougin and Bonnet [28]. In both instances, after specific times nitrocotton of the same nitrogen content was obtained, as shown in Table 75.

TABLE 75

CHANGING NITROGEN CONTENT (% N) IN SAMPLES OF COTTON IMMERSED IN MIXED ACID [28]

After the period of	15 min	1 hr	4 hr	24 hr	4 days	7 days	60 days
Cotton	11.62	11.81	12.84	12.32	12.41	12.62	12.65
Guncotton No. 1	13.33	13.23	13.09	12.99	12.94	12.87	12.66

Demougin and Bonnet reported that both these reactions occurred at the same rate in conc. acids, equilibrium being established after about fourteen days. With nitrating acids containing an exceptionally high percentage of water, i.e. 21.7% water in experiments of Miles and Milbourn [20], or 24.6% in the experiments of Berl and Hefter [27], the balance tends to establish itself very slowly, and considerably altered products are formed due to side reactions. Efforts to achieve an absolute equilibrium fail in such instances.

The results obtained by de Bruin and Witte [28a] make it clear that denitration of nitrocellulose with mixed acid may not reach completion even after one year (e.g. denitration of nitrocellulose of 13.95% N with mixed acid containing 21.9% HNO_3 and 16.9% H_2O which yields nitrocellulose of 12.4% N on nitration).

The authors also denitrated nitrocellulose with nitric acid, obtaining rather non-uniform products.

They pointed out that the rate of denitration is much lower than that of nitration. A theory recently advanced by Trommel [80] explained this in terms of the relative accessibility of the reacting groups in cellulose and nitrocellulose (see p. 239).

Fabel and Fritsche [29] have carried out experiments designed to re-nitrate and denitrate nitrocellulose, as follows. Cellulose was at first nitrated by immersion for 1 hr in one of a series of mixed acids: A, B, C, or D (see Table 76). In succession each sample of nitrocellulose, except D, was divided into 4 parts, to be immersed in the other (or the same) nitrating acid, for 4 hr. Products of nitrogen content shown in Table 77 were obtained.

TABLE 76

COMPOSITION OF MIXED ACIDS USED IN THE EXPERIMENTS OF FABEL AND FRITSCHE [29]

Composition, %	A	B	C	D
HNO_3	20.4	20.4	20.3	20.3
H_2SO_4	65.5	62.0	59.6	58.1
H_2O	14.1	17.6	20.1	21.6

TABLE 77

Nitrating acid	First nitration % N	(% N) Re-nitration in the mixture			
		A	B	C	D
A	13.05	13.07	12.77	12.12	12.01
B	12.24	13.12	12.49	11.69	12.26
C	11.19	13.07	12.48	11.50	10.84
D	10.15	—	—	—	10.53

The figures indicate the result of the additional re-nitration and the effect of denitration, respectively.

Extensive research has been carried out by Wilson and Miles [10] on the denitration of nitrocellulose by the mixed acid. They investigated the influence of acids that varied in chemical composition within wide limits (the content of nitric acid varied from 10 to 70%). A couple of noteworthy rules were formulated. Thus, they found that the higher the proportion of nitric acid, the more rapid the rate of denitration. Sulphuric acid alone or a mixture containing a small amount of nitric acid, e.g. 6% of HNO_3 and 68% of H_2SO_4, has a very weak denitrating effect. The quickest denitration occurs in the presence of acids able to cause cellulose to swell, if such acids are used for the nitration. The higher the nitrogen content of the substance undergoing denitration, the more rapidly denitrating proceeds. Raising the temperature causes the rate of denitration to increase appreciably.

The following example is described by these authors: nitrocotton of 12.2% N was denitrated down to 10.7% N in the presence of acid of 69% HNO_3 and 19% H_2O at 20°C for 5 hr, whilst at 60°C, denitrating to 10.0% N was accomplished within 3 min.

The products obtained by denitrating to below 9.5% N are not completely soluble in acetone.

Craik [30] has determined the influence of temperature, and in consequence the effect of the denitration rate, on the solubility of nitrocellulose (Table 78).

TABLE 78

Denitration	% N		Denitrating acid		Temperature °C	Time hr	Solubility, %	
	Before	After	% HNO_3	% H_2O			Acetone	Alcohol–ether
Slow	13.43	12.78	41.3	20.3	20	72	100 100	2.3 (before the reaction) 99.5 (after the reaction)
Rapid	13.10	9.5	37.2	28.4	55	3/4	100 1.5	5.3 (before the reaction) 0.9 (after the reaction)
Rapid	12.55	10.8	38.8	25.3	35	1/2	100 100	100 (before the reaction) 33.5 (after the reaction)

While regarding the formation of the O-nitro derivative of cellulose as an effective resultant from the nitration and denitration processes, the following picture of the course of reaction leading to the formation of nitrocellulose should be kept in mind.

(1) A portion of the cellulose brought into contact with fresh mixed acid is nitrated to a high nitrogen content. The acid is diluted by water produced during the reaction.

(2) Another portion of cellulose not nitrated so as to form a higher nitrated substance, reacts to give a product containing a lower percentage of nitrogen since the mixed acid has been diluted during stage (1). Gradually further dilution of the acid takes place.

(3) Higher nitrated fractions suffer hydrolysis due to the presence of the more dilute acid.

The process (3) may be slow, hence under industrial conditions it may be broken off before the equilibrium is established. This means that the chemical reaction (3) is not completed. As a final product, a not very homogeneous nitrocotton is obtained. The higher the nitrating temperature, the more rapid the denitration process, the sooner the reaction balance is established, and hence the more uniform the product.

The following formulae, intended for calculating the ratio of components in the mixed acid after equilibrium is established, have been published by Miles [8]:

$$D_n = \frac{100-n}{31.13\dfrac{R}{N} - R-1} \qquad D_w = \frac{40+w}{31.13\dfrac{R}{N} - R - 1},$$

where: N nitrogen content of nitrocellulose as % N,
n the nitric acid concentration in the mixed acid as % HNO_3,
w the water concentration in the mixed acid as % H_2O,
R the weight ratio of mixed acid to cellulose,
D_n the difference in the nitric acid percentage of the mixed acid before and after the nitration,
D_w the difference in the water percentage in the mixed acid before and after the nitration.

Taking into consideration the results of experiments reported by different authors, Berl, Andress and E. Escales [31] have constructed a chart resembling Sapozhnikov's graph, to depict the relationship between the nitrogen content of nitrocellulose and the ratio of spent acid (Fig. 126). In principle the shape of the curves does not differ from those outlined in Sapozhnikov's work and a resemblance exists between those curves and the curves of nitronium ions ($NO_2^{\oplus}$) concentration (Fig. 125).

The same observations apply to the graph of nitrating starch discussed in one of the following chapters, with the exception that the solubility of nitrostarch in nitrating mixtures is, however, a major factor. Thus mixed acids of poor sulphuric acid percentage dissolve nitrostarch, and esterification in such homogeneous systems proceeds more readily.

NITRATION WITH MIXTURES OF NITRIC AND PHOSPHORIC ACIDS

The attempt to substitute phosphoric acid for sulphuric acid was first made by Hoitsema [32] and was also investigated independently at the same time by Lunge and Weintraub [15]. Work in this field has been revived by Krauz and Blechta [33], Berl and Rűff [34], Bouchonnet, Trombe, Petitpas [35], Staudinger and Mohr [35a] and Wannow [36].

Hoitsema obtained a nitrogen content as high as 14.0% N. The works of Berl and Rűff showed that the highest rate of nitration was obtained with mixtures having a phosphoric acid to nitric acid ratio varying within the limits of 3:1 and 1:1. By using these nitrating acids, Berl and Rűff obtained nitrocellulose containing 13.5% N within 1½ min.

Increasing the content of phosphoric acid above 75% of the total mixture is accompanied by a significant reduction in the reaction rate. The nitrogen content of a product prepared by nitrating with mixtures of HNO_3 and H_3PO_4 is higher

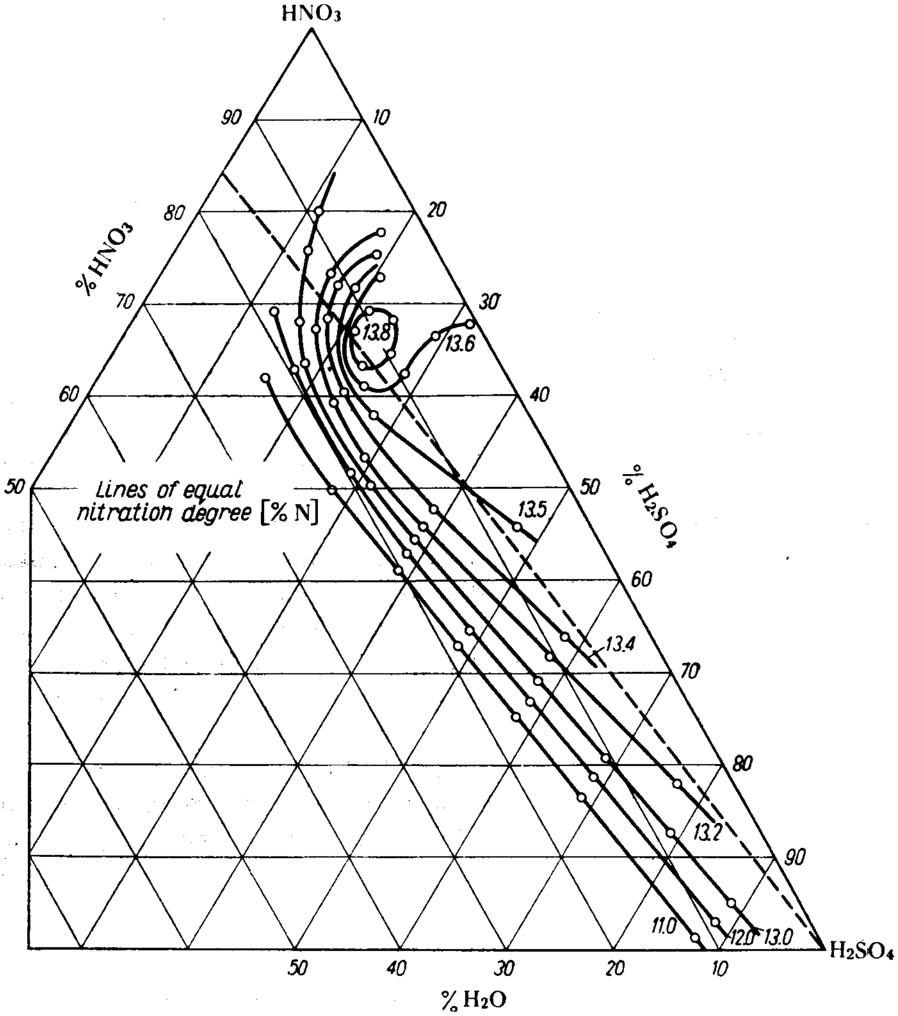


FIG. 126. Nitration of cellulose as a function of the terminal composition of nitrating mixtures (Berl, Andress and E. Escales [31]).

than when mixed acid of HNO_3 and H_2SO_4 are used. This is due to the fact that phosphoric acid does not act as a hydrolysing agent on the cellulose nitrate produced.

The recent systematic investigations carried out by Newman *et al.* [37] were devoted to the viscosity, sedimentation, diffusion and osmotic pressure of nitrocelluloses prepared by nitrating non-purified cotton, purified cotton, and viscose fibres with mixed acid containing phosphoric acid and phosphoric anhydride.

The nitrogen value obtained was reported to be 13.34–13.61% N.

Wannow [36] has stated that the nitration of cellulose by means of mixed nitric and phosphoric acid does not reduce the degree of polymerization of the nitrated substance. The stability of nitrocellulose obtained by treatment with H_3PO_4 and HNO_3 is excellent, as there are no sulphuric esters tending to decompose. Phosphoric acid cellulose esters, if produced, are not characterized by poor stability.

According to Lenze and Rubens [38], the application of concentrated nitric acid with phosphoric anhydride P_2O_5 makes it possible to attain a nitrogen content close to 14.1%, i.e. approximately that of the pure trinitrate.

Several investigators (Berl and Rűff [34], Staudinger and Mohr [35a], Davidson [39], Wannow [36]) have stated that nitrating cellulose by means of a mixture consisting of nitric acid and phosphoric acid gave an appreciably less de-polymerized, although more swollen product than one resulting from the usual nitration by a mixed acid made of nitric and sulphuric acid. For this reason Davidson has recommended nitrating cellulose with mixture of nitric acid and phosphoric acid in order to determine the molecular weight of the nitrocellulose and hence to estimate the molecular weight and the degree of polymerization of the original, untreated cellulose. Davidson reported the following preparative method as suitable for this purpose: one part by weight of cellulose is stirred into 100 parts by weight of a mixture prepared from:

HNO_3	48% by weight
H_3PO_4	50% by weight
P_2O_5	2% by weight

cooled —10°C. After the cellulose has been introduced a temperature of 0°C is maintained for 4–6 hr. The product is filtered off in a suction funnel, and subsequently washed with a mixture of acetic acid and water in a 1:1 volume ratio. During this operation the temperature must be kept at —10°C. The product is rinsed with distilled water until its reaction is neutral. Then it is allowed to stand overnight in a large amount of distilled water, after which it is subjected to a threefold boiling, each lasting 3 hr.

Using the ultracentrifuge sedimenting method, Gralen and Svedberg [40] have determined the molecular weight of nitrocellulose prepared from various types of cellulose. The nitration was carried out at 0°C by means of a mixture composed of 40% of nitric acid, 40% of phosphoric acid, and 20% of phosphorus pentoxide. The results are collected in Table 79.

It follows from these values that the degree of degradation is not inconsiderable, since it corresponds with a two- to three-fold reduction in molecular weight, in spite of the conditions of nitration. The results clearly disagree with those obtained by Staudinger and Mohr [35a] and reported earlier on p. 246.

It has been stated on the basis of trials carried out in the factory at Angoulême, France [41], that the method of nitrating with a mixture composed of nitric and phosphoric acid can be successfully applied commercially for manufacturing high nitrated guncotton (CP_1) containing 13.7% of nitrogen. On the other hand it is less suitable for the production of low nitrated guncotton with a nitrogen percentage of about 12%, since it yields a non homogeneous product.

Nitration by means of nitric and phosphoric acid appears to have prospects of being adopted industrially. However, the use of mixtures containing phosphoric acid involves great technical difficulties, as for instance, the greater tendency of

TABLE 79

Type of cellulose	Cellulose		Nitrocellulose	
	$M \times 10^{-6}$	Polymerization degree	$M \times 10^{-6}$	Polymerization degree
Unbleached cotton Linters	1.75	10,800	0.78	2700
Bleached cotton Linters	0.41	3000	0.40	1360
Sulphite wood pulp	0.46	2900	0.43	1470
Sulphate wood pulp	0.40	2500	0.42	1450

phosphoric acid, as compared with sulphuric acid, to corrode iron and steel. Besides, the recovery of the spent acid is considerably more complicated, since extraordinarily high temperatures for distillation are necessary.

NITRATION WITH MIXTURES OF NITRIC AND ACETIC ACIDS (OR ACETIC ANHYDRIDE)

Acetic acid, or acetic anhydride can be used in the manufacture of nitrocellulose as dehydrating agents. Berl and Smith [42] showed that increasing the proportion of acetic acid mixed with 88% nitric acid favours the nitrating capacity of the mixed acid, since they obtained products containing 13.7–14.0% of nitrogen.

Trogus [43] used the Berl and Smith method to prepare nitrocellulose for X-ray investigations, because it showed the least swelling. Recently Harland [44] has suggested using a mixed acid composed of nitric acid, acetic acid and acetic anhydride when preparing nitrocellulose for the determination of the molecular weight and the degree of polymerization by viscometry. This proposal followed from his observation that cellulose undergoes virtually no de-polymerization when nitrated with a mixed acid of this kind.

Darzens [45] has claimed that nitrating cellulose in a homogeneous mixture of nitric acid, acetic anhydride and chloroform makes it possible to obtain a product containing as much as 13.7% of nitrogen.

It has been established (Bouchonnet, Trombe and Petitpas [35]) that cellulose trinitrate with 14.14% N can be obtained as result of nitrating linters with a mixture composed of 50% of nitric acid, 25% of acetic acid and 25% of acetic anhydride for 5 hr at 15°C. The product was stabilized by alcohol extraction.

NITRATION IN MIXTURES AND SOLUTIONS INCLUDING INACTIVE SUBSTANCES

The earliest attempt to nitrate cellulose in mixtures comprising inactive substances was made by Rogovin and Paradnia [46]. The experiments were aimed at investigating the possibility of replacing the large excess of sulphuric acid which does not take part in the chemical reaction, and exerts an adverse influence on nitrocellulose, for in the presence of a relatively high percentage of water in the mixed acid, it favours side reactions, and oxidizes and hydrolyses the nitrocellulose.

Rogovin and Paradnia substituted carbon tetrachloride or pentane for a part of the mixed acid, and obtained nitrocellulose with different nitrogen values. With a low water content, and a ratio $HNO_3:H_2SO_4$ of 3:1, and by varying the proportion of the inert substance for 75–87%, they obtained nitrocellulose of different nitrogen contents.

Thus for instance, nitration in the mixture composed of

HNO_3	18%
H_2SO_4	5%
NO_2	2%
CCl_4	75%

to which an emulsifying agent (naphthalenesulphonic acids) had been added, gave nitrocellulose containing 11.7% N. An increase of the carbon tetrachloride percentage to 87.5% caused the nitrogen value to decrease to 10.6%.

Kenyon *et al.* [47] published a graph (Fig. 127) showing the effect of the nitric acid concentration in the carbon tetrachloride on the nitrogen percentage of the nitrocellulose produced. The conditions of experiment were as follows: for 5 parts of cellulose, 120 parts of carbon tetrachloride mixed with varying amount of anhydrous nitric acid were used to carry out the chemical reaction for 1 hr.

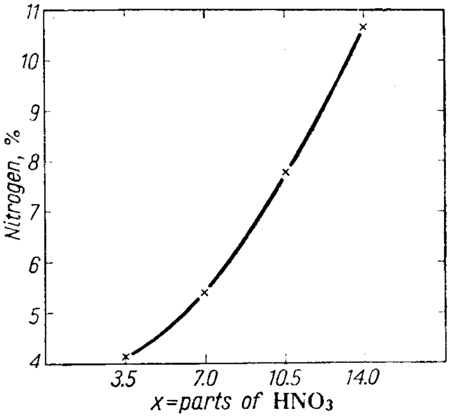


FIG. 127. Nitrogen content in nitrocellulose as a function of HNO_3 concentration in carbon tetrachloride. Ratio of reactants 5:1:x (cellulose: CCl_4:HNO_3) (Kenyon *et al.* [47]).

In addition, there are a few references in the literature describing experiments to nitrate cellulose in media comprising solvents resistant to nitration such as chloroform and other chlorinated hydrocarbons.

Thus, Bouchonnet [48] nitrated cellulose in a solution of nitrogen pentoxide in carbon tetrachloride, to obtain a stable cellulose trinitrate of 14.1% N. Similar products, i.e. with a nitrogen percentage of 13.9–14.1%, have been obtained by this worker, using other solvents, namely chloroform and dichlorodiethyl ether. Ethyl ether includes a characteristically "basic" oxygen atom that forms addition compounds with nitric acid, hence it hinders for the nitration process. Dichlorodiethyl ether, on the other hand, does not behave in this way so that nitration to trinitrate is possible.

In the thirties a new commercial method of nitrating cellulose was invented in Germany by Thinius and Weihe [49]. It consists in acting upon cellulose with anhydrous nitric acid dissolved in organic solvents that do not enter into reaction with this acid, and which do not dissolve nitrocellulose. After being separated, the product is stabilized by ordinary methods. Nitrocellulose produced in this way is characterized by high purity and long-lasting stability.

Rogovin and his colleagues [50] nitrated cellulose by means of nitric acid dissolved in methyl nitrate. Nitrocellulose containing 13.7–14.0% N was obtained with the help of 2 parts of anhydrous acid added to 3 parts of methyl nitrate, allowed to react with the raw material for a period 2 hr at 35°C. Using nitric acid 95% a product containing 10.1% N was obtained under the same conditions. A large proportion of the nitrocellulose containing more than 10% N was dissolved in the nitrating solution. The product can be separated by precipitation with water.

NITRATION WITH NITRIC ACID IN THE PRESENCE OF INORGANIC SALTS

A series of investigations has been devoted to the problem of nitrating cellulose with nitric acid mixed with inorganic salts. Thus for example, Bouchonnet, Trombe and Petitpas [51] have established that the nitration of cellulose by means of anhydrous nitric acid containing an admixture of different salts may yield nitrocellulose with a high nitrogen content shown in Table 80.

TABLE 80

THE EFFECT OF NITRATING CELLULOSE WITH 100% NITRIC ACID IN THE PRESENCE OF DIFFERENT SALTS [51]

Salt	Content of salt in nitric acid, %	Content of nitrogen in nitrocellulose, %
No salt	—	13.3
NH_4NO_3	12	13.87
K_2SO_4	13–15	13.87
KH_2PO_4	20	13.87
$(NH_4)_2SO_4$	10	13.81
KNO_3	30	13.81
$NH_4H_2PO_4$	12–15	13.91

Hence salts exert a characteristic effect that brings about an increase in the nitrogen content of the nitrocellulose.

When 97% nitric acid was used with an addition of 14–16% potassium nitrate nitrocellulose containing 13.37% N was produced.

T. Urbański and Szypowski [52] obtained slightly different results on nitrating linters (98.6% of α-cellulose) by means of fuming nitric acid 98.6% HNO_3, with admixtures of different salts, as shown in Table 81.

TABLE 81

THE EFFECT OF NITRATING CELLULOSE WITH 98.6% NITRIC ACID IN THE PRESENCE OF DIFFERENT SALTS [52]

Salt	Content of salt in nitric acid, %	Content of nitrogen in nitrocellulose, %
No salt	—	12.85–12.90
$NaNO_3$	5	13.35
	9	13.26
KNO_3	5	13.20
	10	13.25
	20	13.07
	30	12.70
NH_4NO_3	5	13.32
	10	13.18
	20	13.02
	35	10.80
$Ca(NO_3)_2$	5	13.20
$Mg(NO_3)_2$	5	13.50
Na_2SO_4	4	13.52
$NaHSO_4$	5	13.42

The maximum nitrogen content of nitrocellulose was reached in these experiments when a 5% solutions of sodium, potassium or ammonium nitrate in nitric acid were used. The highest nitrogen percentage, i.e. 13.5%, was attained when using anhydrous salts that readily form hydrates, namely magnesium nitrate, $Mg(NO_3)_2$, and sodium sulphate, Na_2SO_4.

NITRATION WITH NITROGEN OXIDES

The investigations of Lunge and Bebie [15] made it clear that dinitrogen tetroxide, present in the mixed acid up to 6%, had no adverse influence on the degree of esterification of cellulose. It is known that dinitrogen tetroxide reacts in the presence of sulphuric acid so as to form one molecule of HNO_3 from one molecule of dinitrogen tetroxide:

$$N_2O_4 + H_2SO_4 \longrightarrow HOSO_2ONO + HNO_3 \tag{3}$$

Pinck [53] examined the nitrating activity of such a mixture, and obtained nitrocellulose with various nitrogen contents, rising to 13.36%, when nitric acid containing 15% N_2O_4 mixed with 95% sulphuric acid was used.

An important contribution was made by Rogovin and Tikhonov [54] who followed the nitration of cellulose by means of nitric acid including different quantities of nitrogen trioxide N_2O_3, dinitrogen tetroxide N_2O_4, or nitric anhydride N_2O_5. In every instance the degree of nitration was higher than could be achieved by nitration with nitric acid alone. The presence of nitrogen trioxide and tetroxide causes cellulose to de-polymerize during nitration. Because of this, the viscosity of nitrocellulose prepared in this way is lower than that made by esterification in the presence of nitrogen pentoxide. Likewise the stability of nitrocotton produced in the presence of N_2O_3 and N_2O_4 is lower than that of nitrocellulose yielded in effect of nitration accompanied by N_2O_5.

Nitration by means of 96% nitric acid enriched with 4% nitrogen pentoxide results in a nitrocellulose containing 13.7% N of good stability, while nitration with 96% nitric acid alone yields a product with 13.0% N. This has been confirmed by many research workers, using N_2O_5 in various ways for nitration. Thus Hoitsema [32] obtained nitrocellulose containing 14% N, while Berl and Klaye [24] produced one with 13.86% N. Lenze and Rubens [38], using nitrogen pentoxide dissolved in nitromethane, obtained nitrocellulose of 14% N. Dalmon, Chédin and Brissaud [55] showed that a solution of N_2O_5 in carbon tetrachloride produced nitrocellulose which contained 14% N.

T. Urbański and Janiszewski [56] have confirmed the results of their predecessors, using nitrogen pentoxide plus a small amount of nitric acid, intended for preparing a liquid nitrating solution. Within 40 min at 20°C or after 35 min at 45°C, a product containing 14.0% N was reached. This kind of nitrocellulose is characterized by its high stability.

Rogovin and Tikhonov [54] reported cellulose nitrated in solutions of nitrogen trioxide N_2O_3 in nitric acid formed the nitrates described in Table 82.

TABLE 82

THE EFFECT OF NITRATING CELLULOSE WITH SOLUTIONS OF N_2O_3 IN NITRIC ACID [54]

Concentration of N_2O_3 %	Nitrogen content of nitrocellulose %	Viscosity of a 2% acetone solution	Stability at 110°C hr
—	13.03–13.06	312	4.5
2	13.3 –13.4	—	4
3	13.4 –13.5	159	4
4	13.4 –13.5	96	1.75
10	9.6 – 9.4	12	1.33

On carrying out the nitration by means of nitric acid plus N_2O_4, these investigators observed results intermediate between the action of N_2O_3 and N_2O_5 (Table 83).

Examining the action of dinitrogen tetroxide alone in liquid or gaseous form, or dissolved in nitric acid, Shorygin and Khait [57] found that N_2O_4

TABLE 83

THE EFFECT OF NITRATING CELLULOSE WITH SOLUTIONS OF N_2O_4 IN NITRIC ACID [54]

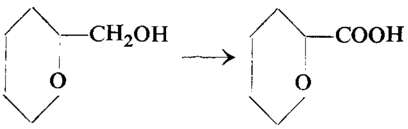
Concentration of N_2O_4 %	Nitrogen content of nitrocellulose %	Viscosity of a 2% solution in acetone	Stability min
—	13.0	312	240
2	13.35	150	—
4	13.65	175	150
10	13.65	193	90

caused considerable degradation of the cellulose, but no nitration. Only oxidation products of acid character soluble in sodium carbonate solution are formed under these conditions. Nitric acid with dinitrogen tetroxide dissolved in it gives nitrocellulose of a higher nitrogen content, if the content of N_2O_4 is kept within the limit of 20–30%. In the presence of a larger percentage of N_2O_4 the degree of nitration falls.

Cellulose regenerated by treatment with ammonium sulphide suffered extensive degradation on nitration in the presence of dinitrogen tetroxide.

Shorygin and Khait [57] first drew attention to the fact that cellulose brought into contact with nitrogen dioxide is converted into a substance totally soluble in alkali solution. This reaction was then investigated in more detail by Kenyon *et al.* [58] as well as by Rogovin *et al.* [59].

It has been made clear that the primary hydroxylic groups undergo oxidation, and as a result macromolecules comprising units of glucuronic acid are formed:



It is possible to oxidize all the CH_2OH groups to carboxylic groups, if the conditions of reaction are sufficiently severe, when the content of COOH may reach 25%. The product obtained in this way is a polyanhydroglucuronic acid, known as carboxycellulose or celluronic acid. When half the CH_2OH groups present in the cellulose are oxidized, a product with a 13% COOH content is obtained, soluble in dilute solutions of caustic soda, ammonia and sodium carbonate. Celluronic acid can form esters with nitric acid. The properties of these esters will be discussed later.

According to the more recent investigations of Nabar and Padmandabhan [60] and Nevell [61], and Kaverzneva, Ivanov, Salov and Kist [62] not only the primary alcoholic groups in cellulose molecules but also secondary ones undergo oxidation by dinitrogen tetroxide. Kaverzneva *et al.* have confirmed that N_2O_4 attacks primarily the carbon atom 6, oxidizing the groups CH_2OH to carboxylic groups.

Further, these authors assume that some carboxylic groups are formed by opening and oxidizing the pyran ring.

Oxidation of CHOH groups results, of course, in the formation of carbonyl groups, but the number of aldehyde groups formed is virtually nil. Kaverzneva and others have calculated that for every 100 anhydroglucose rings, 19 CO and 65 COOH groups are formed, but no more than 0.3 aldehyde groups. Such a product is unstable and tends to decompose readily in the presence of moisture or alkalis.

The content of nitrogen, which is all present in the form of ONO_2 groups, does not exceed 2.5% N.

Kenyon *et al.* [47] suggest that the action of dinitrogen tetroxide on cellulose proceeds in three stages:

(1) Nitric acid is produced by the chemical reaction of N_2O_4 and water, a small amount of which is present in the cellulose, formed in the course of oxidizing or nitrating cellulose:

$$2N_2O_4 + H_2O \longrightarrow 2HNO_3 + N_2O_3 \tag{5}$$

(2) Nitration of cellulose:

$$[C_6H_7O_2(OH)_3]_n + nHNO_3 \longrightarrow [C_6H_7O_2(OH)_2ONO_2]_n + nH_2O \tag{6}$$

(3) Hydrolysis of the cellulose nitrate produced and oxidation of the primary alcohol groups under the influence of nitrogen dioxide:

$$[C_6H_7O_2(OH)_2ONO_2]_n \xrightarrow{N_2O_4} [C_5H_7O_2(OH)_2COOH]_n \tag{7}$$

To show the effect of the percentage of dinitrogen tetroxide in the carbon tetrachloride solution on the nitrogen content and on the carboxyl group content of the reaction product, Kenyon reports the following data, collected in Table 84.

TABLE 84

$N_2O_4:CCl_4$ ratio	Nitrogen content, %	Content of carboxyl groups, %
1:1	0.32	21.1
1:2	0.33	12.8
1:3	0.35	9.3
1:4	0.37	7.6
1:5	0.39	7.4
1:6	0.40	7.0
1:7	0.40	6.3
1:8	0.39	5.9

The degree of cellulose oxidation decreases markedly as the concentration of N_2O_4 in the solution decreases. The nitrogen content, on the contrary, rises slightly as a result of the initial dilution, remaining constant during further decrease in concentration.

Other characteristics of the reaction of cellulose with nitrogen dioxide solution in carbon tetrachloride in the presence of anhydrous nitric acid, are shown in Table 85.

TABLE 85

Anhydrous HNO_3 parts	CCl_4 parts	N_2O_4 parts	Reaction time hr	Nitrogen content %	Content of carboxyl groups %
3.5	120	—	1	4.1	10.12
7.0	120	—	1	5.4	13.23
10.5	120	—	1	7.8	17.28
14.0	120	—	1	10.6	17.18
7.0	120	—	2	7.2	14.40
7.0	120	—	4	7.2	16.50
7.0	120	—	6	7.6	15.65
7.0	120	—	8	6.7	14.45
	60	60	2	0.58	11.94
	60	60	4	0.78	16.97
	60	60	6	0.76	19.33
	60	60	8	0.67	19.76
7.0	60	60	2	2.30	15.87
7.0	60	60	4	1.90	17.11
7.0	60	60	6	0.58	18.92
7.0	60	60	8	0.80	20.27

Cellulose oxidized by means of dinitrogen tetroxide can have surgical applications as a material for dressing wounds, since it is assimilated by the human body (Kenyon *et al.* [58]).

A nitrogen content of about 5.7% N can be attained after 1 hr on treating 5 parts of cellulose with 60 parts of dinitrogen tetroxide dissolved in 60 parts of carbon tetrachloride, mixed with 7 parts of anhydrous nitric acid. The relationship between the nitration time under the conditions mentioned above and the variation of nitrogen content of the product is shown in Fig. 128.

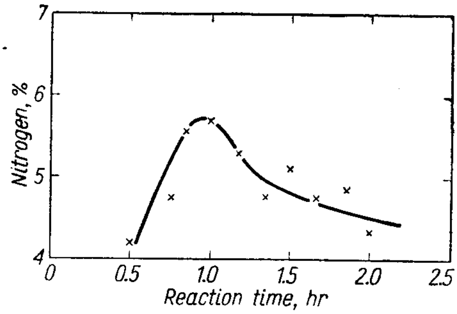


FIG. 128. Nitrogen content in nitrocellulose as a function of time of action with N_2O_4-HNO_3 solution. Ratio of reactants 5:60:60:7 (cellulose:N_2O_4:CCl_4:HNO_3) (Kenyon *et al.* [47]).

The shape of the curve indicates that after 1 hr, denitration begins.

Cellulose nitrated by fixed quantities of N_2O_4 and CCl_4, whilst the quantity of nitric acid varied from 0 to 40 parts, after one hour yielded products differing in nitrogen content. The highest nitrogen content was reached by adding 8–20 parts of nitric acid (Fig. 129).

Kaverzneva [63] and Nevell [61] have detected 1–1.5% of ketone groups (carbonyl groups), among the oxidation products of cellulose formed by oxidation of secondary alcohol groups.

The experiments cited are of great importance in practice. Mixed acids always contain a certain amount of nitrogen dioxide, hence the investigations described have disclosed the possibility that cellulose oxidation reactions may occur during nitrating. This may be regarded as confirmation of K. Smoleński's view (already mentioned, p. 229) that cellulose can be converted into pentosans through an intermediate stage involving uronic acids, more so, since it has been shown experimentally that the amount of pentosans could increase during nitration.

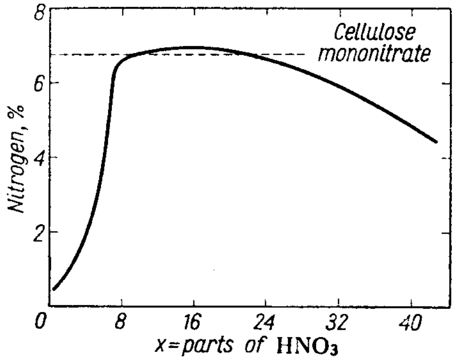


FIG. 129. Influence of the content of HNO_3 in nitric acid–N_2O_4 solution in CCl_4 on nitrogen content of nitrocellulose. Ratio of reactants 5:60:60: x (cellulose: N_2O_4:CCl_4:HNO_3) (Kenyon *et al.* [47]).

Celluronic acid nitrates (carboxycelluloses nitrates). Celluronic acid obtained by treating cellulose with nitrogen dioxide may then be esterified by means of nitric acid.

It has been found that even in the presence of a small number of carboxyl groups an appreciable change in the properties of the nitric ester is brought about, as compared with nitrocellulose.

To characterize the properties of the product obtained by esterifying celluronic acid with nitric acid, Rogovin, Treyvas and Shorygina [64] have reported the following numerical data, collected in Table 86.

These figures show that the nitric ester is scarcely soluble in a good solvent for nitrocellulose such as acetone when it contains 2 or 3% of COOH groups, i.e. one carboxylic group for 8–10 pyran rings.

In order to explain the low solubility of celluronic acid nitrates Rogovin *et al.*

TABLE 86

Carboxyl group content of the substance %	Nitrogen content %	Solubility in acetone %
1.56	13.5	18.2
3.6	13.0	9.7
8.0	11.5	13.2
18.5	7.0	2.5

suggest that cross-linkages are formed between the carboxyl and free hydroxyl groups, thus binding neighbouring molecular chains.

Due to partial substitution of the primary alcoholic groups by carboxyl groups, the strength of the glucosidic linkages joining the pyran rings is appreciably weakened, hence carboxycellulose containing 2–3% of COOH groups is de-polymerized if treated with dilute solution of alkalis even at room temperature.

NITRATION OF CELLULOSE IN THE GASEOUS PHASE

Investigations into the possibility of nitrating cellulose in nitric acid vapour on a commercial scale were first carried out by Deutsche Celluloidfabrik [65]. Later the process was described by Baker and Bateman [66]. The experiments were carried out as follows. Vapours of nitric acid, either at atmospheric pressure, or under reduced pressure of 20–90 mm Hg, or in a stream of carbon dioxide, were passed through a layer of cellulose at room temperature. None of these methods gave a product containing over 10% N, however, because the nitric acid was condensed on the cellulose fibres and gelatinized them. Better results were obtained by nitration with the vapours of nitrogen pentoxide in a stream of carbon dioxide, the products having a nitrogen content approaching 13.6% N. Even so, the surface of the fibres was gelatinized and the nitrated product was very non-uniform.

The next published paper was that of Berl and Rűff [67]. They treated cellulose by means of nitric acid vapours at 0°C for periods of 60–80 hr and attained a product containing only 4–8% N. From the X-ray diagrams, the authors concluded that a mixture composed of nitrated cellulose, non-nitrated cellulose, and Knecht compound (see p. 321) was formed. Later the question was investigated by Rogovin and Tikhonov [54] who subjected cotton to the action of vapours of 96% nitric acid. They have found that the time necessary to reach a specific nitrogen content by means of gaseous phase nitration was appreciably longer than that needed for nitrating in the liquid phase. Cellulose treated with liquid nitric acid of this concentration at 20°C yields a product of 12.65% N in $2\frac{1}{2}$ hr, whereas in the gaseous phase the same degree of nitration is scarcely achieved within 48 hr.

By nitrating cellulose by means of nitric acid vapours at pressures of 50–150 mm Hg and at temperatures from 38 to 65°C, Bouchonnet *et al.* [68] obtained products containing 10.9–13.7% N in periods of 15 min to 3 hr.

The most detailed research on nitration in the gaseous phase has been carried out by Wilson and Miles [69]. They concluded that there were no prospects of introducing this method in practice, since the nitrocellulose produced is non-homogeneous, and the nitration is inadmissibly slow. Thus, to reach a nitrogen content of 10% N by vapour phase nitration, at a vapour pressure of 16 mm Hg, a period of 48 hr was needed.

Similar conclusions have been reached by Champetier and Foëx [70] and by Trombe, Foëx and Champetier [71]. Wilson and Miles also studied the kinetics of nitration in nitric acid vapour. On the basis of these investigations they concluded that two molecules of nitric acid take part in the reaction with one OH group:

$$-OH + 2HNO_3 \longrightarrow -ONO_2 + HNO_3 \cdot H_2O \qquad (8)$$

Acid of the composition $HNO_3 \cdot H_2O$ is a strong denitrating agent and this may account for the difficulty in obtaining a highly nitrated product when using HNO_3 vapour. Instead of the ordinary equation of the second order

$$\frac{dx}{dy} = Ky^2$$

Wilson and Miles suggest the following second order equation for the rate of nitration with nitric acid in vapour phase:

$$\frac{dx}{dy} = K(y-r-s)^2$$

where s is the acid combined with the water formed and present in the fibre and r is a correction for the absorptive capacity of the nitrate groups in the cellulose, deduced from the determined absorption of nitric acid by fully nitrated cellulose.

Shoryghin and Khait [57] brought cellulose into contact with vapours of nitrogen dioxide at room temperature and obtained a product largely oxidized and degraded, that contained up to 3.2% N.

Dalmon [72] reacted the fibre of Chinese nettle (ramie) with nitric anhydride in a stream of dry air. Nitrocellulose containing as much as 14.12% N, i.e. cellulose trinitrate (within the limits of analytical error), was obtained. T. Urbański and Janiszewski [56] obtained a nitrogen content of 13.90–13.95% on repeating these experiments with cotton (linters) at 25°C.

The nitration of polysaccharides with nitrogen pentoxide in the gaseous phase has the advantage of not degrading the large molecule (Vollmert [73]).

During World War II, a method of two-stage cellulose nitration was used in Germany on a semi-plant scale (10 tons a month). Cellulose was first treated with air saturated with nitric acid vapours, and then the partially nitrated cellulose was immersed in 98% nitric acid. The initial treatment of the cellulose with vapours of nitric acid prevents the surface gelatinization that ordinarily occurs if cellulose is introduced direct into concentrated nitric acid. The product obtained in this way contained 13.65–13.8% N, and was very easy to stabilize since no sulphuric acid had been used in the nitration process.

According to a description by Buhs [74] the method was developed by Dietsch, Mesket and Hechler. See also [84].

NITRATION WITH NITRONIUM CHLORIDE

T. Urbański and Siemaszko [75] examined the nitration of cellulose with NO_2Cl in the vapour phase. Gaseous NO_2Cl was drawn through cellulose at 20°C for 4 hr, and the nitrocellulose than subjected to the usual treatment. A product with 12.2% N was obtained with 168% yield. The product does not contain chlorine. Its stability is higher than that of nitrocellulose of the same nitrogen content prepared by means of the usual nitrating mixture.

It is interesting to note that NO_2Cl dissolved in chloroform or carbon tetrachloride was a much less efficient nitrating agent and only yielded a product of 9.5–10.0% N.

KINETICS OF NITRATION. HEAT OF REACTION

It was demonstrated in the early investigations of Lunge [15] and Berl [31] (see pp. 327 and 341) and more recent work of Chédin and Tribot [76] on the nitration of cellulose that the nitration reaction proceeds very rapidly for the first few minutes, whereupon the rate decreases gradually, slowing down as the maximum nitrogen content is approached. At 20°C and above, this stage is reached within 20 min.

A striking example of the great rapidity of nitration, particularly in the first few minutes can be seen from the diagram by Spalding [76a] (Fig. 130). The figures

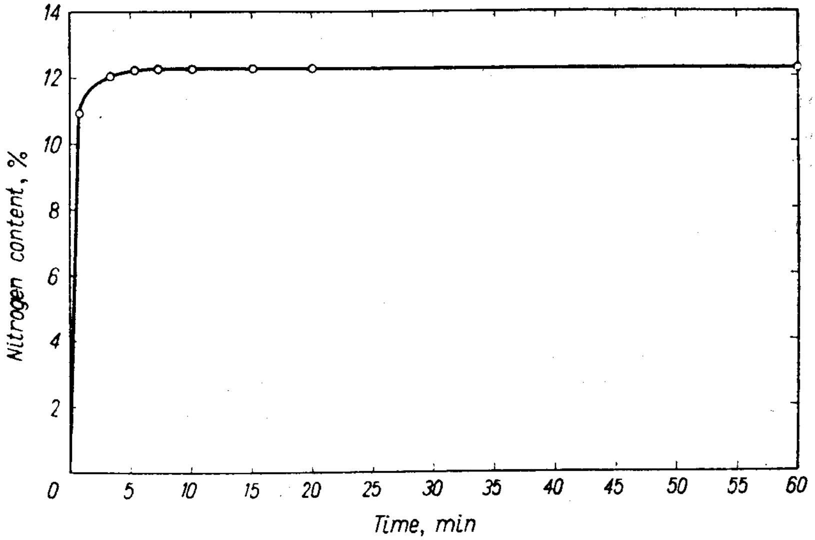


FIG. 130. Rate of nitration of cellulose in a laboratory dipping pot, according to Spalding, Hercules Powder Co. [76a].

refer to the nitration of cellulose with a mixed acid containing 21.0% HNO_3, 61.5% H_2SO_4 and 17.5% H_2O.

At a lower temperature the process is slower. Hence in order to bring about a thorough nitration in a short period, a more concentrated nitrating acid should be applied. The rate of nitration depends not only on the composition of the mixed acid and its temperature, but also on the rate of diffusion of the acid within the cellulose fibre.

Atsuki and Ishivara [77] have established that the rates of diffusion and of esterification are of the same order, but that diffusion proceeds more rapidly.

According to Sakurada [78] bleached cellulose is nitrated in a shorter time than an unbleached one since diffusion through the bleached tissue is quicker. Nitration was carried out at 0°C by means of a 1:2 mixture of nitric acid, density 1.52 g/cm^3 and sulphuric acid, density 1.84 g/cm^3. The results are shown in Table 87.

TABLE 87

THE EFFECT OF NITRATING BLEACHED AND UNBLEACHED COTTON (AFTER SAKURADA [78])

Bleached ramie-cellulose			Unbleached ramie-cellulose		
Time of nitration sec	Nitrogen content of nitro-cellulose %	Nitrate group number in one $C_6H_{10}O_5$ unit	Time of nitration sec	Nitrogen content of nitro-cellulose %	Nitrate group number in one $C_6H_{10}O_5$ unit
—	—	—	15	1.53	0.20
45	3.18	0.42	45	2.11	0.27
90	3.91	0.52	90	2.71	0.35
300	5.63	0.78	300	4.55	0.61
600	7.67	1.18	599	5.86	0.82
1800	11.07	2.00	1800	9.08	1.49
3600	12.65	2.48	3600	11.82	2.20
18,000	13.85	2.89	18,000	13.80	2.87

Taking into consideration the factor of diffusion Sakurada expresses the nitration rate of cellulose by the equation

$$x = kz^m$$

where: x is the amount of cellulose that has entered into reaction, z — the time of reaction, k, m — constants depending on the capacity of the acid to diffuse into the fibre. The kinetics of nitration of cellulose in nitric acid vapour was reported earlier (p. 354).

Recently Kunz *et al.* [79a] examined the nitration of pulverized cellulose and found it to be extremely rapid.

To emphasize the importance of diffusion into the solid phase as a factor affecting the nitration of cellulose, an observation of Hackel and T. Urbański [79] (see

p. 428) may be cited. Thus the nitration of starch by means of mixtures rich in nitric acid results in a higher nitrogen content than obtained from cellulose under corresponding conditions, because the starch is dissolved in such acids. (This has already been discussed on p. 341.)

A new concept of the mechanism of O-nitration of cellulose and denitration of nitrocellulose was recently advanced by Trommel [80]. On the basis of his experiments on the nitration equilibrium of cellulose he came to the conclusion that various reacting groups in cellulose and nitrocellulose molecules differ in their accessibility to nitration and denitration respectively.

The accessibility of the OH groups in cellulose is 96–99% when nitrated with mixed acids. The accessibility of ONO_2 in cellulose trinitrate on denitration is only *ca.* 70%. The latter value is much lower than the former because of the much higher crystallinity of the trinitrate compared with that of the lower substituted cellulose nitrates. The difference may explain why the rate of nitration is higher than that of denitration. The inaccessible regions in the nitration are to be attributed to cellulose "junction points" and in the denitration of cellulose trinitrate to trinitrate "junction points".

On the basis of his studies on the kinetics of the O-nitration of cellulose, Miles [8] concluded that the reaction of O-nitration of cellulose should be expressed as follows:

$$-OH + 2HNO_3 \rightleftarrows -NO_3 + HNO_3 \cdot H_2O \tag{9}$$

the water produced during the nitration being combined with a molecule of nitric acid.

Hence the equilibrium value can be expressed by the equation

$$K_1 = \frac{[-NO_3][HNO_3 \cdot H_2O]}{[-OH][HNO_3]^2} \tag{10}$$

Nitric acid hydrate exists in balance with its components. Therefore there is a further equilibrium value:

$$K_2 = \frac{[HNO_3 \cdot H_2O]}{[HNO_3][H_2O]} \tag{11}$$

Thus the final total equilibrium value of the process is expressed by the ratio

$$K = \frac{K_1}{K_2} \tag{12}$$

According to other investigations (Sendo [25], Kagawa [26]):

$$K = \frac{a_w}{a_n} \cdot \frac{a}{3-s} \tag{13}$$

where: a_n – the activity of nitric acid, i.e. the ratio of the vapour pressure of the nitric acid in the mixture to that of pure nitric acid;

a_w—the activity of water, i.e. vapour pressure ratio of the water in the mixture to that of pure water;

s —the number of nitrated hydroxyl groups for every C_6, in which for every anhydroglucose unit there are $3 - s$ non-nitrated groups.

Heat of nitration. During O-nitration of cellulose heat is evolved. Wilson, in 1937 [81] first carried out measurements of the thermal effects of this reaction with both nitric acid–water, and mixed acid.

The results of his measurements (in cal/g of cellulose) are summarized in Table 88.

TABLE 88

Final percentage of nitrogen %	Total heat evolved during nitration	Heat developed due to the change in acid composition		Heat of absorption by nitrocellulose	Heat of nitration (and $-\Delta H_n$ kcal/mole HNO_3)
		$-HNO_3$	$+H_2O$		
10.57	69.3	−10.1	33.0	26.7	19.7 (1.74 kcal /moleHNO_3)
13.28	111.4	−13.1	64.2	13.8	30.5 (1.86 kcal/mole HNO_3)

Kagawa [82] established that the heat of nitrating cellulose to 10.4% N is 77.5 cal per 1 g cellulose, from which he calculated the heat of nitrating one —OH group to be 2.11 kcal. Calvet and Dhers-Pession [83] reported a value of 2.0±0.2 kcal.

Kunz *et al.* [79a] determined the heat of nitration of pulverized cellulose at 0°C with nitric acid. They found it be 61.6 cal per 1 g cellulose or 1.696 kcal per one nitrated OH group.

The heat of nitration has been also calculated from the heat of combustion of nitrocellulose (Miles [8]), as 1.17 kcal per one hydroxyl group. Measurements of the heat of combustion are extremely accurate, hence this value appears to be close to the actual value although it differs considerably form the values obtained by direct measurement by earlier authors.

Temperature coefficient of nitration. Experiments have shown that in a moderate range, e.g. from 0 to 45°C, temperature affects the degree of nitration very little. A decrease in temperature usually results in some decrease in degree of nitration on a technical scale, where nitration time is limited, but this is because equilibrium is not reached, and the rate of the reaction is the governing factor. From a knowledge of the heat of nitration it should be possible to predict the course of the reaction from the known equation:

$$\frac{d\ln K}{dT} = \frac{\Delta H}{RT^2} \tag{14}$$

However, the experiments by Miles [8] do not confirm these thermodynamic calculations, due to our incomplete and faulty knowledge of the mechanism of the nitration reaction.

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CHAPTER XIII

NITROCELLULOSE MANUFACTURE

PREPARATION OF CELLULOSE MATERIALS FOR NITRATING

In the following section information is given about the industrial methods of obtaining cellulosic raw materials, such as cotton and wood pulp cellulose, for the purposes of nitration. The question is discussed more extensively in special handbooks devoted to the technology of cellulose. For this reason the description that follows will be limited to general information only.

The basic sources of raw material for the manufacture of cellulose are cotton, and wood cellulose.

COTTON

Cotton is the richest source of cellulose, since cotton fibres contain as much as 85–97% cellulose. Cotton consists of the nap covering the seeds of the cotton plant (*Gossypium*) which grows throughout the whole year in a warm, moderately damp climate (Egypt, southern areas and of United States, and U.S.S.R., India, and China Pacific Islands). The length, thickness and colour of the nap depend on the variety of the plant and on the climate in which it is cultivated.

Every cotton fibre consists of a single cell, filled with air and albumin residues, breakdown products of protoplasm. It also contains certain colouring matter.

Two kinds of cotton are obtained from the cotton plants:

1. Long fibre cotton 20–50 mm in length and 0.01–0.04 mm dia., which is the raw material for the textile industry. Waste from this cotton is utilized in the production of certain sorts of high viscosity nitrocellulose, e.g. dynamite nitrocotton.

2. Short fibre cotton, 10–20 mm in length, known as linters, which is the nap remaining on the surface of the cotton seeds after the long fibres of cotton destined for spinning have been separated. Short cotton fibres are separated from the seed by special machines and compressed into bales so as to reduce the bulk of the product to be sent for purification.

The purification of linters consists in removing all non-cellulosic substances, such as fats and waxes, lignin, proteins, non-cellulosic carbohydrates and mineral substances. The process is carried out in two stages:

(a) mechanical cleaning and (b) chemical purification.

The mechanical cleaning consists in passing the linters through toothed rollers, which remove the large types of foreign body. Thus the cotton is teased out on the rollers and transported by conveyer to autoclaves in which it undergoes chemical purification under pressure.

Linters in batches of about 3000 kg are kiered in a 1–3% solution of caustic soda for a period of 2–6 hr, at a temperature of 105–140°C. The access of air must be prevented during this operation. During kiering the fats and waxes are hydrolysed, pectins are decomposed, and at the same time hydrolysis and dissolution of the residual lignin in the chaff takes place. The duration and the temperature of treatment depend on the cleanness of the linters, and must also be correlated with the viscosity desired in the product. The higher the temperature and the longer the time of boiling the lower the viscosity of the cellulose produced and hence that of the nitrocellulose. After kiering is finished a large valve in the bottom of the autoclave is opened, the hot mass being expelled by the pressure within the autoclave into a double-bottomed tank. The upper false bottom acts as a strainer, on which the cotton is rinsed with a large amount of water until all traces of sodium hydroxide are removed. About 150 m^3 of water are consumed for 1 metric ton of linters.

The colour of cotton purified in this manner is pale to dark brown. The product is then bleached by means of chlorine or hypochlorite solutions at room temperature. Vats provided with a vertical stirrer or trough-shaped vessels with a horizontal or vertical stirrer are usually used for this purpose.

During chlorination, destruction of the colouring matter and further decomposition of other substances accompanying the cellulose proceeds, all these substances being oxidized by chlorine or hypochlorite.

The bleached cotton is thoroughly washed with water to remove residual chlorine and its compounds and then the alkalis are neutralized by acidifying with dilute sulphuric acid. The product is then rinsed again with water to remove the mineral constituents.

If the linters are to be used for the manufacture of particularly pure, white collodion cotton intended for production of varnishes or celluloid, it is necessary to remove any iron compounds from the cellulose. This can be carried out by washing the cotton with an oxalic acid solution, followed by a water rinse.

The results achieved by linters purification are shown in Table 89.

The moisture content of the raw linters is 5–10% depending on the climate of the country in which it is stored.

In general, linters are considered the best raw material for nitrocellulose manufacture, having the following advantages as compared with long-fibre spinning cotton: (a) low price, (b) easier handling, (c) shorter time of pulping the product preceding stabilization. The advantages (b) and (c) result from the fact that the linters are composed of short fibres.

If long-fibre cellulose is to be used as a nitration material then noils from combing machines or waste from a spinning mill are usually used. Such wastes are usually contaminated with lubricating oils and before the chemical treatment they should be

TABLE 89

THE EFFECT OF PURIFYING LINTERS

Components	Raw linters %	Purified linters %
α-Cellulose	75–85	99.0
Fats and waxes	0.5–1.0	0.2
Proteins	1.0–1.5	0.2
Mineral components (including iron compounds)	(0.06)	(0.002)
Hemicelluloses	5	0.3
Lignin	3	0.2

subjected to an extraction with petrol or other solvent, e.g. trichloroethylene or carbon tetrachloride. Subsequently they are boiled for a short period in dilute caustic soda solution so as not to lower the viscosity, since cotton with long fibres is used for manufacturing nitrocellulose of the highest viscosities. For the same reason such cotton is not usually bleached.

During alkaline kiering and bleaching, cellulose does not undergo purification only. Simultaneously a certain modification of its tissue takes place: it grows more spongy and permeable, and is therefore able to take up rapidly liquids such as mixed acid. This makes the process of nitration considerably easier.

In commercial specifications for cotton destined for nitration, the following approximate values are required:

moisture percentage	*ca.* 6%
mineral (as ashes), up to	0.5–0.7%
fats and waxes in average up to (oily places can contain up to 1%)	0.30%
mechanical impurities (determined by hand sorting of a sample) up to	0.01–0.02%
organic impurities, undergoing carbonization by conc. sulphuric acid, and insoluble in this acid, up to	0.75–1.0%
chlorine, free	absent
chlorine, bonded, determined in ash, up to	0.05%

WOOD CELLULOSE

The question of substituting wood pulp cellulose for cotton as a raw material in the production of nitrocellulose arose at the beginning of the present century due to the big increase in nitrocellulose manufacture, which was followed by an expansion in the demand for cotton.

A particularly acute shortage of cotton occurred in Germany during World War I, and wood pulp cellulose was widely used there for nitration, although the product was inferior in quality than that made from cotton. Towards the end of World War I (about 1918), due to the shortage of cotton in the U.S.A. (despite the very large production there), attempts were made to nitrate wood cellulose. They were accompanied by serious difficulties. It was found that wood pulp in the form of crepe paper tended to swell significantly in the course of nitration. After nitration the product retained much more acid than nitrocotton, while the yield of nitrocellulose was smaller, since from 100 parts of cellulose 120 instead of 150 parts of nitrocellulose were obtained. Nitrocellulose made from wood pulp and intended for powder manufacture, when dehydrated with alcohol, gave up its water with difficulty owing to its peculiar fibrous structure. Therefore, during the transition period the nitration of mixtures of linters and wood cellulose was widely practized in many countries. The mixtures are still in use for some rocket propellants where high mechanical properties are required.

Eventually, the problem of using wood cellulose as a nitration material was solved successfully during the interwar period, and during World War II, wood pulp cellulose was commonly used for nitrocellulose manufacture.

Raw wood contains 45–60% of cellulose. Morphologically this kind of cellulose is distinguished from cotton cellulose by the smaller size of its fibres. Chemically it is more reactive.

Spruce wood for example consists of the following components:

cellulose	55–56%
carbohydrates, other than cellulose	10–14%
lignin	20–30%
oils, resins, mineral matter	13–15%
albumins	0–0.7%

The separation of cellulose from the wood is carried out by one of three methods: the soda process, the sulphate process, and the sulphite process. Nitration cellulose is prepared chiefly by the sulphite and sulphate methods.

In the sulphite pulping process wood cut into pieces is subjected to kiering in a calcium bisulphite solution under a pressure of 3–8 kg/cm^2, at 120–145°C for 7–30 hr. The higher the temperature, the shorter the time of boiling. Substances accompanying cellulose dissolve in the liquor. Lignin is converted into a soluble lignin sulphonic acid. Cellulose is isolated from the solution, known as sulphite cellulose lye, and washed with water.

The sulphite process produces cellulose pulp readily bleached, pale in colour, containing a high percentage of α-cellulose and a low content of lignin and of pentosans. The large quantities of waste sulphite cellulose lye obtained as a by-product can be used for various purposes, i.e. alcoholic fermentation, production of fodder yeast, manufacture of tanning agents, production of vanillin, etc. Nevertheless, sulphite lyes in general cause much trouble, since the amount of liquor produced is usually larger than can be rationally utilized.

The average composition of crude cellulose sulphite pulp is as follows:

cellulose	85%
lignin	2%
pentosans	4%
hexosans	5%

The "sulphate" process consists in kiering pieces of wood in a solution composed of sodium hydroxide, sodium sulphide and sodium carbonate in a 65:15:20 ratio. The concentration of the solution is 10–12% of NaOH. Boiling at a temperature of 170–175°C under pressure lasts about 6 hr, of which 3 hr are required for heating, the other 3 hr being the kiering proper. Cellulose is then separated from the lye, washed with water, bleached, and subjected to final purification. The lye is condensed, evaporated to dryness, then sodium sulphate is added, and the whole is calcined. The sodium sulphate is thus reduced to sodium sulphide. Unchanged sulphate and the excess of carbonate are removed by addition of milk of lime.

The sulphate process yields cellulose pulp of high purity, though it contains more lignins. This pulp has a darker colour and does not undergo bleaching so readily. This is probably due to the presence of relatively stable, coloured sulphur compounds. Further, the content of undecomposed pentosans is higher in the sulphate pulping process than in the sulphite method. One of the advantages of the sulphate method lies in the recovery of the whole "sulphate lyes". When coniferous trees are used, certain amounts of turpentine and of "sulphate oil" ("tall oil") are also obtained.

Cellulose for nitration is subjected to bleaching and to final purification.

Bleaching. Crude wood cellulose is bleached by means of calcium or sodium hypochlorite in large tanks, "bleachers", equipped with stirrers. Bleaching cellulose is of great importance for nitrocellulose manufacture, particularly in the case of nitrocellulose intended for the production of smokeless powder. It is essential that the powder should be pale in colour, as a change in the colour of the powder often indicates decomposition. Similarly, cellulose destined for manufacturing collodion cotton, for varnishes, celluloid and film, should be carefully stripped of colour so that the final products are colourless.

Finishing wood cellulose. The finishing process is made to obtain a higher α-cellulose content and to endow the wood pulp with a shape conducive to easy nitration. This is the last operation prior to nitration. It consists in removing hemicelluloses, pentosans, and hexosans, which are undesirable ingredients of wood pulp. An insufficiently purified wood pulp may contain 5–6% of pentosans, straw cellulose even as much as 20%, whereas cotton does not contain more than 0.5–0.6%.

According to the present theory (e.g. Zherebov [1]) most of the hemicelluloses, pentosans and hexosans are removed during sulphitation, because calcium sulphite is capable of forming addition compounds with pentosans. Complete removal of hemicelluloses is only possible however after lignins have been removed, as lignin seems likely to be chemically combined with hemicellulose and thus with pentosans or hexosans. Only rupture of these bonds and the separation of lignins makes it possible to attack the non-cellulosic polysaccharides (Heuser and Haug [2]).

Generally after each operation including bleaching, the cellulose is washed with sodium hydroxide solution, so as to increase the content of α-cellulose.

The final purification is designed chiefly to remove pentosans, as these undergo nitration with difficulty to yield products of low nitrogen content that are insoluble or only partly soluble in organic solvents. Hence the presence of pentosans can have an adverse effect on the nitrogen content and solubility of the nitrated product. The imperfect solubility causes the solutions to be turbid, which is particularly detrimental in nitrocellulose for manufacturing varnishes and films.

A high proportion of lignin also reduces the solubility of nitrocellulose. According to Bryde and Rånby [3], the solubility in acetone is reduced only when the lignin content approaches 18%.

The physical nature of nitration cellulose is very important. In general it is prepared in the form of thin paper sheets, 16–20 g/m^2 in weight. It is also possible to produce wood cellulose in the form of loosened fibres resembling linters by "carding", i.e. tearing cardboard in two opposite directions.

The form of the cellulose affects its permeability to acid, and the retention of spent acid in the fibres. Schur and McMurtrie [4] report that wood pulp cellulose from coniferous trees retains the more acid, the larger the diameter of the cellulose fibres.

An extensive discussion, explaining which forms of cellulose are the most suitable for nitrating, appears in a paper by Schur and Hoos [5].

In Great Britain, according to the patents of Picton [6] small flakes of sheet wood-cellulose have been nitrated, while in the United States shredded cellulose prepared by the Stern method [7] was most widely used (shreds made of loosely felted cellulose fibres in a special machine). This last form of cellulose is especially suitable for uniform penetration and imbibition of the nitrating acid. Normal nitrators, as used for linters, are also suitable for nitrating this type of cellulose.

Wood pulp for nitration is made exclusively from coniferous trees, since it has been found that conifers give cellulose with long fibres, and hence mechanical losses are small.

OTHER SOURCES OF CELLULOSE

In the view of the limitations governing cotton growing and the necessity of preserving existing areas of woodland, the problem of finding alternative sources of cellulose for nitration other than cotton or wood cellulose, has received attention. To solve this question investigations were made at the turn of the present century, and later during World War. I. Experiments on the nitration of cellulose fibres from maize stalk, agave, hop, hemp, flax, alfalfa and ramie, have been described. The majority of these experiments were devoted to the nitration of expensive fibres, of high value in the textile or paper industry. It is clear that work of this kind could not receive great attention due to economic considerations, and the experiments were limited for the most part to the laboratory scale.

More important, from the practical point of view, was the extensive work of Pšenica [8] devoted to the question of nitrating fibres of cellulose isolated from nettle, fibres of little interest for the textile industry. By nitrating nettle cellulose in the same way as cotton, nitrocellulose containing 13.4% of nitrogen was produced, of adequate chemical stability provided the cellulose was well purified before the nitration.

Another cheap and readily available source of cellulose is the straw of annual plants. This raw material usually contains exceptionally large quantities of mineral matter. In order to separate cellulose the chlorine process is often used. It consists in treating the cellulosic raw material (previously boiled in a 10% sodium hydroxide solution and then in water) with chlorine. The decomposition of lignin, pentosans and other substances takes place and at the same time the cellulose is bleached. Crude cellulose prepared in this way contained 80–92% of α-cellulose and about 1% of mineral matter.

Naiman and Troitskii [9] have carried out extensive investigations to compare the nitration of cotton with that of cellulose differing in origin and purity from wood pulp, with hydrocellulose and oxycellulose, and with pentosans. The results are collected in Tables 90 and 91.

TABLE 90

COMPOSITION OF DIFFERENT CELLULOSIC RAW MATERIALS FOR NITRATION

No.	Material for nitrating	Cellulose content %	Copper number	Pentosans content %	Lignin content %	Fats, waxes content %	Ash content %
1	Cotton cellulose	99.55	0.06	—	—	—	0.08
2	Wood cellulose	98.50	0.59	1.38	0.36	0.23	0.20
3	Surgical cotton	98.86	0.49	1.43	0.37	0.24	0.12
4	Linters	99.38	0.13	2.14	0.10	0.37	0.36
5	Purified wood cellulose	96.08	0.29	2.90	0.02	0.21	0.44
6	Bleached wood cellulose	87.36	1.20	5.63	0.77	0.91	0.29
7	Unbleached wood cellulose	87.76	1.10	4.86	4.23	1.22	1.30
8	Bleached spruce paper	86.64	1.13	4.77	0.55	0.41	0.54
9	Unbleached spruce paper	87.90	1.14	4.93	1.61	0.57	0.88
10	Straw cellulose, bleached	71.96	1.39	27.45	2.78	0.27	3.25
11	Spruce sawdust	60.45	2.4	10.92	29.26	7.27	0.16
12	Cotton hydrocellulose	93.45	3.91	1.31	—	0.18	0.49
13	Oxycellulose	69.72	8.91	1.09	0.12	0.10	0.76
14	Pentosans	—	—	90.75	—	—	0.47

Nitration was carried out with acid of composition:

22.2%	HNO_3
68.5%	H_2SO_4
9.0%	H_2O
0.3%	NO_2

The ratio acid: cellulose was 60. The nitration was carried out for 1 hr at 15–18°C.

From the values obtained the deleterious effect of pentosans is noticeable since the presence of these compounds reduces the yield and the solubility of the product. The adverse effect of a high percentage of pentosans is less evident when only lower

TABLE 91

THE RESULTS OF NITRATING MATERIALS LISTED IN TABLE 90

No.	Nitrogen content %	Solubility %		Viscosity	Ash %	Yield %
		in ether–alcohol	in alcohol			
1	13.1	—	—	—	—	171.1
2	13.1	18.9	0.51	1.1	0.04	163.3
3	13.2	1.6	0.27	23.2	0.14	—
4	13.15	3.3	1.03	7.3	0.11	167.5
5	13.1	4.0	0.18	8.1	0.7	167.0
6	13.0	7.0	0.62	10.0	0.20	163.2
7	12.95	8.8	0.35	10.0	0.33	153.5
8	12.95	8.3	1.26	6.5	0.12	—
9	12.95	8.6	0.97	9.4	0.07	—
10	12.55	9.5	1.86	5.4	0.3	132.1
11	11.7	14.8	2.33	4.8	0.3	96.0
12	13.2	17.5	—	1.4	0.11	151.9
13	12.8	5.5	1.72	—	0.6	140.3
14	10.7	17.3	3.5	—	0.4	102.5

nitrated products are produced, probably because pentosans treated with less concentrated acids are decomposed by oxidation and hydrolysis, and dissolve in the acid.

Oxycellulose produces a product difficult to stabilize, in low yield. Hydrocellulose, on the other hand, yields a product more soluble in ether–alcohol mixture, and containing more nitrogen than the nitrated oxycellulose.

From their experiments Naiman and Troitskii concluded that wood pulp cellulose should be subjected to specially careful purification before nitration.

More recently attempts to nitrate viscose fibres have been reported, e.g. Newman [10], Okajima, Hayama, Watanabe [11] nitrated viscose fibres by means of a mixture containing nitric acid and acetic anhydride.

DRYING CELLULOSE BEFORE NITRATION

Cotton or wood pulp as delivered to nitrocellulose plants contains 6% or more of moisture. This moisture should be removed prior to nitration so that it does not bring about any dilution of the mixed acid and thereby change the course of the reaction. Cotton is usually transported in the form of compressed bales, which are opened and shredded before drying. Wood cellulose, in the form of pressed cellulose pulp or of crepe paper, is dealt with similarly. Dryers for dehydrating cotton or cellulose may be of various types. The simplest is the shelf drier, equipped with mechanical ventilation and heaters situated at the bottom, supplied with water or steam so as to maintain a temperature of 80–100°C inside the drier.

More thorough and quicker drying is attained in the formerly widely used Schielde semi-continuous driers. A simple design of this type of drier is shown in Fig. 131. It comprises two drying chambers I and II, separated by partitions. The whole is made from sheet-iron. In the lower part of one chamber and between the chambers heaters are installed. Air sucked from above by means of a ventilator enters one of chambers (I) from underneath and is heated there. Flowing upwards, it passes a range of shelves on which cellulose material is spread. Subsequently the air passes via the central heater to the other chamber (II), where again it flows upwards and escapes through a ventilator.

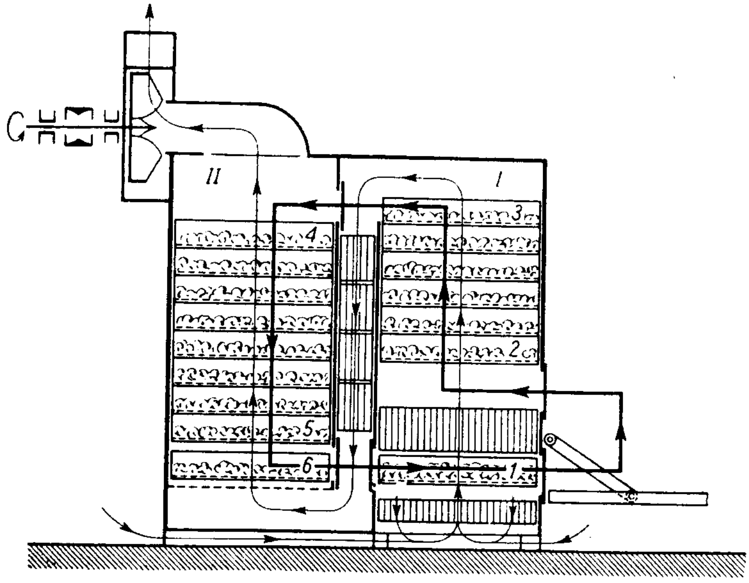

FIG. 131. Schielde drying oven for cellulose.

Cotton or wood cellulose is introduced into an iron box *1* equipped with a metal mesh bottom occupying the outside position. By means of a chain and sprocket mechanism the box is moved in position *2* and later to the position *3*. Meanwhile another box *1* is loaded and so on. Finally the box from position *3* is transferred to the neighbouring chamber, position *4*, to be shifted gradually downwards to the positions *5* and *6*, and thereafter to the position *1* and outside again. There the dried cotton is unloaded and replaced by a fresh batch. Drying cellulose in chamber (I) is co-current process, while in the chamber (II) a counter-current process is carried out. The movement of shelves carrying the cellulose is marked as a thick line, while a thin line indicates the direction of air.

A continuous drier of the Petrie type is outlined in Fig. 132. This drier is a sheet-iron box about 4.5 m high, about 6.0 m long, and 1.25 m wide. In this box five or six slatted shelves are constructed. Between the slats a system of movable slats is arranged so as to propell the cotton in one direction, by a series of upward and forward movements. After each forward movement the slats are lowered and return

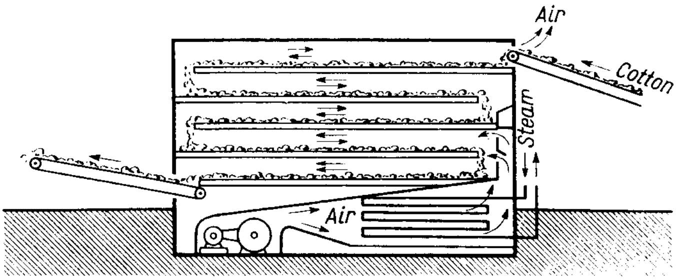

FIG. 132. Petrie drying oven for cotton.

to their original position, to repeat the cycle. In this way wet material falling from a conveyer onto the uppermost shelf of the drier is gradually pushed towards the lower shelves, till it ends on the bottom conveyer which removes the dried material.

Air, blown through a steam heater situated in the lower part of the drier, is warmed and then flows to the upper part of the unit in co-and counter-current with the cotton. It has been found that application of the counter-current principle can readily cause a blockage in the lower part of the drier.

The Petrie drier is unsuitable for drying wood pulp in the form of thin paper sheet, as such a material is readily carried away by the air stream, the mechanical device alone is not sufficient to shift cellulose of this sort.

Among other systems of driers, continuous apparatus transporting cellulose on a conveyor belt in a stream of warm air are widely used (Fig. 133).

During World War II pneumatic driers of cellulose were developed in Germany and they are in use in modern industrial practice. They are based on the

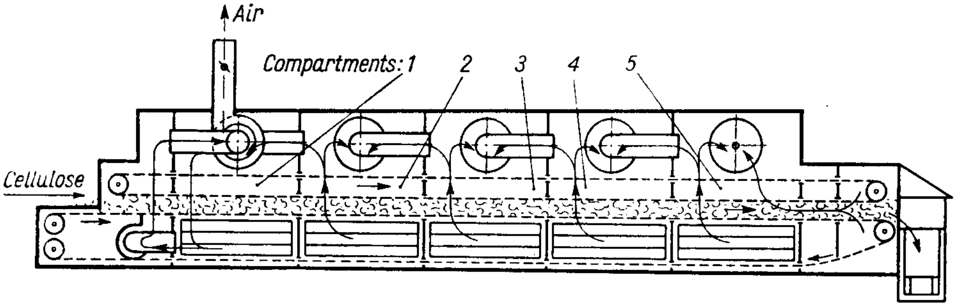

FIG. 133. Diagrammatic presentation of Hass drying oven [12].

principle of introducing cellulose into a stream of hot air. Air is heated to 110°C and cools down to 80–90°C when contacting cold cellulose with the normal moisture content (6–8%). The stream of air with cellulose enters "a cyclone" where the air velocity is rapidly reduced and the cellulose falls down. A diagrammatic presentation of pneumatic drier is given in Fig. 134. Air filtered through (*1*) is blown by a fan (*2*) into a heater (*3*). Cellulose enters (*4*) and passes with air along the wide pipe to a cyclone (*5*). From here moist air leaves (*6*) and dried cellulose falls through (*7*).

The advantage of pneumatic driers is that they serve both for drying and transporting the cellulose. Drying is very quick.

The disadvantage of the method is that it is difficult tolower the moisture content below 2% (this is the consequence of the co-current system). Also the air consumption is high (*ca.* 10 m^3/kg of cellulose). This is much higher than in ordinary mechanical driers.

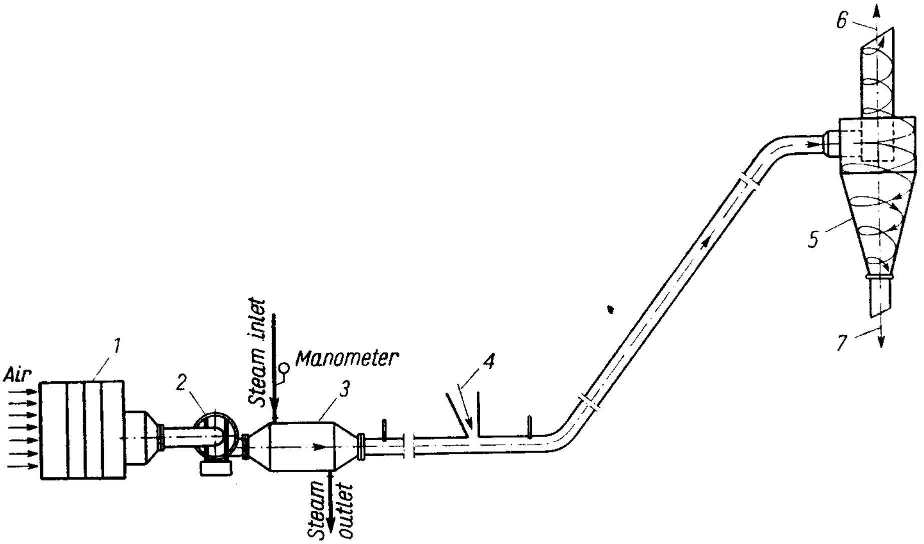

FIG. 134. Cellulose drier with a pneumatic transport [12].

Cellulose material, such as cotton or wood cellulose, is dried until the moisture content is below 1%, or in the pneumatic drier to *ca.* 2%, and then loaded into sealed sheet metal containers or bags, to cool to room temperature.

Care should be taken that the temperature inside the driers does not exceed 105–110°C, as otherwise the material may ignite. Further, there exists a danger of inflammation of the cotton dust present in the air, for it can be kindled by static electricity. For this reason both the driers and all auxiliary equipment must be earthed.

INDUSTRIAL NITRATION OF CELLULOSE

The types of nitrocellulose produced commercially and their properties are listed in Table 92.

Data on the viscosity of different types of nitrocellulose, particularly varnish nitrocellulose have been given above (see p. 277).

TABLE 92

TYPES OF NITROCELLULOSE

Nitrogen content	Amount of NO	Solubility	Name of nitrocellulose type	Specific gravity
%	cm³/g subst.			
13.45–12.9	214	Insoluble both in alcohol and in ether–alcohol, soluble in acetone and ethyl acetate	Guncotton, coton-poudre No. 1, (CP_1), nitrocellulose No. 1 (NC_1), Schiessbaumwolle S (13.2–13.4% N)	1.659–1.654
12.6–12.8	203	Partly soluble in ether–alcohol	Pyroxyline, pyrocollodion cotton, pyrocellulose	1.653
12.3–11.0	196–176	Soluble in: ether–alcohol, acetone, ethyl acetate, insoluble in alcohol, soluble in nitroglycerine	Collodion cotton (colloxyline), coton-poudre No. 2 (CP_2), nitrocellulose No. 2 (NC_2), Schiessbaumwolle PE (11.3–12.6% N)	1.653
10.5–10.0	162	Soluble in alcohol and other organic solvents	Low-grade collodion cotton	

MIXED ACIDS

Clearly composition of the nitrating acids used to nitrate cellulose depends on the type of nitrocellulose required. Nitrocellulose showing specific properties can be produced by means of mixed acid of widely different composition. Hence the composition of the nitrating acid should be chosen to secure the most advantageous operating conditions, as for instance the most economic mixture with the highest safety factor during nitration. The use of mixtures of high nitric acid content increases the risk of the product igniting during nitration.

In practice the H_2SO_4 to HNO_3 ratio ranges from 2.5–3, while the water content should be varied according to the required degree of nitration, the solubility of nitrocellulose, etc.

For manufacturing high nitrated guncotton (coton-poudre No. 1 or CP_1 in France, Schiessbaumwolle S in Germany) the mixed acid should contain 5–13% of water. For the production of lower nitrated guncotton (coton-poudre No. 2 or CP_2 in France, Schiessbaumwolle PE in Germany) 15–20% of water is used and for collodion cotton 18–25%. A more or less exact rule is that varying the water content by 0.5% causes the nitrogen percentage of the nitrocellulose to vary by about 0.1–0.2%. The quantity of acid to be used for the nitration of cotton or wood pulp cellulose is chosen so as to make it possible to saturate the cellulosic material with acid quickly and uniformly. The composition of the mixture changes during nitration owing to the consumption of nitric acid and the production of water during the reaction. Hence a large excess of acid should be used, so that the change in its composition is negligible during nitration and hence a more uniform nitration is achieved. The use of a large excess of acid also makes it possible to use a less concentrated acid, as the dilution during nitration is relatively less.

The ratio of cellulose to acid used in practice ranges from 1:40 to 1:60, and in exceptional cases may be 1:80. A larger excess of acid is also recommended for nitrating poor quality material, which is much more difficult to wet with mixed acid.

The cellulose to acid ratio also depends on the method of nitration. Thus if nitrators equipped with mechanical stirrers are used, the nitration proceeds quietly and evenly so that a smaller excess of acid can be used.

The exact composition of mixed acids and the cellulose to acid ratios are included in the detailed descriptions of particular methods of nitration.

Economy in the consumption of acid in a nitrocellulose plant is achieved by fortifying the spent acid with concentrated nitric acid, sulphuric acid and oleum (see Vol. I) for further use.

The loss of acids is due mainly to the ability of nitrocellulose to retain a considerable amount of waste acid after being centrifuged. It has been established that 100 kg of nitrocotton retain as much as 100 up to 150 kg of acid. In addition, there is some loss in handling, and a further loss of acid vapours, mainly those of nitric acid, carried away by the ventilation air.

NITRATION IN POTS

The oldest method of nitrating cotton consisted simply in immersion in acid. The cotton was allowed to remain for a certain time in the acid and then the combined charge of a dozen pots was transferred to a centrifuge to separate the nitrocotton.

An improvement to the pot method was introduced by Abel. It consisted in dividing the process of nitration into two operations. First the cotton was immersed for a short time in a very large volume of acid. Then it was removed and transferred to pots in which the cotton was nitrated slowly by the acid taken up in the first operation.

About 200 kg of nitrating acid mixed in the ratio indicated in Table 93 are used for each charge.

The temperature of the acid at the beginning of the process lies within 20 and 25°C, and as the nitration proceeds, it may rise to 30, or even 35°C if there is no cooling. 800–900 g of cotton are introduced rapidly into the vessel containing acid, and pressed down to the bottom. To facilitate this operation, the cotton is held with tongs. It is removed after some 5–6 min. Subsequently it is laid on the net attached to the upper edge of the pot and the excess of acid is pressed out of the cotton (which is already nitrated to some extent), by means of an aluminium spade operated by a handle (Fig. 135). The cotton still contains 9–12 times its weight

TABLE 93

THE POT PROCESS FOR PRODUCING GUNCOTTON

Type of nitrocellulose	Composition of the acid	HNO_3	H_2SO_4	H_2O	NO_2
CP_1	mixed acid	15.5	72.5	11.5	0.45
	spent acid	12.3	74.2	13.0	0.48
CP_2	mixed acid	16.5	65.5	17.5	0.50
	spent acid	14.3	66.5	18.5	0.70

of acid after pressing. It is transferred into the covered stoneware or aluminium pot standing nearby, and a series composed of several pots is transported on a truck to concrete basins, to be cooled with running water (Fig. 136).

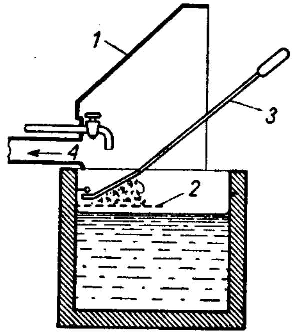

FIG. 135. Nitration pot according to Abel (no cooling jacket is shown): *1*—fume hood, *2*—net, *3*—aluminium spade with a handle, *4*—ventilation pipe.

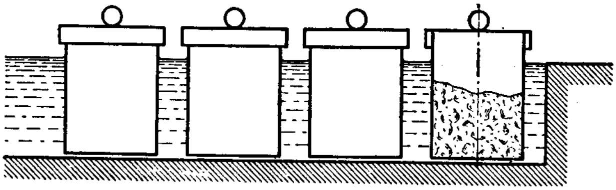

FIG. 136. Nitrating pots for "ripening" of nitrocellulose.

Here the nitrocotton ripens for the following period:

CP_1	for 6–10 hr
CP_2	for 3– 4 hr

Spontaneous decomposition of the nitrocotton may occur during the process of ripening, provoked by a variety of causes, e.g. the entrance of water into the pots due to careless handling or to a defect in the pot itself, such as a crack, or the use of too warm cooling water in the summer, which permits the temperature in the pot to rise.

After the ripening is finished the contents of a dozen up to twenty pots, i.e. about 25 kg of guncotton, are transferred to a centrifuge to extract the excess of acid. The content of acid is reduced in this way to some 100–150%. Safety precautions during centrifugating and the removal of the centrifuged guncotton are described later.

After the cotton has been removed from the nitration tank (Fig. 135) the composition of the acid in the tank is adjusted so that in quantity and strength of it remains unchanged throughout. The waste acid from the centrifuge is low in nitric acid. The regeneration of this spent acid by addition of oleum and fresh nitric acid is uneconomic. Spent acid is denitrated.

According to French data the consumption of raw materials in the production of 100 kg of guncotton CP_1 (coton-poudre No 1) is as follows:

cotton	63 kg
nitric acid	126 kg
sulphuric acid	123 kg

From 100 parts of cotton, 159 parts of guncotton are obtained. The consumption of raw materials for the manufacture of lower nitrated (CP_2) nitrocotton is less economic.

The pot process of nitration is very simple, no elaborate plant is required, and it can be used for nitrating low grade cotton. Because of the long nitration time it is possible to make use of nitrating mixtures containing little nitric acid, thus reducing the hazards involved in nitration and centrifugation.

A disadvantage of this method is that it involves handling small amounts of raw material, and therefore labour requirements are high. The output per worker per 8-hour shift is only 40 kg of guncotton. The unhealthy working conditions are a serious drawback; the atmosphere is contaminated by nitrous fumes, which escape because the reaction vessels are not tightly closed.

Although the pot process should be considered as obsolete and not competitive with more modern mechanical nitrators, it may still be considered as an auxiliary method, useful when it is necessary to organize production quickly and for a low outlay or when cellulose of low grade must be nitrated.

The pot process was widely used in Russia, France and Great Britain, during World War I.

CENTRIFUGAL NITRATION

For a long time nitration of cellulose in a centrifuge was the commonest method used in all countries. The process developed as a result of the centrifuge constructed by Selwig and Lange [13] that produced considerable amounts of nitrocellulose from one charge during a relatively short time.

The centrifuge shown in Figs. 137 and 138 is the principal unit of the plant.

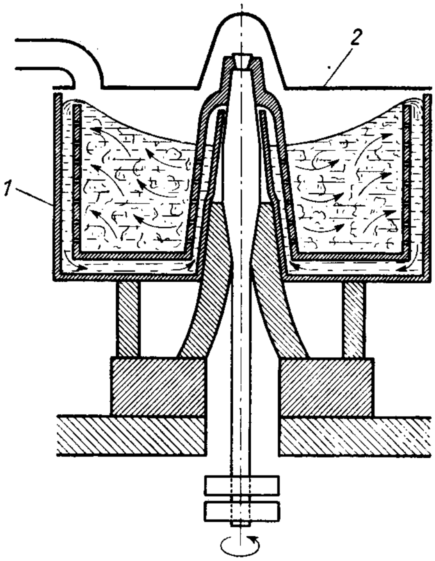

FIG. 137. Diagram of a nitration centrifuge of Selwig and Lange, according to Pascal [14].

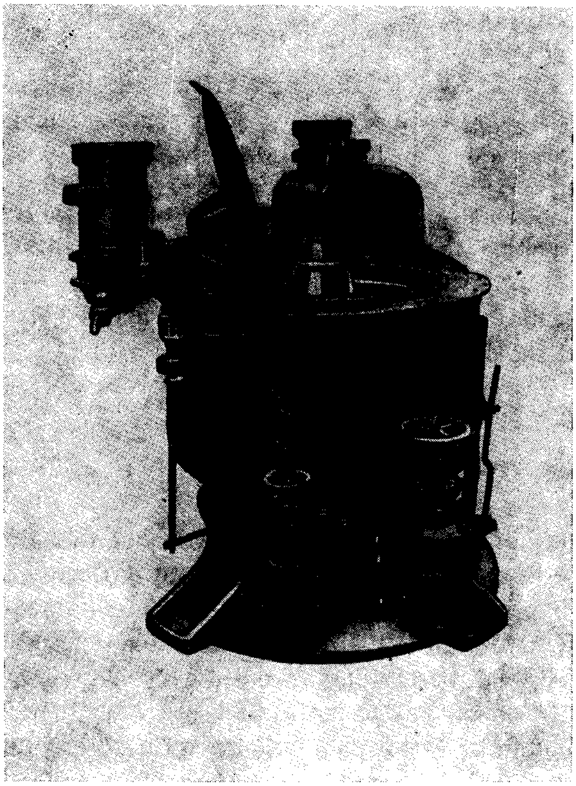

FIG. 138. Nitration centrifuge of Selwig and Lange [13].

The nitration centrifuge is a cylindrical steel vessel (*1*), 0.55–0.65 m high and 1.1–1.3 m dia., suspended on a fixed support erected on a strong foundation. Inside the vessel there is a basket of stainless steel sheet with 5 mm perforations, mounted on a rotating vertical shaft. It is made in various sizes: diameter 1.0 m, height 0.4 m (small model) or diameter 1.2 m, height 5.5 m (large model). An important constructional detail of steel vessel (*1*) is the protection of the shaft against corrosion by the nitrating acid. The shaft can run at both high and low speeds. The whole is closed at the top by an aluminium cover (*2*), equipped whith an exhaust duct through which acid vapours are removed. Acid is fed in and removed through a pipe in the bottom of the vessel (not shown in the sectional view) which is branched to connect with: (a) the metering tank for the mixed acid (inflow), (b) the spent acid tank (outflow).

The process of nitration is carried out as follows: according to the size of centrifuge, either 600–650 kg or 1000–1200 kg of nitrating acid mixed in the ratio given in Table 94 are introduced into the centrifuge.

TABLE 94

THE CENTRIFUGAL NITRATION PROCESS OF GUNCOTTON MANUFACTURE IN FRANCE [14]

Type of nitrocellulose	Composition of the acids	HNO_3	H_2SO_4	H_2O	NO_2	Specific gravity (at 15°C)
CP_1	mixed acid	21.25	66.25	120	0.50	1.738
	spent acid	18.75	67.50	13.2	0.55	1.734
CP_2	mixed acid	20.00	61.75	17.5	0.75	1.694
	spent acid	17.30	63.30	18.6	0.80	1.692

In the manufacture of high nitrogen guncotton (13.45% N) a more concentrated mixed acid should be used, composed of:

HNO_3	22.1%
H_2SO_4	68.4%
H_2O	8.5%
NO_2	0.5%

The temperature of the acid for the production of this nitrocellulose should be 20–30°C, while in the production of lower nitrated guncotton (CP_2) a temperature of 25–33°C is permitted. The acid is maintained at the required temperature in special tanks (temperature stabilizers) situated above the metering tanks. The stabilizers are heated with warm water or cooled with cold water, usually by means of a coil.

A charge of cotton or wood pulp cellulose of 11–15 kg for a small unit or 20–22 kg for a large one is immersed in the acid so that it is rapidly and evenly distributed in the basket.

This task is carried out by means of a special aluminium or aluminium tipped steel fork. Local overheating followed by decomposition of the nitrocellulose can occur at the boundary of the acid-wet and dry substance, if immersion is not uniform. This danger is particularly liable to occur with insufficiently purified cellulose, which does not readily take up the mixed acid.

The cotton to acid ratio should lie within the limits 1:40 to 1:60. The most widely used range is 1:50 to 1:55.

After the centrifuge is loaded it is shut, and put in motion at about 20–25 r.p.m. for a period of 20–45 min.

The rotatory movement forces the acid to circulate through the appertures in the basket into the fixed outer case whence it flows down, below the basket towards the shaft and so back into the basket again. Due to the circulation of acid uniform and rapid nitration is achieved.

It has been demonstrated experimentally that the maximum nitrogen content of the product is attainable in this process yet within 15–20 min. For the time of nitrating cotton in a centrifuge at 25°C, Pascal [14] reports the figures listed in Table 95.

TABLE 95

THE TIME OF NITRATING COTTON IN A CENTRIFUGE (AFTER PASCAL)

Time min	Nitrogen content in CP_1 %	Amount of unnitrated substance %	Nitrogen content in CP_2 %	Amount of unnitrated substance %
5	11.75	5	10.95	10
10	12.93	—	11.30	—
15	13.10	—	11.65	—
20	13.10	—	11.95	—
25	13.10	—	—	—

After nitration is finished, the centrifuge is run at high speed (1000–1100 r.p.m. for the smaller centrifuge or 600–800 r.p.m. for the larger unit), in order to separate the nitrocotton from the spent acid. The nitrocellulose obtained still contains 100–150% of spent acid. After 5–7 minutes' centrifuging, the nitrocellulose is removed by means of aluminium forks, as illustrated in Fig. 139.

During nitration nitrocellulose occasionally catches fire. It has now been made clear that these accidents are caused mainly by the nitrocellulose's greater absorptive power for HNO_3 than for H_2SO_4 from the spent acid (p. 327). As the result, the composition of the absorbed acid differs from that of the liquid phase and corresponds to a higher degree of nitration. The acid retained by the nitrocellulose causes secondary nitration during centrifuging, a phenomenon which is accompanied by the development of a certain amount of heat. Towards the end of nitration, there is

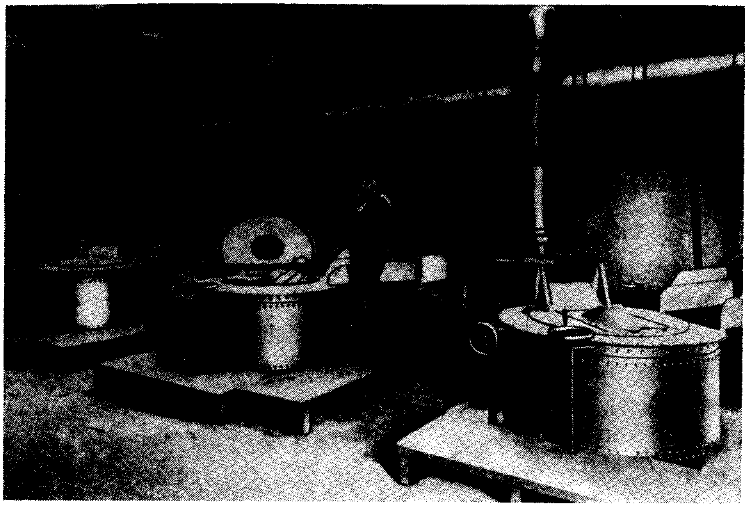

FIG. 139. General view of nitration centrifuges. Discharge of nitrocellulose with aluminium forks (Bofors Nobelkrut, Sweden).

no large volume of acid left to play the part of a thermostatic liquid. Hence the temperature of the product may rise sufficiently to provoke self-ignition. Spontaneous ignition of this kind is particularly frequent while manufacturing higher nitrated guncotton during the summer. Insufficiently purified cotton or wood cellulose catches fire more easily than a pure material owing to decomposition of the impurities or to uneven nitration.

Other stimuli can also cause nitrocellulose to ignite: a drop of lubricant, or a drop of water falling upon the centrifuged nitrocotton, e.g. off the wet fork, may cause a fire, rapid decomposition or even explosion.

Further, too much haste to unload the product by means of the fork, before the centrifuge has stopped, may bring about an explosion, due to the friction between the fork and the inner surface of the moving basket. The use of a steel fork is particularly dangerous and has caused many accidents.

If the decomposition is not of a rapid character, then it can be controlled by immediately pouring cool acid into the centrifuge.

As a precaution should fire occur, the workers should be provided either with protective helmets, equipped with a fresh air supply, or with masks and absorbers, and they should also wear protective clothing of asbestos or thick wool. If a violent fire occurs, the building must be evacuated, since to remain in an atmosphere containing a high concentration of nitrogen dioxide, even for a short time, is very dangerous. This is discussed in more detail on p. 407.

The centrifugal nitration process is reasonably economic. However, it requires well instructed personnel, it is troublesome for the workmen, and its electric power requirements are high.

For each centrifuge, two workers are required, and the rated output per hour of the smaller type centrifuge is 35 kg of nitrocellulose, but taking into account delays and minor repairs, the average hourly output rarely exceeds 30 kg of nitrocellulose, i.e. 120 kg of guncotton per man per 8-hour shift.

According to French calculations dating from World War I, the consumption of raw materials and the power requirements per 100 kg of guncotton produced was:

cotton	61 kg
HNO_3	140 kg
H_2SO_4	81 kg
electric power	6.5 kWh

During World War I attempts were made to recover the absorbed nitric acid from the guncotton after centrifuging, by washing with sulphuric acid. No satisfactory results were attained, however as the sulphuric acid failed to penetrate deeply into the closely packed layer of nitrocellulose, and the quantity of recovered nitric acid was insufficient to cover the cost of the operation.

However, during World War II a method of recovering nitric acid by washing the nitrocellulose in the centrifuge was taken out in Germany, covering the use of spent acid, as will be discussed later (see p. 390).

After being spun in the centrifuge the nitrocellulose is transported via a stoneware channel to a neighbouring shop, in which the preliminary stabilizing operations, i.e. water washing, is carried out.

Usually two centrifuges are connected to a common channel, as shown in Fig. 140.

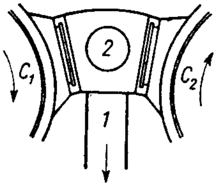

FIG. 140. Diagram showing two centrifuges combined with a drowning trough: C_1 and C_2—two centrifuges, *1*—ventilation pipe, *2*—syphon, according to Pascal [14].

The channel comprises a stoneware funnel, having a collar through which a powerful stream of water enters from different sides, and a stoneware pipe with a U-bend to form a siphon, sketched in Figs. 141 and 142. The diameter of the pipe should be at least 30 cm. Above the funnel there is a hood connected with the fume ducting system. Nitrocellulose is carried by the water flowing down the channel, and thus transported to the next building.

It is extremely important to supply the runway with an abundant quantity of water when the nitrocellulose is introduced. Explosion may occur if nitrocellulose is unloaded from the cetrifuge to the trough while the latter is empty due to an oversight by the worker, or to an interruption in the water inflow. The explosion is caused by the contact between the acid nitrocellulose and the small amount of water remaining in the channel after the preceding load was emptied.

In order to avoid such dangerous errors, automatic safety devices may be incorporated, so that for instance, the cover of the channel cannot be opened unless a full stream of water is flowing through it.

The consumption of water is large, amounting to some 120–150 l. per 1 kg of guncotton.

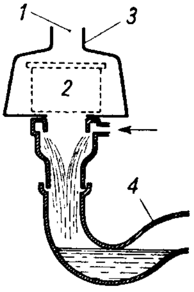

FIG. 141. Diagram of the drowning trough: *1*—ventilation pipe, *2*—aperture to discharge nitrocellulose, *3*—fume hood, *4*—syphon, according to Pascal [14].

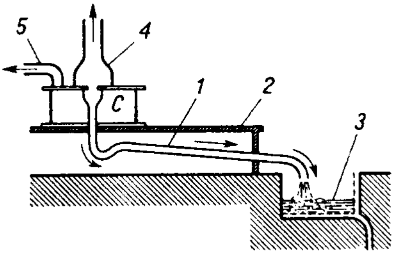

FIG. 142. Diagram of the connection of a centrifuge (*C*) with a drowning trough: *1*—syphon, *2*—service platform, *3*—trough, *4, 5*—ventilation pipes, according to Pascal [14].

THOMSONS' METHOD

The process patented by the Thomsons in 1903 (J. M. Thomson and W. T. Thomson [15]) was used only in Great Britain, though during World War I it was used to a lesser extent also in France. It has now been superceded by the use of nitrators with mechanical stirring.

The principle features of Thomsons' method are: (*1*) immersing the cotton in the acid, and (2) after nitration washing out the acid with water.

The nitrator sketched in Fig. 143 is a cylindrical stoneware vessel of internal diameter 1.1 m and depth 0.4 m, strengthened with an iron belt. Its conical bottom is fitted with an outlet pipe. A three-way valve is provided for evacuating and filling the vessel with acid. Inside the vessel there is a perforated stoneware plate to support the cotton charge. Twenty five to twenty nine centimeters above this plate supports carry a perforated aluminium plate 15 mm thick, which acts as a false

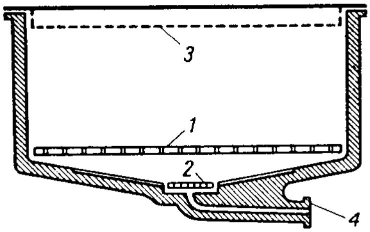

FIG. 143. Diagram of Thomsons' nitrator: *1*—perforated bottom plate of stoneware, *2*—filtering stoneware plate, *3*—perforated aluminium plate, *4*—discharge pipe, according to Pascal [14].

bottom. The nitrator is covered with an aluminium hood connected to the fume duct. The units are grouped in batteries of four nitrators.

Nitration in the Thomsons' plant is carried out as follows. Some 500–540 kg of nitrating acid mixed in the ratio reported in Table 96 are introduced from beneath into the vessel.

TABLE 96

THE NITRATION OF COTTON BY THE THOMSONS' METHOD, AS APPLIED IN FRANCE [14]

Type of nitrocellulose	Composition of the acids	%			
		HNO_3	H_2SO_4	H_2O	NO_2
CP_1	mixed acid	21.5	69.75	8.55	0.25
	spent acid	18.2	71.0	10.5	0.30

The nitration is performed without stirring, and hence with a more concentrated nitric acid than in the centrifugal method, so that the process proceeds more rapidly. The temperature of the acid is 24–25°C. A charge of 14–18 kg of cotton is immersed in the acid so that it is spread uniformly throughout the vessel. The proportion of cotton to acid varies within the range 1:30 to 1:38.

When the cotton has been introduced, the aluminium plate is placed in a position such that the meniscus of acid lies halfway up the perforations (Fig. 144).

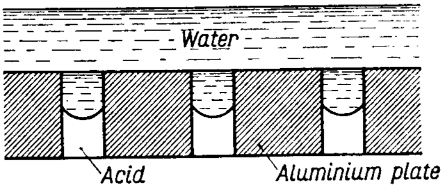

FIG. 144. Diagram of hydraulic closure of a Thomsons' nitrator.

Water is then led in carefully by means of a rubber pipe lying on the aluminium plate so as to form a hydraulic seal, i.e. the water in contact with the acid in the plate perforation creates two layers of liquid immiscible owing to the difference in their specific gravities. Moreover, the small diameter of the perforations makes mixing of the two liquids difficult.

Due to this water seal, acid vapours do not escape from the nitrator, and the atmosphere in the nitration shop is unpolluted. After the nitrator is loaded the ventilation hood is removed to a neighbouring vessel which is then charged in exactly the same way.

The nitration process lasts 1½–2 hr for the manufacture of high nitrated guncotton. For the production of lower nitrated guncotton 1–1½ hr is long enough.

After nitration is finished the apparatus is slowly emptied at the rate of about 150 l. of acid per hour. At the same time cold water supplied by a rubber pipe is allowed to flow at the same rate onto the surface of the aluminium plate so as to maintain the same level of liquid in the nitrator. During this operation acid is displaced by water that also mixes with the acid retained in the guncotton. The boundary between the two liquids falls in the vessel at a rate of 2.5 mm/min.

Smoothness of the displacement and dilution of the acid by water depends to a large extent on the quality of cotton used; only the best grade of cotton is suitable for this system of nitration.

The admixture of water with the acid remaining in the guncotton is accompanied by the development of an appreciable quantity of heat. Water used for this purpose should therefore be cooled at least to 4–8°C in order to prevent the temperature rising above the permitted limit, which would otherwise cause decomposition. In spite of this precaution, on mixing with the acid retained by the nitrocotton, a partial denitration always takes place, so the highest nitrated guncotton cannot be obtained by the Thomson process.

Unstable esters formed during nitrating also undergo decomposition, when water is added. Nitrocotton prepared by Thomsons' method is therefore more stable than the product obtained by other methods. Due to partial denitration, the solubility of the guncotton in an ether–alcohol solution is increased.

Sometimes, e.g. when low-grade cotton is used, sudden evolution of heat and rapid denitration is unavoidable, and simultaneous decomposition followed by inflammation of the guncotton can take place, causing the stoneware vessel to break.

The acid flowing out of the nitrating vessel gradually changes its strength and composition. At the beginning, for 1½ hr, about 250 l. of concentrated spent acid flows out. Its average composition is given in Table 96.

This concentrated spent acid is collected separately, and within the next 15–20 min a further 50 l. of diluted acid is collected. Thereafter acid wash-water flows out, and is neutralized before being allowed to escape to the drains.

The composition of the spent acid varies, as shown in the graph (Fig. 145). At first it contains a relatively small proportion of nitric acid, the $HNO_3:H_2SO_4$ ratio being 0.24, since nitrocotton absorbs more nitric acid than sulphuric acid. This $HNO_3:H_2SO_4$ ratio increases significantly when acid partially diluted by water begins to flow out, because nitric acid absorbed and retained in the guncotton is now washed out with water. After about an hour, the ratio of nitric to sulphuric acid is approximately 0.8.

Concentrate ($d = 1.766$) and dilute acid ($d = 1.16$) are collected in separate tanks, and the acid wash water goes to a neutralizing basin. After washing, the water supply is turned off, and the nitrocellulose is conveyed in trucks to the stabilization house.

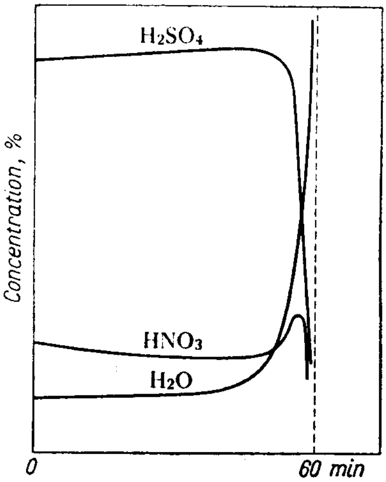

FIG. 145. Change of composition of acid flowing from a Thomsons' nitrator, according to Pascal [14].

Thomsons' process is advantageous for many reasons: the actual operation is simple and the atmosphere in the nitration shops is free from health hazards. The nitrocotton removed from the nitrators contains only a small quantities of acid, and is easier to stabilize than nitrocellulose produced by other methods. The loss of acid is negligible indeed, and this is the chief advantage of the process.

The drawbacks of the method lie in the necessity of using high grade cotton, in the difficulty of achieving a high nitrogen value, and in the need for preparing well-cooled water.

The raw materials consumed in the manufacture of 100 kg of guncotton accordingly to French reports from World War I [14] are:

cotton	58 kg
HNO_3	106 kg
H_2SO_4	84 kg

thus from 100 kg of cotton 172.5 kg of nitrocellulose are manufactured.

From each nitration lasting 4 hr, 22.4 kg of CP_1 were produced corresponding to a daily output of 134 kg in all. The same French sources report that 22 nitrators, served by an 8 man crew, produced 115 kg of product per worker during an 8-hour shift.

NITRATION WITH MECHANICAL STIRRING

Nitrating in vessels equipped with mechanical stirrers is now the most widely used method. It was first introduced by du Pont de Nemours in U.S.A. It was described in 1922 [16].

A nitration unit is composed of four nitrators (Figs. 146–149) constructed of acid resistant steel. Each nitrator (Figs. 146) is fitted with two stirrers that rotate at about 45 r.p.m. either in the same or in opposite directions. A centrifuge installed below each nitrator receives the contents of the nitrator and separates the nitrocotton from the spent acid. The centrifuge is constructed in such a way that lifting a cone in the centre of the movable basket opens the discharge outlet for the acid allowing it to flow down into a gutter in the storey below. Nitrocotton from this gutter enters a washing tank where the product is freed from acid, and is then sent to the stabilizers. The complete installation is illustrated in Fig. 148.

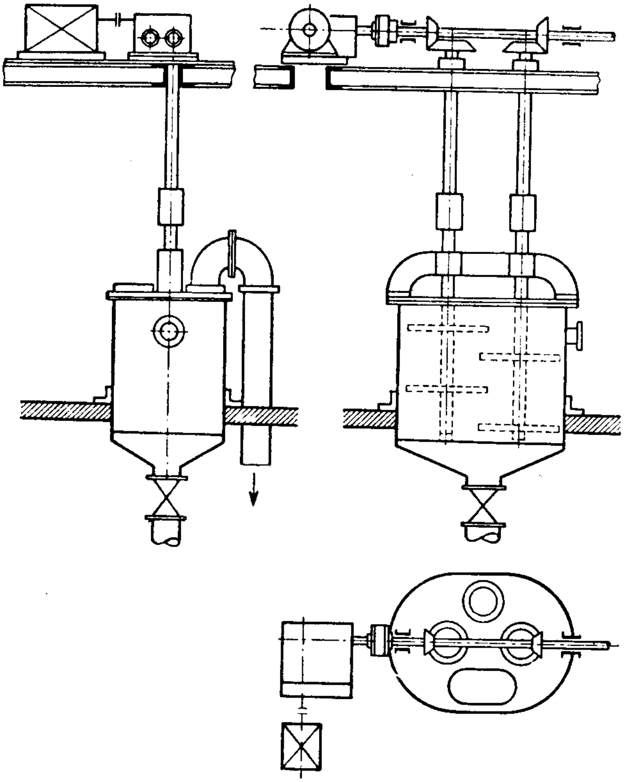

FIG. 146. Diagram of mechanical nitrators (according to Bonwitt [17]).

The process of nitration is as follows: The nitrator is charged with 750 kg of mixed acid of the composition shown in Table 97.

Then 17 kg of cellulosic material are loaded into the nitrator, with the stirrers

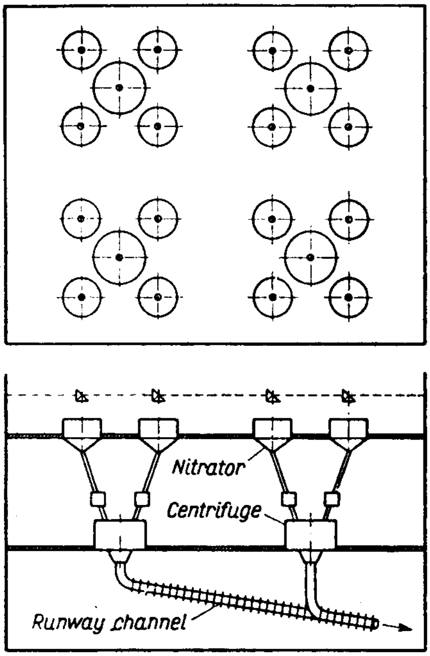

FIG. 147. A plant of four batteries of four nitrators with one centrifuge each (according to Bonwitt [17]).

TABLE 97

THE NITRATION OF COTTON WITH MECHANICAL STIRRING

Composition of the mixed acid, % / Type of nitrocellulose	HNO_3	H_2SO_4	H_2O
Guncotton CP_1	24	66–67	9–10
Collodion cotton CP_2	24	61–62	14–15

running all the time. After 20–25 min the nitration is finished, and the contents of the nitrator are discharged into the centrifuge (Fig. 149).

Centrifugation lasts 5 min, followed by unloading, which takes the same time. In order to maintain continuous operation, the four nitrators are used in turn: while the first nitrator is being loaded with acid and cotton, in the second nitration is just starting, nitration in the third is nearing completion, and the fourth nitrator is being emptied.

Fume ducting connected to the nitrators and to the centrifuge keep the atmosphere in the building pure.

The numerous advantages of the method include absence of complicated operations, low energy requirement, and the fact that it can be used for the nitration

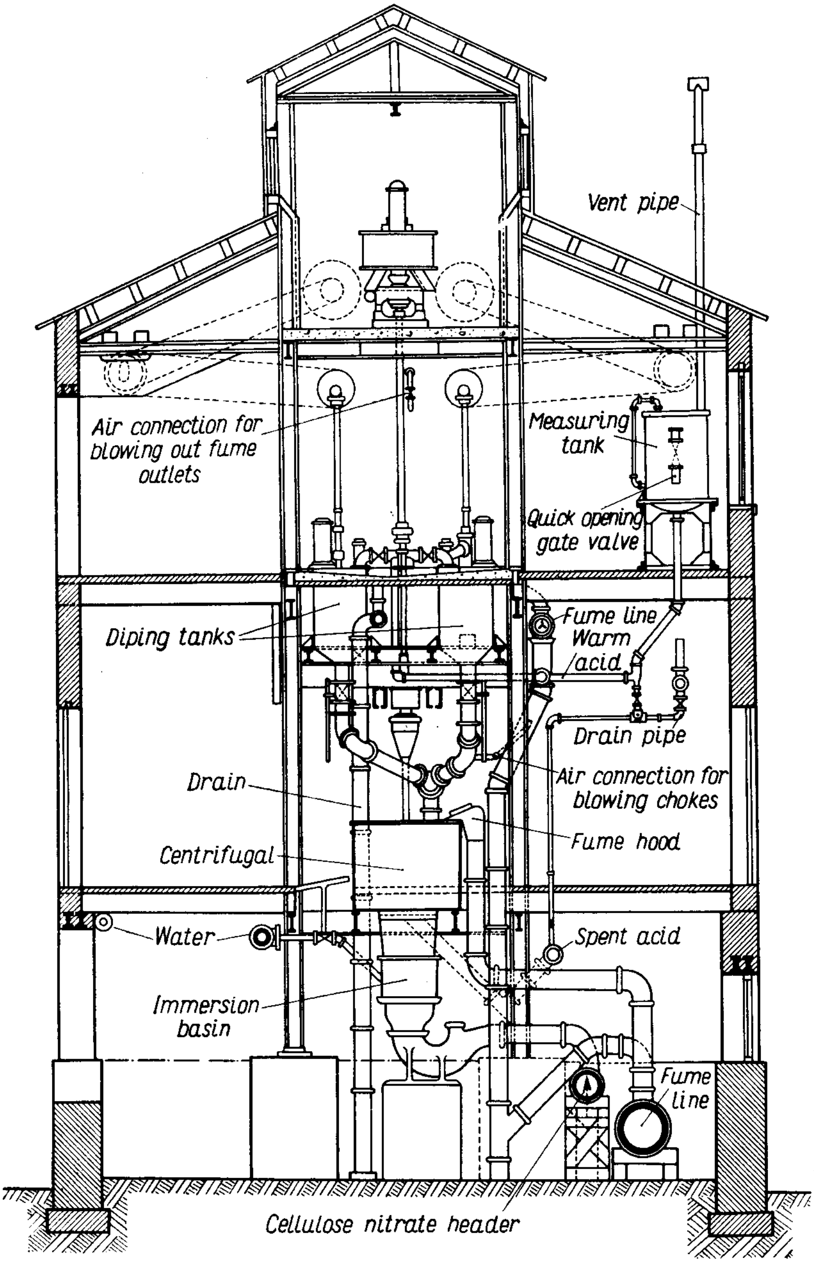

FIG. 148. Diagram of a plant for nitration of cellulose in mechanical nitrators, du Pont system (according to du Pont de Nemours [16]).

of low grades of cotton as well as wood pulp cellulose, from which very uniform products are obtained. The disadvantage of the method is the neccessity for multistorey buildings.

A modification also exists in which the nitrator is loaded with half the total acid,

FIG. 149. General view of centrifuges in a mechanical nitration plant (Hercules Powder Co., [18]).

the cellulose is then immersed in the acid as quickly as possible and at the same time the remainder of the mixed acid is added.

GERMAN METHOD

The process of nitrating cellulose described below was used in the German factories at Krümmel [19] and Aschau [20] during World War II.

The nitration plant was identical in principle with that described above, with mechanical stirring. In the German method cellulose in the form of crepe paper prepared from 70% birch and 30% spruce was nitrated. Cellulose, torn to pieces in rollers, was dried to reduce its moisture content from 6–7 to 1.2%. Towards the end of the war the drying stage was omitted at Krümmel, and cellulose containing 6–7% of moisture was nitrated, since the time saved and the economy in steam achieved then was reckoned sufficient compensation for the need to make use of more concentrated acids.

The mixed acid was warmed to the required temperature (30°C at Krümmel and 18°C at Aschau) by means of temperature stabilizers. These were cylindrical tanks provided with a coil to heat or to cool the content, and a mechanical stirrer.

The data collected in Table 98 show the composition of the mixed acid used in the German plants. The cellulose to acid ratio was 1:45.

The nitration process consisted in immersing cellulose in the mixed acid. At Krümmel a charge of 25 kg was immersed for 30 min, while at Aschau 21 kg of cellulose were immersed for 40 min. Towards the end of nitration the temperature was around 25°C. The nitrators were provided with stirrers able to revolve at a speed of 200 r.p.m. This rate was maintained during the addition of cellulose to the nitrators, after which the rate of rotation was slowed down to 100 r.p.m. After the nitra-

TABLE 98

NITRATING CELLULOSE BY THE GERMAN METHOD

Type of nitrocellulose \ Composition of the acid, %	HNO_3	H_2SO_4	H_2O	NO_2
Krümmel				
Type S: 13.2–13.3% N	22.5	67.5–68.5	9–10	
Type PE: 11.25–11.5% N	20	62–64	16–18	
Aschau				
13.2–13.3% N	22.0	67.8	10.2	2.0
12.4–12.6% N	22.0	62.5	15.5	2.0
11.2–11.5% N	22.0	59.5	18.5	2.0

tion was finished, the contents of the nitrator were let down into the centrifuge, from which separated solid material was removed through the bottom, while the spent acid went to denitration.

At Krümmel, from 100 kg of cellulose 164 kg of high nitrated nitrocellulose (Schiessbaumwolle S) containing 13.2–14.3% of nitrogen and 144 kg of lower nitrated nitrocellulose of 11.2–11.5% N were obtained.

A distinctive feature of the process used at Aschau was the recovery of the acid retained by the nitrocellulose by washing with dilute spent acid in a centrifuge. Three subsequent washings using more and more dilute acid, and finally a water wash, were used.

The composition of the acids used for the successive washings is reported in Table 99.

TABLE 99

COMPOSITION OF SPENT ACIDS USED FOR WASHING NITROCELLULOSE

Washing	Composition of the acids, %		
	HNO_3	H_2SO_4	H_2O
I	18	47	35
II	17	28	55
III	16	14	70
IV	0	0	100

Every acid rinse lasted 30 sec, to be followed by centrifugation for 20 sec. The total washing took 170 sec.

In order to utilize the recovered acids, the liquor from the first washing was sent back to tank I. Half the acid from the second washing was sent to tank I and half to tank II, while half of the third acid rinse went to tank II and half to tank III. The final rinsing water also went into tank III.

The concentration of the dilute acid in the tanks I, II and III, was maintained more or less constant, so that the acid could be used again for washing nitrocellulose. Excess acid went to the denitration plant.

At Aschau the consumption of nitric acid for 100 kg of nitrocellulose of 12.0 to 12.6% N was 90 kg of nitric acid, whereas without the arrangement for recovering the acid, the consumption was 110 kg of HNO_3.

This utilization of the dilute acid produced by washing nitrocellulose is of interest for economic reasons. In former methods the acid wash water had to be neutralized before being discharged to waste. Thus it involved both loss of acid and a large consumption of calcium and sodium carbonate.

While the nitrocellulose was being washed in a centrifuge as described above "fume off and inflame" frequently occurred, generally during the first wash. The accidents were attributed to traces of water remaining in the pipe-line after the final water wash of the preceding charge, for small amounts of water dropped onto a fresh centrifuge charge readily caused it to inflame. One of measures adopted to prevent these ignitions was to push aside the mouth of the water pipe, so as to make it impossible for any water to drop into the centrifuge. A special nozzle was also installed to produce an even spray of acid or water.

Nitric acid recovery included the recovery of the acid vapours from nitrating installations and all tanks, metering tanks and stabilizers holding nitric acid. These vapours were led by means of fume ducts from the nitration plant and by suction pipes from the tanks into towers, where they were sprayed with water or with dilute nitric acid, to produce 50% nitric acid.

CONTINUOUS METHODS OF NITRATION

Numerous methods for continuously nitrating cellulose are to be found in the patent literature. For instance, several patents propose passing cellulose laid on a moving belt through a nitrating bath. The same belt conveys the nitrated cotton to a tank, where it is separated from acid. Subsequently the guncotton produced is unloaded into water. Arrangements of this type were patented [21].

The main drawback of these methods consists in the difficulty of maintaining constant composition of the mixed acid, hence there is liable to be a significant lack of uniformity in the resulting nitration product. A more uniform product can be obtained by using nitric acid vapour [24].

Another method which enables a more homogeneous product to be made by more uniform nitration, was proposed by Juer [22]. The nitrator comprises a rotatory drum inside which is a plate, bent in a spiral form. As the drum turns, this spiral moves the charge in one direction. In a separate pre-nitration vessel provided with a stirrer, cotton and acid are metered and mixed to feed the nitrator batch-wise. The length of the drum and its speed of rotation are arranged so that completely nitrated cotton is delivered. The guncotton produced is separated from the spent acid by conventional methods, e.g. in a centrifuge.

Meissner [23], in a patent for the continuous nitration of cellulose suggests using several U-shaped nitrators coupled together. Cellulose is introduced to one of the nitrators, while another is fed with acid. By means of suitable stirrers it is possible to transfer the contents of one nitrator successively to the following nitrator. Acceptably uniform nitration is achieved by this system.

Up to the present, continuous processes for the cellulose nitration have not been introducted in practice.

New ideas in the manufacture of nitrocellulose consist in nitrating cellulose in the presence of a solvent (e.g. methylenedichloride [25], nitromethane) which is not subjected to nitration but dissolves nitrocellulose and forms a separate phase. The solution of nitrocellulose is then washed with water to stabilize the product. The operations can be made continuous.

Nitrocellulose precipitated from the solution can be subjected to an additional, very brief stabilization (e.g. a 1-hour boil).

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CHAPTER XIV

STABILIZATION OF NITROCELLULOSE

THERE are many methods of stabilizing nitrocellulose. In different countries and in various plants, a variety of techniques are in use, partly as a result of local conditions, e.g. the quality of the water available for stabilization boiling, but influenced also by tradition and by the development of earlier processes.

However, certain fundamental operations are common to all stabilization methods, namely:

(1) Primary washing of nitrocellulose by means of water and boiling in kiers, either in pure water or in dilute acid (the alkaline kiering formerly in use has now been abandoned).
(2) Additional kiering in autoclaves under pressure (in more up to date plants).
(3) Pulping (grinding) nitrocellulose in beaters and in mills respectively.
(4) Poaching (final boiling) in boilers, in water containing alkalis (not always applied).
(5) Certain kinds of collodion cotton for industrial purposes, e.g. for varnishes, celluloid, films, are also subjected to a bleaching process.
(6) Decanting and rinsing the stabilized nitrocellulose.
(7) Removal of mechanical impurities, e.g. sand or long fibres.

Other operations also in use include:

(8) Blending batches of nitrocellulose to form large homogeneous stocks of product.
(9) Centrifuging the nitrocellulose in order to remove excess water.
(10) Semi-hermetic or hermetic packing for transport.

During the various operations enumerated samples are taken to be checked in the laboratory for stability (Abel heat test), degree of fineness, etc.

PRIMARY WASHING AND BOILING IN KIERS

Nitrocellulose delivered from the centrifuges is washed with water either in special vats with stirrers (Fig. 150), or directly in kiers in which the product is then boiled. In the latter case water is introduced into the kier loaded with nitrocellulose and then let out again, the washing being repeated several times.

The drum (*1*) made of perforated plate is equipped with paddles both inside and outside. Nitrocellulose picked up by the outer paddles is thrown over to the neighbouring compartment, while the inner paddles remove water. To the second

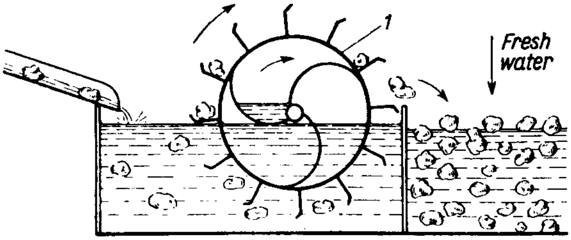

FIG. 150. Diagram of washing nitrocellulose.

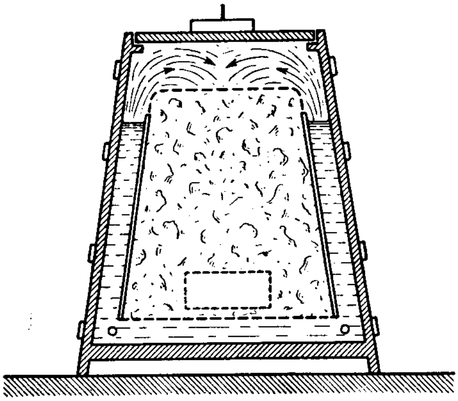

FIG. 151. Diagram of a digester (kier) for stabilizing boiling nitrocellulose, according to Pascal [1].

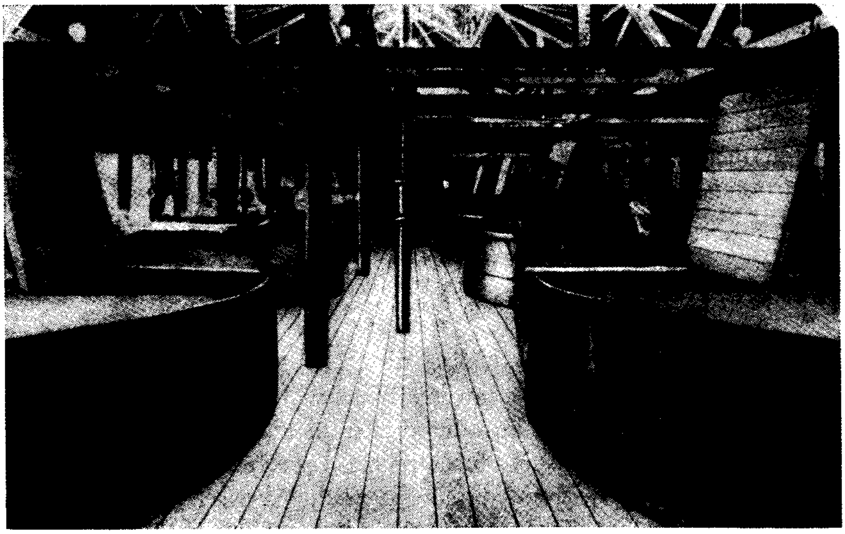

FIG. 152. General view of digesters for stabilization of nitrocellulose (Hercules Powder Co., [3]).

tank fresh water is introduced and a similar drum removes water and transfers nitrocellulose to the next compartment and so on.

The kiers are vats made from wood in the form of a cylinder or truncated cone (Figs. 151 and 152), of 2–50 m^3 capacity (10–20 m^3 is the most common).

Recently, an improvement in construction has been introduced that consists in lining the kiers with stainless steel plates. 100 kg of nitrocellulose is loaded for every 1–2 m^3 of volume of the vat.

The kiers are double-bottomed, the upper "false" bottom being made of perforated acid-resistant sheet or a wood frame lined with perforated stoneware bricks. Live steam at about 3 atm pressure is introduced into the space below the false bottom. In order to ensure a better circulation of hot water and steam in the kier, in many installations boilers are provided with one or more pipes (e.g. four), which are open at both ends and arranged so that the lower opening is situated above the steam inlet. Water and steam rise in the pipes and spout from the top. In this way a vigorous circulation is maintained inside the boiler. An outlet tap is situated in the lower part of the boiler. The kier is loaded with nitrocellulose transported in water, which then flows out leaving the nitrocellulose inside. With this method, which was used in Germany, it is impossible to attain a higher loading density than 50 kg/m^3.

Wet nitrocellulose can be pressed down manually in the kier by workers dressed in protective clothing, rubber shoes and woollen clothing for entering the boiler. In this way, as used in France, the loading density can be increased to 100 kg/m^3.

Although better use is made of the capacity of boiler, the high density of loading has an adverse effect on water circulation, thus making it necessary to prolong the period of stabilization boiling.

Below examples are given of stabilization boiling as carried out in France in CP_1- and CP_2-guncotton manufacture.

The stabilization boiling comprises the following stages:

(a) three water washes, each of 15 min (each wash consists in filling the vat with water, allowing it to remain for 15 min and then removing it);

(b) one 4-hr boil followed by change of water;

(c) one 72-hr boil for CP_1 or one 36-hr boil for CP_2, followed by a change of water;

(d) three boils, each of 1 hr in the presence of calcium carbonate (about 0.5% calculated on the weight of guncotton). Each of the boils is followed by rinsing the load with cold water.

This method of stabilization is very expensive, and takes an exceptionally long time — several days. It is therefore necessary to arrange a considerable number of kiers and hence a large and costly installation is required. Pascal [1] states that in a factory to produce 100 tons of nitrocotton a day some 400–500 vessels of 2–4 m^3 should be installed.

Furthermore, the operation of an installation is also expensive, since 4–5 kg of steam are consumed for every 1 kg of nitrocellulose. A boiler house to supply the kiers with steam should be situated near to the stabilizing house.

The stabilization of guncotton produced by the Thomsons' method is slightly less expensive, as this product is easier to purify. According to Robertson [2] 10 successive boiling and washing operations are to be carried out:

(a) two 10-hr boils.
(b) washing with cold water;
(c) five 4-hr boils;
(d) three 2-hr boils;

The water is changed after each boil. In spite of the relatively short time needed for stabilization, the Thomsons' method is too expensive.

The introduction of autoclaves, which considerably reduced the time required for boiling, brought about a marked improvement in commercial methods of stabilization. The high installation costs for the high pressure system are fully compensated by the very much shorter stabilization process.

In the plant at Krümmel [4] nitrocellulose was boiled with water in kiers of 14 m^3 capacity. S-type was boiled for 6–8 hr, and collodion nitrocellulose (PE-type) for only 3 hr.

In the factory at Aschau [5], boiling was carried out using water acidified with 0.5% of sulphuric acid, the operation lasting up to 10 hr for S-nitrocellulose, or up to 8 hr for PE-nitrocellulose. In both plants, nitrocellulose was then kiered under pressure.

BOILING UNDER PRESSURE (KIERING IN AUTOCLAVES)

According to the stabilization method used in German factories, after primary stabilization in boilers, the nitrocellulose was subjected to a short kiering in autoclaves made from acid-resistant steel with a hot-water circulation (Fig. 153).

At Aschau [5] autoclaves of 5 m^3 capacity were used, loaded with 400 kg nitrocellulose and 4 m^3 of water. The autoclave was equipped with a stirrer, and was heated by means of both direct and external heat, under a pressure of 12 atm until the desired temperature of 140°C was reached, after which the temperature was maintained exclusively by means of external heating. Kiering took about 15 min.

At Krümmel [4] kiering was carried out for 6 min at a temperature of 142–145°C.

After kiering, the contents of the autoclave were transported by means of a pump or in a water conveyer to the beaters, where the fibres were broken down.

Treatment in autoclaves was also used in earlier years to reduce the viscosity of collodion cotton intended for the manufacture of varnishes. For the same purpose, a water slurry of nitrocellulose may be "boiled" under hydrostatic pressure in tubes, as a continuous process. These methods are discussed in detail in the chapter devoted to the manufacture of collodion cotton for varnish production.

According to Miles [7] at Ardeer, rotary autoclaves, spherical in shape, made from stainless steel are used. A pressure of about 3.5 kg/cm^3 and a temperature of *ca.* 142°C are maintained inside the autoclave. The nitrocellulose to water ratio is 1:10, and since the nitrocellulose contains less than 0.25% of acids (as H_2SO_4), the acidity of the water in which the kiering is performed is less than 0.03%.

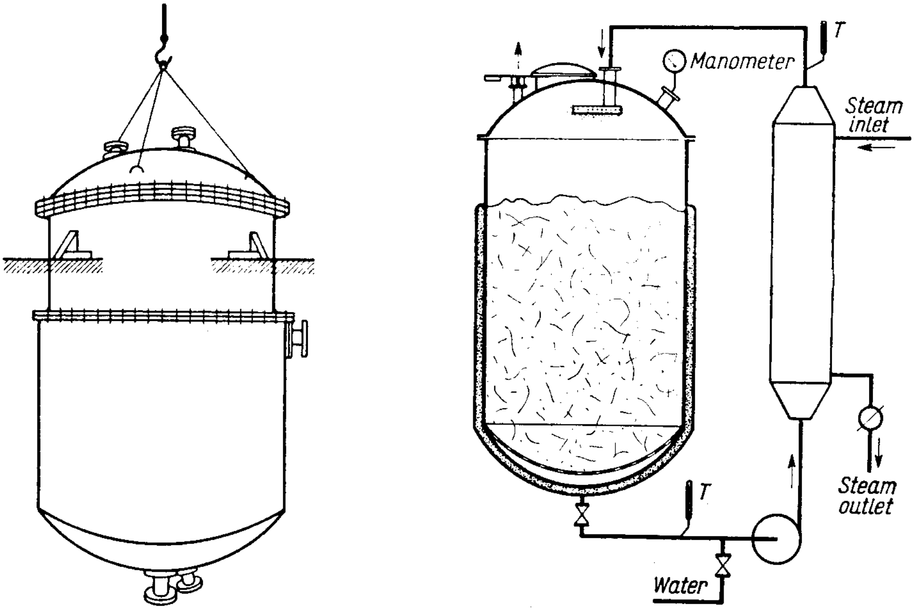

FIG. 153. Autoclave for stabilizing nitrocellulose [6].

During kiering a partial degradation of the nitrocellulose takes place, followed by the dissolution of part of the product. The loss thus caused is higher in the case of lower nitrated cellulose, e.g. 10.8% N, than with higher nitrated products, e.g. containing 12.2% N. On the other hand the denitration is more severe with higher nitrated products. This is most evident in the initial stage of boiling. A phenomenon of this kind was described by Desmaroux [8].

The viscosity of nitrocellulose is also reduced. For instance, during 2 hr kiering nitrocellulose with a polymerization degree P of 200 undergoes a de-polymerization to $P = 50$, at the same time losing 0.12% of nitrogen.

The autoclave is equipped with a device to remove any gases produced during pressure boiling. The composition of the gases evolved varies within the range:

20–50%	CO_2
25–35%	NO_2
10–25%	NO

PULPING

An important operation in the stabilization of nitrocellulose, particularly for materials containing over 11.5% N involves cutting the fibres into short pieces. Only nitrocellulose of low nitrogen content, below 11.5% N (collodion cotton) can be stabilized adequately without such a treatment.

Generally, shortening the fibres is carried out in beaters, equipment adapted from the paper industry. The operation is known as pulping.

The majority of paper beaters are of the type illustrated in Fig. 154, which comprises a cast iron tub divided by a vertical partition (*1*). In one half of the tub a cutting drum (*2*) is placed, provided with steel teeth lying parallel to the axis of the drum. As it rotates, the drum meshes with identical fixed teeth (*3*) attached to the bottom of the vessel.

The tub is filled with nitrocellulose and water. The semi-liquid slurry passes between the teeth, where the fibres are cut by the knives (*2*) and (*3*) that function like shears. Due to the high speed of rotation of the drum (100–150 r.p.m.), the semi-liquid slurry is drawn between the knives and thrown on to the other side. A considerable slope at the bottom helps to maintain a high velocity. The stream of pulp follows to the second half of the beater whence it returns to the first compartment, to be drawn once more by the revolving drum between the knives, and so on.

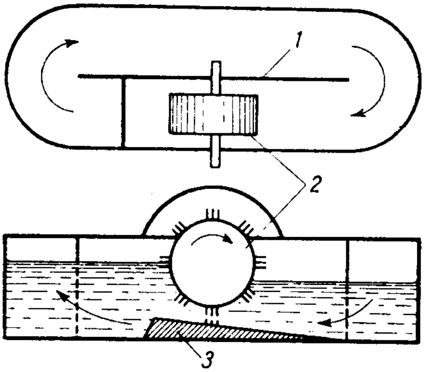

FIG. 154. Diagram of a beater (small size), according to Pascal [1].

At the beginning, the circulation of the slurry is difficult owing to its uneven consistency, so movement of the mass is aided by wooden paddles. Gradually the fibres and lumps of nitrocellulose are cut, the consistency of pulp becomes more and more uniform, and the slurry flows more easily as the nitrocellulose becomes finer. The paddles should however be kept ready to use until the end of pulping, to move the mass by hand should any congestion occur. As pulping proceeds, the bearings that support the shaft of the cutting drum are gradually lowered, so that the distance between the fixed teeth and the drum's knives is gradually reduced.

The time required for pulping depends on the design of the beater and on the type of nitrocellulose. Thus, the more highly nitrated the cellulose, the lower the mechanical strength of fibres, i.e. the more brittle they are and the more easily torn to pieces.

Very large beaters (capacity 25 m^3), may be used (Figs. 155 and 156). Here, the cutting drum is situated at one end of the tub which is made either of cast iron, from a couple of units to be assembled together, or of concrete. Concrete vessel are lined internally with glazed tiles. The trough is divided into two by means of a vertical baffle plate. In these compartments the bottom is inclined in opposite directions in order to facilitate the circulation of the pulp.

The dimensions of the equipment used in France are as follows: length 5.5 m, width 2.4 m, height 1.2 m drum diameter 1.35 m and length 1.75 m. The drum is equipped with 80 knives.

Vessels of these dimensions are loaded with a pulp charge of 1000 kg guncotton. The tub is filled with 15 m^3 of water, and gradually 1000 kg of boiled nitrocotton (dry weight), are added during a period of 2 hr. The drum revolves at a rate of 125 r.p.m. During loading, the men move the material with paddles to cause the mass to get under the cutting drum. After the total charge of guncotton has been loaded pulping is continued for 2–4 and 4–6 hr for high and lower nitrated guncotton, respectively.

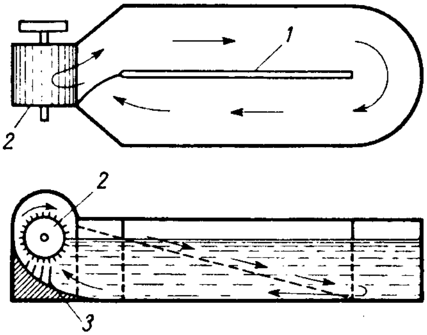

FIG. 155. Diagram of a beater (large size), according to Pascal [1].

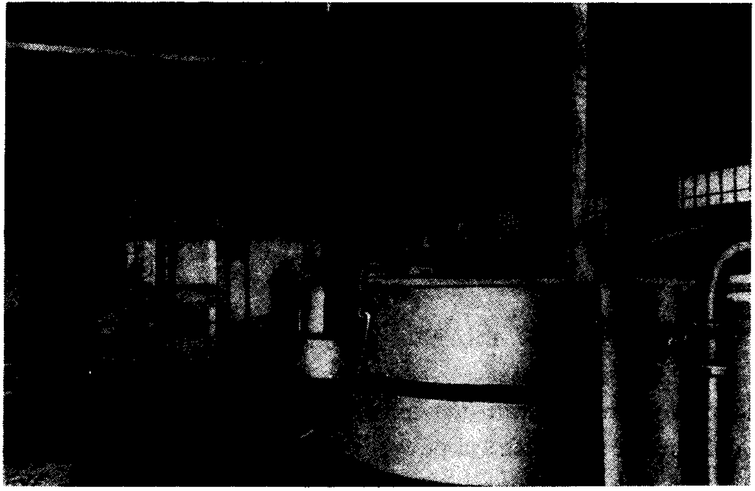

FIG. 156. General view of a beater plant (Bofors Nobelkrut, Sweden).

During the pulping, sodium carbonate or calcium carbonate is added to neutralize the residual acid freed from inside the cut fibres. Initially enough sodium carbonate is added to prepare a solution of about 0.1% of Na_2CO_3 concentration. Later on, during the process, more sodium carbonate is added to keep the pH-value within the range 7.0–9.0. The admixture of carbonate prevents the acidification of the reaction medium, and protects the cutting knives against corrosion. Calcium carbonate is used in excess so that a certain amount of it remains in the nitrocellulose.

The adjustment of the knives of the cutting drum so as to maintain close contact is carried out in accordance with the indications of an ammeter. Using a 100 HP motor the consumption of electrical power is 30 kWh per 100 kg nitrocotton.

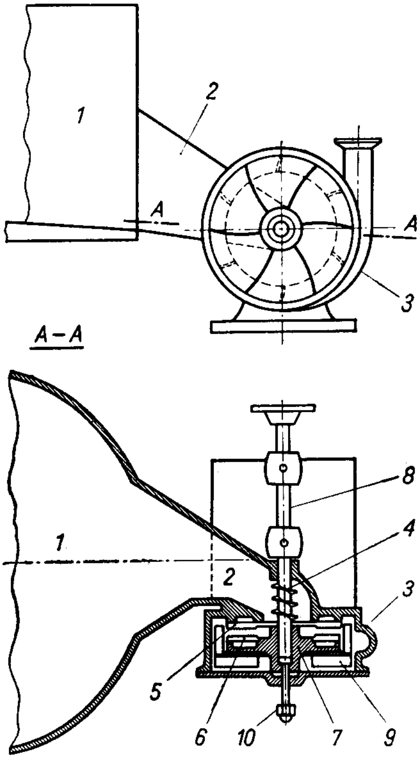

FIG. 157. Disk mills, Raczyński system [9].

In the factory at Krümmel [4] beaters of 14.5 m^3 capacity were used, their effective capacity approaching 2400 kg of guncotton. In this machine S-type nitrocellulose was pulped for 5–6 hr, whereas for PE-type nitrocellulose pulping time was extended to 10–12 hr. The fibre length after pulping was 0.2–0.5 mm. The operation was regarded as complete when a specimen taken from the beater demonstrated a fineness characterized by a value of 80–100 cm^3. The test consists in stirring 10 g nitrocellulose with 250 cm^3 of water in a graduated cylinder, the volume occupied by the nitrocellulose being measured after a few hours. Under these conditions a well pulped nitrocellulose occupies a volume less than 140 cm^3 corresponding to a mean fibre length of 1 mm.

Raczyński [9] replaced the beaters for pulping nitrocellulose by disk mills (Fig. 157). A nitrocellulose water suspension flows down from a tank (*1*) through the channel (*2*) into the mill (*3*). The mill simultaneously acts as a draw-lift pump. By means of the worm (*4*) the suspension is conveyed to the milling disks (*5*) and (*6*). The disk (*5*) is fixed, and the disk (*6*) is attached to the outside of a rotor (*7*) which revolves about the spindle (*8*). The other surface of the rotor (*7*) is equipped with paddles (*9*) which throw the slurry through a vertical outlet during rotation. The screw (*10*) presses the rotor carrying the disk (*6*) into the fixed disk (*5*).

Markiewicz, Zenftman and Raczyński [10] included the Raczyński mills in a pulping plant (Fig. 158) which comprised a battery of eight mills (*1–8*) and two

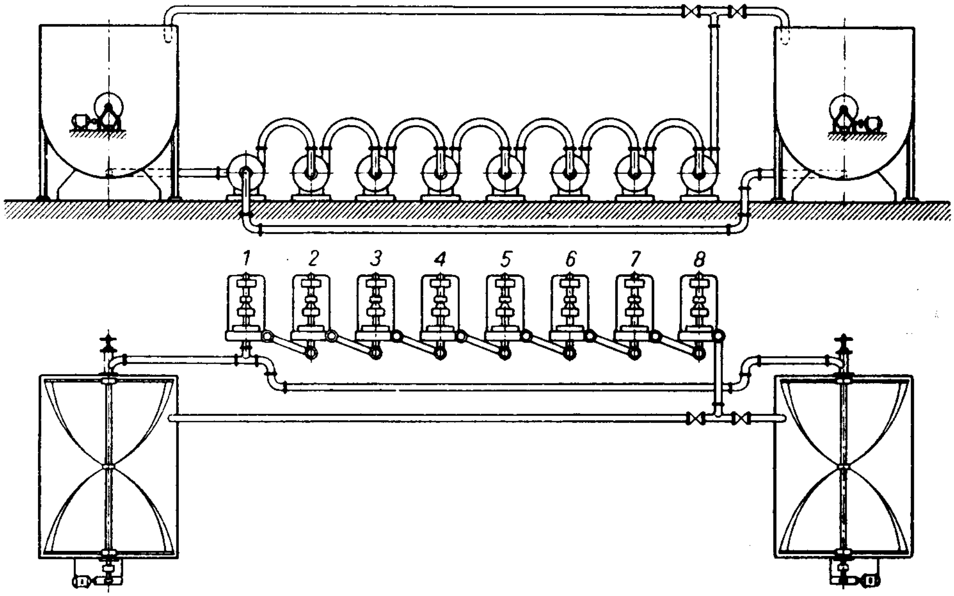

FIG. 158. Diagram of a Raczyński milling plant [10].

tanks in which nitrocellulose was kept in suspension in water by means of stirrers. The suspension from one tank proceeds through the disk mills into the other tank. When the whole contents of one tank have been transferred to the other one, the direction of flow of the slurry is reversed.

The introduction of the Raczyński mill revolutionized the pulping of nitrocellulose fibres. Their most important advantage is that they require only 25–30% of the power needed for beaters. The design of the Raczyński mill has since been improved by Wrocławski [11].

Attempts have also been made to replace the beaters by conical mills in which conical knives on the rotor mesh with fixed knives. Owing to its shape and to the inclination of the knives, the mill also acts as a pump, drawing the suspension of nitrocellulose from the tank and returning it to the same or to another tank. These mills have not been wider adopted in practice, since they have no material advantage over conventional beaters.

After being pulped, the nitrocotton fibres are pumped into the poacher. If the consistency is insufficiently liquid then water is added to the slurry during pumping. The beaters or mills are emptied through a discharge pipe in the base.

A diagram illustrating the layout of a beater or a mill with a poacher, the position of the mixer and the final purification unit, is outlined in Fig. 159.

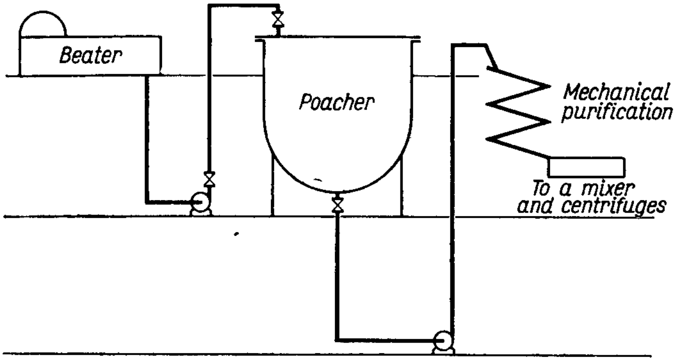

FIG. 159. Diagram of a plant composed of a beater, a poacher and a purifier.

Between the beaters or mills and the boilers, an apparatus for separating long fibre nitrocellulose from the cut fibres is inserted. This is a tank carrying a vertical cylindrical screen drum, with apertures 0.4 mm dia. The drum rotates and the cut fibres pass through the sieve into the drum, whence the contents flows to the boilers. The uncut fibres are caught on the surface of the screen from which they are removed by means of a brass knife and recycled to the beaters.

Alternatively, the uncut fibres can be retained in trough-shaped settlers with baffle-plates. This method is usually used for separating nitrocellulose already completely stabilized, as will be seen in the description that followings.

BOILING IN POACHERS

The suspension of cut nitrocellulose fibres in water is transferred with the help of a pump into a boiler (poacher). This is a vertical (Fig. 160) or horizontal (Fig. 161) cylindrical vessel of 10–20 m^3 capacity, constructed of sheet-metal, equipped with a stirrer and heated by direct steam injection.

In France it is customary to add 1–2% of calcium carbonate to the water in which the pulped nitrocellulose is poached for at least 4 hr. The stability of the resulting nitrocellulose is examined by means of the heat test, and if necessary poaching is repeated. This is carried out by allowing the contents of the boiler to settle for several hours, so that the nitrocellulose sinks to the bottom. The water is then decanted from above the nitrocellulose layer, fresh water and calcium carbonate are added, and the poaching is started again, and continued for 2–4 hr.

This procedure is repeated as often as necessary, using fresh water each time.

The weight of calcium carbonate added is equivalent to 0.1–0.5% that of the nitrocellulose.

With high nitrated guncotton (CP_1) the stabilizing process usually consists of two 4-hr poachings, each boil being followed by decantation, for which an outlet tube ending with a funnel is usually used. The stability of the nitrocellulose is then tested, and one or more further poachings in the presence of calcium carbonate, lasting 2 hr, and a couple of water washings are carried out, if necessary. The water washing consists in agitation of the nitrocellulose with cold water, followed by settling and decantation of the water.

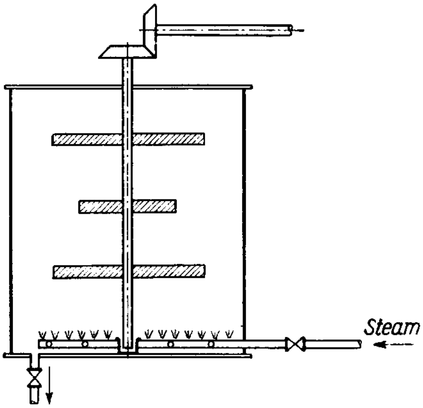

Fig. 160. Vertical boiler (poacher).

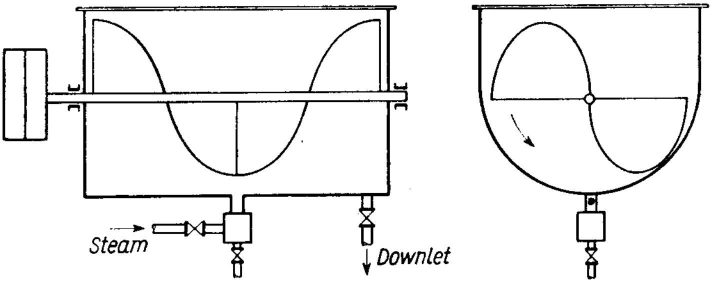

Fig. 161. Horizontal boiler (poacher).

In Germany during World War II, cylindrical boilers, provided with mixers, of 10–14 m^3 capacity, were used. The vessels were made of sheet-iron or of concrete lined internally with an acid-resistant material, for instance ceramic plates joined by means of a phenol-formaldehyde resin, "asplit".

In the plant at Krümmel [4] the water suspension of the pulped nitrocellulose of low nitrogen content was stabilized by heating it to boiling point, cooling and refrigerating it, and then washing with water. Nitrocellulose of high nitrogen value, on the other hand, was boiled for several hours until a sample taken from the poacher passed the standard heat test. Sampling was carried out after 2, 3, 5 and 8 hrs' poaching. Thereafter, if the sample failed to show sufficient stability, the test was repeated every 3 hr.

In the factory at Aschau [5] 13 m^3 boilers were loaded with 1100 kg of pulped nitrocellulose. Nitrocellulose of 11.2–11.6% N was poached for 2–3 hr, whereas nitrocellulose containing 13.2–13.4% N was poached for 5 hr, in water containing 0.25% by weight of sodium carbonate calculated with reference to nitrocellulose.

In Great Britain instead of hot poaching, the pulped nitrocellulose is subjected to repeated washing. This consists in thoroughly stirring the nitrocellulose with water, decanting the water and repeating the procedure with fresh water.

Washing is most usually performed in "washing poachers", rectangular tubs (Fig. 162) divided by a partition into two parts. The slurry of nitrocellulose in water is transferred by a rotary pump from one part of the trough to the other. The bottom of each section of the vessel slopes in opposite direction so as to facilitate circulation. After being stirred with water for some 15–20 min the contents of the vessel are allowed to settle for half an hour, and then the water is decanted from above the nitrocellulose.

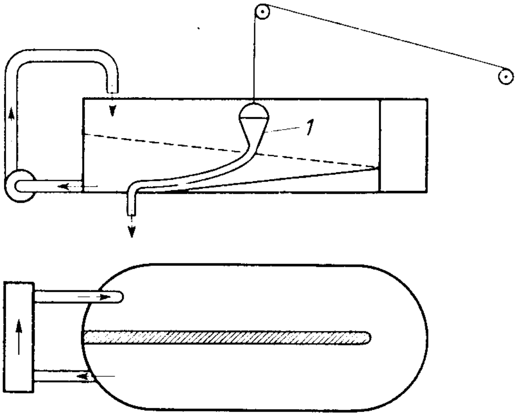

FIG. 162. Washing poacher.

Fresh water is then introduced and the stirring is re-started. Washing is repeated at least three times.

In many factories washing of this kind is carried out as a supplementary operation after stabilization of the nitrocellulose by boiling.

BLENDING

In order to produce a homogeneous product, a couple of charges of nitrocellulose are blended after stabilization to make at least 10,000 kg. The mixing is carried out in various types of equipment. For instance large concrete vessels 25 m long, 4 m wide, 2 m high divided by a partition wall into two troughs, and equipped with a pump to circulate the water suspension of nitrocellulose are used in France. The charge totals 10,000 kg of the material plus 100 m^3 of water (Fig. 163).

In German plants cylindrical concrete tanks equipped with stirrers are the most widely used. The capacity of these tanks is 100 m^3, and they are charged with 10,000 kg of nitrocellulose. After mixing the product for several hours with water, it is removed through a valve in the bottom of tank and subjected to a final purification.

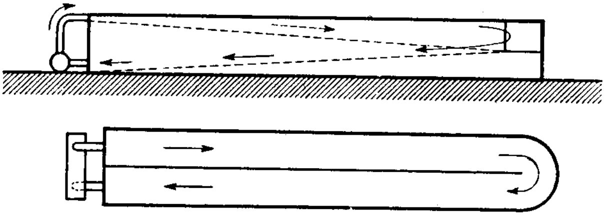

FIG. 163. Mixing tub (according to Pascal [1]).

FINAL PURIFICATION

The final purification stage (screening) removes insufficiently cut fibres, sand, particles of iron and other mechanical impurities picked up by the nitrocellulose during manufacture.

Two types of plants are in use for this purpose. One is a kind of settler, constructed in the form of a sharply inclined, wooden gutter, with a large number of bends. Wooden baffles are placed at intervals along the bottom of the gutter, interspersed with "honeycomb" sections intended to detain sand. After leaving the settler the slurry of nitrocellulose passes through vibrating sieves where the residual uncut fibres are retained. Finally the suspension flows between the poles of an electromagnet which removes iron. Alternatively, the screens for removing long fibres may be situated between the beaters and the poacher, when further screening during final purification is superfluous.

DECANTATION

After the final purification, the suspension of nitrocellulose in water is led into cylindrical decantation tanks, 6–8 m high and 1.5–2.5 m dia. equipped with stirrers. The contents of the tanks are allowed to stand for a time, and then the water is decanted either by means of a funnel (Fig. 163) or through a valve in the side of the tank. The stirrer is then set in motion and the "thickened" pulp of nitrocellulose in water is delivered to a centrifuge.

Most of the water can also be removed from nitrocotton by introducing the pulp into a tank containing a revolving screen drum. The nitrocellulose is retained on the surface of the screen drum, the water passing through and being removed from the inside of the drum.

DEHYDRATION

The water content of the "thickened" nitrocellulose pulp is reduced to 30–40% in centrifuges of the type similar as those used in the manufacture of sugar. In many plants, additional dehydration is carried out in hydraulic presses, in which the nitrocellulose is subjected to a pressure of about 20 kg/cm^2 and formed into blocks or "cakes" in which the water content is 20–30%. Clearly this is advantageous from the point of view of transport.

The dehydration and pressing of nitrocellulose is often combined with an additional blending. Thus, for example, after centrifuging, the nitrocellulose is placed in a large wooden box in horizontal layers, from which vertical slices are then removed for pressing.

PACKAGING AND TRANSPORTING

Wet nitrocellulose containing 20–40% of water is packed in galvanized iron drums or in semi-hermetic wooden boxes lined with zinc sheet or sometimes only with paraffin wax paper. Rubber gaskets are fitted under the lids. The box lids are fastened down by means of brass screws. Nitrocellulose packaged in this way is accepted for railway transport in separate waggons.

DRAIN WATER

Prior to being discharged to waste, water acidified during the stabilization of nitrocellulose should be neutralized by means of calcium carbonate. Further, all wash-water should be freed from particles of nitrocotton. This is usually accomplished in large settling tanks in the form of divergent cones. Waste water is introduced into the tank at a point roughly half way up. The velocity of water flow is therefore reduced as its level rises, so that the nitrocellulose sinks to the bottom, while water freed from nitrocotton overflows and is discharged. From time to time nitrocellulose (strongly contaminated as a rule) is removed from the bottom of settlers and is destroyed either by means of boiling with milk of lime or by careful burning.

SAFETY IN A NITROCELLULOSE PLANT

Danger exists in nitrocellulose plants even during the first stage of the manufacturing process, while shredding and drying the cellulosic material. Too high a temperature in the drier or contamination of the cotton with lubricating oils are sufficient to cause it to catch fire. Under the influence of a discharge of static electricity, cotton dust present in the air may to explode. Therefore the electric installation must be designed and built with particular care.

Another danger point in nitrocellulose manufacture lies in the nitrating arrangements, particularly in centrifugal nitration processes. If low-grade nitrocellulose catches fire in the centrifuge, sometimes its rate of burning is slow enough to permit the fire to be extinguished quickly, by introducing cool nitration mixture into the centrifuge. The burning of high-nitrated nitrocellulose, on the other hand, is extremely violent, and is difficult or impossible to check and it may pass into explosion (see p. 316).

In the event of inflammation of the centrifuge charge all employers should leave the building immediately, since large volumes of nitrogen tetroxide are evolved, and the atmosphere becomes poisonous. Alyavdin [14] reports that nitrogen tetroxide in air becomes toxic at a concentration of 0.15 mg/l. The inhalation of nitrogen tetroxide at this concentration causes inflammation of the upper respiratory tract and prolonged contact produces inflammation of the lungs. According to the U.S.S.R. industrial health standards (NSP 101–51) the permissible concentration is 0.005 mg/l., a quantity undetectable by smell, since the limiting concentration capable of detection by smell is 0.02 mg/l. (Lazarev [15]).

In a paper by Valada [16] the lethal dose of NO_2 in the air (DL_{50}) in experimental animals was estimated at 1 g/m^3 i.e. 1 mg/l., when breathed for half an hour. According to that author, the symptoms of poisoning are emphysema of the lungs, and the presence of iron pigments in the liver, kidneys and spleen, all indicative of severe globulosis. Should accidental poisoning with nitrogen dioxide occur, the patient should be taken out into the fresh air immediately. In severe cases, oxygen can be administered to relieve the respiration, and intravenous injection of glucose and calcium chloride should be given. In addition the action of heart should be sustained by means of caffeine, camphor or heart glucosides.

Undue haste in unloading centrifuges with forks made of acid-resistant metal, even if it is soft like aluminium, is also dangerous. Explosion of the centrifuge charge have been reported due to attempting to unload the basket before the centrifuge was stationary: friction between the forks and the inside of the basket caused an explosion to occur. It should also be kept in mind that nitrocellulose wet or damp with spent acid is especially liable to decompose. The higher the nitrogen content, the more dangerous it is to handle. Numerous accidents have been caused by touching acid guncotton with wet forks or by allowing water to drip into it (see p. 380).

The later stages of nitrocellulose production are considered less hazardous since the nitrocotton is handled in suspension in water. It is important to prevent the nitrocellulose from becoming dry. Particular attention should be paid to washing down of the clinker bricks or asphalt floor regularly with water.

In the building where stabilization and the final purification of nitrocellulose are carried out meticulous cleanness must be observed. The workmen should wear shoes with rubber or wooden soles, and this footwear must be kept in special boxes or on shelves situated in the rooms in which it is to be worn. It is forbidden to walk outside these rooms while wearing the special footwear so that neither sand nor mud are carried in.

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CHAPTER XV

MANUFACTURING SPECIAL TYPES OF NITROCELLULOSE

DYNAMITE COLLODION

COLLODION nitrocotton for manufacturing blasting gelatine and dynamite, also called dynamite cotton or dynamite collodion, is characterized by the very high viscosity of its solutions in organic solvents. It is produced by selecting a suitable cellulosic raw material, and performing the nitration at a low temperature, followed by a brief stabilization boil in a neutral or nearly neutral medium. The most important factor is the choice of suitable raw material.

Cellulosic raw materials. The best raw material for manufacturing dynamite nitrocotton is unbleached or very slightly bleached long-fibre cotton. Usually cotton wastes from spinning mills are used. The raw material is purified as described earlier (p. 363).

Too drastic purification should be avoided, as this can have an adverse effect on the product, lowering the viscosity of its solutions. Thus it is particularly undesirable to subject the cotton to bleaching.

Nitration. In order to keep the viscosity of the product as high as possible, the cotton is nitrated at a low temperature: 10–12°C. The reaction rate is not high at this temperature. It is therefore necessary to use a mixed acid relatively rich in nitric acid, for example:

HNO_3	22–24%
H_2SO_4	61–62%
H_2O	15–16%

The nitration is carried out in nitrators with mechanical stirring (or — in earlier days — in pots), the cotton to acid ratio being kept within the limits 1:45 to 1:50. In this way nitrocellulose containing 12.1–12.3% of N is obtained.

Stabilization. Dynamite nitrocotton, after being spun in the centrifuge, is immersed in the usual way in cold water, rinsed, and subjected to stabilization boiling. Stabilization must be carried out under conditions which make impossible to bring about a significant decrease of viscosity. Since a greater reduction of nitrocotton viscosity is caused by boiling it in acidified water than when it is boiled in pure water several preliminary boiling operations, carried out for short periods are recommended. For instance, a series of three 2-hr boils, between each of which the water is changed, may be followed by one or more 4–8 hr boil also interspersed by a change of water. In some plants the product of nitration is first washed for 2 hr in hot water at 90°C (poaching), and is boiled several times for longer periods of time only after the acid has been removed.

Dynamite nitrocotton is pulped within as short a period of time as possible, e.g. 2 hr, because excessive beating of the product reduces the viscosity of the nitrocellulose solutions. The pulping is followed by washing or by a short poaching in boilers, after which the purity is checked by means of the heat test. After stabilization, the nitrocotton is freed from sand and other impurities.

Properties of dynamite nitrocotton. The most important test consists in dissolving dry dynamite nitrocotton in nitroglycerine in a porcelain dish at 65°C. To 97.5 g of nitroglycerine, 2.5 g of dynamite cotton are added. The ingredients are mixed for 20 min by means of a horn spatula. After being cooled the gelatine produced should be of such a consistency that it can be taken out of the porcelain vessel like a piece of dough. The gelatine should be neither too viscous, nor too fluid. Frequently an exudation test is carried out at a temperature slightly above room temperature. To this purpose a cylinder of gelatine is kept on a filter paper at 30–33°C for 144 hr. The relevent specifications in different countries allow different diameters for the liquid exuded into the filter paper.

LACQUER-GRADE NITROCELLULOSE

Nitrocotton used for lacquer manufacture is characterized by the following properties:

(1) complete solubility in organic solvents, proved by its capacity to give clear solutions;

(2) a viscosity appropriate to the specific purpose for which it is intended.

The nitrogen content should be within the range 11.0–12.3% N, i.e. within such limits that ensure complete dissolution in organic solvents. For cheaper varnishes, in which ethyl alcohol is used as a solvent, nitrocellulose of lower nitrogen value, e.g. 10–10.5%, is used. Such a nitrogen content endows the product with complete solubility in ethyl alcohol.

Cellulosic raw materials. Linters or wood pulp cellulose are in use as raw material for manufacturing lacquer nitrocellulose. It is essential to use very well purified and bleached raw material. Wood cellulose should contain mainly α-cellulose. The admissible pentosan content is limited to traces only, because these compounds are a source of products insoluble in organic solvents. Cellophane can also be utilized for nitration.

An essential, important test is the measurement of the viscosity of a cuprammonium solution of the cellulose, as by this method it is possible to classify cellulosic material into grades suitable for manufacturing lacquer nitrocellulose of the desired viscosity.

Nitration. The nitration is usually carried out under conditions that promote the production of a low-viscosity product. Hence the process is carried out primarily with linters, at a relatively elevated temperature, commonly between 30 and 35°C. The clarity of nitrocellulose sulution increases with nitration time to an optimum and then decreases [1].

Stabilization. After being thoroughly washed free from acid, the nitrocellulose is subjected to stabilization either in boilers and afterwards in autoclaves (Fig. 153), or directly in autoclaves. Pressure boiling nitrocellulose in autoclaves makes it possible to control the viscosity of nitrocellulose with a high accuracy, since both time and temperature are controlled. The kiers for lacquer nitrocellulose manufacture are constructed of stainless steel or welded sheet iron, enamelled inside. The capacity of the autoclaves ranges from 5 to 25 m^3, their charges varying from 400 to 1500 kg, at a nitrocellulose to water ratio of about 1:10. It is very important to ensure and maintain thorough mixing of the collodion cotton with the water, in order to prevent the nitrocellulose from getting dry, for this may cause decomposition, often followed by explosion. The autoclave is equipped with an external heating jacket as well as with a direct steam injection system.

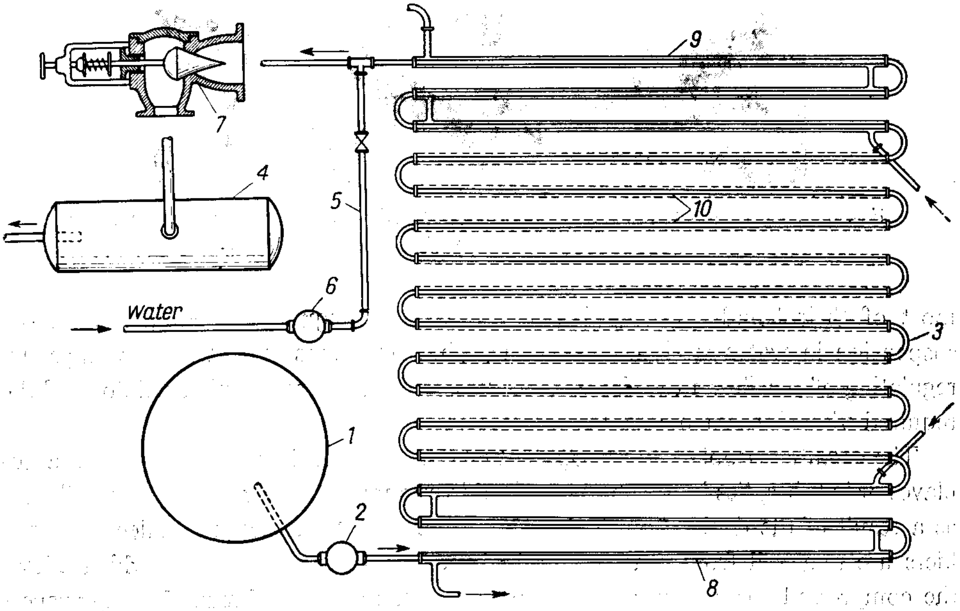

FIG. 164. Continuous digester for nitrocellulose, Hercules Powder Co., [2, 3]: *1*—mixer to prepare a slurry of nitrocellulose with water, *2*—pump, *3*—tube autoclave, *4*—collector of stabilized nitrocellulose, *5*—immergency water pipe with a pump (*6*), *7*—reduction valve, *8*—heated part, *9*—cooled part, *10*—insulated part.

A considerable advance in the practice of stabilizing lacquer nitrocellulose was made by the development of a continuous process of boiling under pressure in acid-resisting tubes, 100 mm dia., up to 1500 m long (Figs. 164 and 165). The tubes are warmed or cooled by means of outer jackets being heated throughout

FIG. 165. Continuous digester for nitrocellulose (Hercules Powder Co.) according to Milliken [2, 3].

most of their length, and cooled at the outlet. Lacquer nitrocellulose as a 4% suspension in water is circulated in the tubes by means of centrifugal pumps. By regulating of the flow rate, the temperature, and the pressure, nitrocellulose of the required viscosity can be produced.

The essential problem in the operation of kiering whether it takes place in autoclaves or in tubes, lies in the removal of acid vapours evolved from the nitrocellulose as a result of the denitration of unstable cellulose esters. Vapours collected in the kiers are removed from time to time by opening a gas-release valve which allows the compressed gases to pass into a special duct. In the continuous boiling process in pipes, the gases are entrained with the suspended nitrocellulose.

Great attention should be paid during the manufacture of lacquer nitrocellulose to the purity of the water used for washing and stabilization. The water should be carefully freed from iron, the maximum permissible concentration of which is 0.002 g/l. Water used in the production of film nitrocellulose should be of even higher purity and also must not contain calcium salts.

Bleaching. It is often necessary in the manufacture of lacquer nitrocellulose to remove all traces of coloured substances by bleaching. One method consists in oxidizing with potassium permanganate in the proportion of 1 kg $KMnO_4$ to 100 kg of lacquer nitrocellulose in the presence of a little sulphuric acid. After the reaction is over the nitrocellulose is rinsed with water, and the brown colour of manganese dioxide is removed by the action of sulphur dioxide or sodium sulphite.

It is also possible to bleach collodion by means of a 1% solution of chlorine or calcium hypochlorite applied for 30–60 min, after which the traces of chlorine are removed with sodium sulphite, and the product is washed.

CELLULOID-GRADE NITROCELLULOSE

Nitrocellulose of 11.8–12.3% N intended for celluloid manufacture is obtained in a way resembling the production of lacquer-grade material with the exception that the viscosity of the product is not of such decisive importance. Low viscosity of the nitrocellulose can cause the celluloid gel to be brittle, however. For this reason care should be taken to keep the viscosity above a certain limit. The essential stabilization can be carried out in boilers without recourse to autoclaves, but in order to shorten the stabilization process it is possible to carry out the kiering in autoclaves, the process then requiring only a few minutes.

LOW-GRADE NITROCELLULOSE

Recently interest was evinced in nitrocelluloses of very low nitration grade, e.g. 0.5–2.0% [4]. They were obtained by nitrating cellulose with mixtures containing 32% HNO_3, 31–38% H_2SO_4 and 32–37% H_2O at 8–30°C.

A noticeable degradation accompanies the reaction (lowering of molecular weight, appearance of carboxyl and carbonyl groups).

The most interesting property consists in their solubility in aqueous 6% NaOH at low temperature (e.g. —7°C). Products containing 0.9–1.0% N possess the best solubility. The viscous solutions can be used to form transparent film by treating with coagulating agents (e.g. C_2O) and washing with water (to remove alkali). The films possess high tensile strength and resistance to bending [5].

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CHAPTER XVI

NITRIC ESTERS OF POLYSACCHARIDES OTHER THAN CELLULOSE. NITRO-DERIVATIVES OF LIGNIN AND ABIETIC ACID

HEMICELLULOSES AND PENTOSAN NITRATES

EXPERIMENTS on the nitration of hemicelluloses composed mainly of pentosans were carried out by Will and Lenze [1]. These authors treated hemicelluloses with strong nitric acid, and isolated the nitration product by precipitation with water or sulphuric acid. The product obtained was insoluble in ether–alcohol.

Rassow and Dörr [2] nitrated hemicelluloses using the mixed acids applied for nitrating cellulose. Thus, making use of a mixture composed of

25.10%	HNO_3
66.85%	H_2SO_4
8.05%	H_2O

that normally produces nitrocellulose with a nitrogen content over 13%, they established that from hemicelluloses an insignificantly nitrated product was obtained in a small yield (Table 100).

The nitration products obtained by Rassow and Dörr were partially soluble in ether–alcohol, and completely soluble in amyl acetate.

As a result of nitrating hemicelluloses by means of more dilute acids, including 16.5–21.0% of water, at 20°C, a product containing even less nitrogen (5.8–7.2%) was obtained. It was scarcely soluble in mixtures of ether and alcohol.

Rassow and Dörr have also nitrated pure xylan, isolated from straw cellulose. By applying a concentrated nitrating acid, mixed at the proportions mentioned above they prepared nitroxylan in the form of a white powder containing 8.76% N, in 115.7% yield.

This product contains only 61% of substances soluble in ether–alcohol. This fraction contains 7.13% of nitrogen, whereas the nitrogen content of the insoluble part is 9.22% N. Other investigations in this field have been mentioned earlier, in Tables 89 and 90.

TABLE 100

THE RESULT OF NITRATING HEMICELLULOSE (AFTER RASSOW AND DÖRR [2])

Temperature °C	Nitrogen content of product %	Yield of nitro-hemicellulose produced from 100 g of hemicellulose g
20	7.24	50.75
10	8.30	107.5
0	8.88	113.2

PECTIN NITRATES ("NITROPECTINS")

Before World War II attempts were made in Germany to nitrate pectins prepared by extracting sugar beet shavings. However, the properties of the nitropectins were of no great interest, and they have not found any practical application.

Until recently, published data concerning pectic acid nitrates was lacking. Schneider and Ziervogel [3] obtained nitric esters of pectins as intermediate products which were then esterified by means of acetic anhydride to the corresponding acetates.

In 1949, Rogovin, Treyvas and Shorygina [4] prepared pectin nitric esters in order to investigate their properties. Pectic acid was nitrated for 4 hr at 20°C in a mixture composed of: 48% HNO_3, 50% H_3PO_4 and 2% P_2O_5 to yield a product containing 9.2% of nitrogen and 7.5% of carboxylic groups.

The number of COOH groups remained unchanged during nitration, and in contrast, say, with celluronic acid nitrates, the product is completely soluble in acetone. In order to explain this behaviour Rogovin *et al.* suggest that a part of the carboxyl groups in pectic acid are esterified, and therefore incapable of participating in ester cross-links between carboxyl and hydroxyl groups. These links are mentioned by the same investigators while discussing the structure of celluronic acids (see below).

ALGINIC ACID NITRATES

Rogovin, Treyvas and Shorygina [4] have examined the product of nitration of alginic acid obtained after 4 hr at 20°C by means of a mixed acid consisting of: 48% HNO_3, 50% H_3PO_4, and 2% P_2O_5.

The product contained 9.3% N and 16% COOH. During nitration the number of carboxylic groups did not increase. The product was almost completely soluble in acetone (96.4%).

To explain the appreciable solubility of the product, Rogovin *et al.* suggest that the carboxylic groups of alginic acid are probably internally esterified with hydroxyl groups. Thus (as with pectic acid nitrates, see above) no cross-links can be formed of the type assumed by the same authors to exist in celluronic acids and in celluronic acid nitrates (see below).

CELLURONIC ACID (CARBOXYCELLULOSES) NITRATES

Celluronic acid produced by treating cellulose with nitrogen tetroxide may then be esterified by means of nitric acid. It has been found that even in the presence of small number of carboxylic groups a considerable change in the properties of the nitric esters is brought about, as compared with cellulose.

To characterize the properties of the product of esterification by means of nitric acid, Rogovin, Treyvas and Shorygina [4] have determined the values collected in Table 101.

TABLE 101

THE RESULT OF NITRATING CELLURONIC ACID (AFTER ROGOVIN, TREYVAS, SHORYGINA [4])

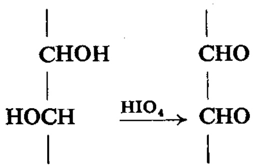
Content of COOH groups in the original substance %	Nitrogen content of product %	Solubility in acetone %
1.56	13.5	18.2
3.6	13.0	9.7
8.0	11.5	13.2
18.5	7.0	2.5

It is clear from the figures that owing to the presence of 2–3% COOH, i.e. one carboxylic group for 8–10 anhydroglucose rings, the product is made very poorly soluble even in such a good solvent of nitrocellulose as acetone.

As for the negligible solubility of celluronic acid nitrates, Rogovin *et al.* consider that it is brought about by the formation of cross-links between the neighbouring long-chain-molecules of oxidized cellulose, owing to the participation of carboxylic groups and free hydroxylic groups. The strength of the glycosidic bonds that link the anhydroglucose units together is considerably weakened by a partial substitution of the primary alcoholic groups by carboxylic groups. Thus, carboxycellulose containing 2–3% of COOH undergoes de-polymerization in the presence of dilute alkalis even at room temperature.

DIALDEHYDE CELLULOSE NITRATES

In the anhydroglucose units of cellulose oxydized by means of periodic acid two aldehyde groups are present produced as a result of the oxidation reaction of the neighbouring secondary alcoholic groups (α-glycols) detected by Hudson and Jackson [5]:



$$\begin{array}{c} | \\ \text{CHOH} \\ | \\ \text{HOCH} \\ | \end{array} \xrightarrow{HIO_4} \begin{array}{c} | \\ \text{CHO} \\ | \\ \text{CHO} \\ | \end{array}$$

Rogovin, Yashunskaya and Shorygina [6] have studied the products of esterification of dialdehyde cellulose by means of nitric acid. The raw material, containing various quantities of aldehyde groups, was nitrated at 0°C with mixture composed of 48% HNO_3, 50% of H_3PO_4 and 2% of P_2O_5.

The product is distinguished from nitrocellulose by its higher hygroscopicity and poorer solubility in organic solvents. Data illustrating the point are listed in Tables 102 and 103.

TABLE 102

THE HYGROSCOPICITY OF ALDEHYDE CELLULOSE NITRATES

Degree of oxidation (number of aldehyde groups contained in every 100 anhydroglucose units)	Nitrogen content of product %	Hygroscopicity (absorbed water) %
0 (cellulose)	13.85	0.82
7.0	13.66	1.02
43.8	12.69	2.64
72.0	11.91	3.50
144.6	9.42	11.02

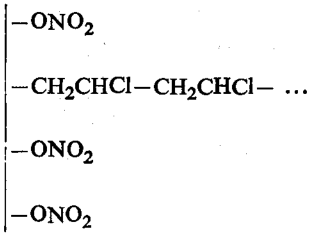
TABLE 103

THE SOLUBILITY OF ALDEHYDE CELLULOSE NITRATES

Degree of oxidation	Nitrogen content of the product %	Solubility in acetone %
0 (cellulose)	13.85	100
5.2	13.75	44.4
14.0	13.11	27.6
43.8	12.7	3.4
73.3	11.8	3.8
117.4	10.3	3.3
144.6	9.4	1.6

COPOLYMERS OF NITROCELLULOSE

Recently Kargin, Usmanov and Aikhodzhayev [7] prepared a grafted copolymer of nitrocellulose with vinyl chloride or vinylidene chloride. The method roughly consists in the formation of free macro-radicals of nitrocellulose (through γ-irradiation or — more effectively — ozonization of nitrocellulose). After that, the monomer of vinyl chloride or vinylidene chloride is reacted with the macro-radical in the presence of a redox catalyst. This eventually gives a copolymer of the following diagrammatic structure:



The main property of such a copolymer is a much lower ignitability and combustibility than that of nitrocellulose. This may be of value in making heat resistant and non-inflammable films, lacquers, celluloid, etc.

On cross-linking nitrocellulose — see p. 303.

NITROSTARCH

Braconnot, who first nitrated cellulose, was also the first to nitrate starch, in 1833 [8]. He dissolved potato meal in conc. nitric acid, and then precipitated the nitration product by adding water. These experiments were repeated by Pelouze [9] and Buijs Ballot [10], whereas in an experiment of Rheinsch [11] the starch was nitrated like cellulose in modern methods, by means of a mixture of nitric and sulphuric acids. For a long time nitrostarch was not distinguished from nitrocellulose. Eventually, attention was drawn to their difference by Béchamp [12]. By reduction of starch nitrate he recovered the initial carbohydrate, i.e. starch in a form that differed from the non-nitrated original starch by its solubility in water. (In accordance with our knowledge it was most probably dextrin). Béchamp [13] tried to apply various methods for isolating nitrostarch dissolved in nitric acid. He used both water and sulphuric acid, and obtained nitrostarch with different nitrogen contents, and has observed that the product separated by means of sulphuric acid was the less stable, readily undergoing spontaneous decomposition. Mühlhäuser [14] expressed a far-sighted view that the low stability of this nitrostarch was due to partial sulphonation brought about by sulphuric acid.

The most extensive of the researches carried out in the nineteenth century were those of Mühlhäuser [14], who dissolved starch in a ten-fold quantity of nitric acid, sp. gr. 1.50 and precipitated the product with thirty times as much sulphuric acid. In this way he introduced 13.5% N, but the nitration product was unstable.

Experimenting with a still stronger nitric acid, sp. gr. 1.52, Will and Lenze [1] prepared nitrostarch characterized by a nitrogen content of 14.04%. They established that it is possible to produce nitrostarch of high nitrogen percentage and adequate stability providing it is subjected to a stabilization boil in ethyl alcohol.

Moreover, Will and Lenze established that starch can be nitrated in a manner resembling cellulose nitration, by means of a mixture of nitric and sulphuric acid, to obtain a product containing 13.9% N. The same method was tried by Sapozhnikov [15]. However, he did not wholly confirm the results published by Will and Lenze, since the maximum nitrogen content in his product was 13.5%.

Starch nitrated by Brown and Millar [16], by dissolution in nitric acid and subsequent precipitation with the help of sulphuric acid, was stabilized by washing in ether and chloroform.

Soluble starch was nitrated by Syniewski [17]. The most extensive published researches devoted to the preparation, purification and properties of nitrostarch are those of Hackel and T. Urbański [18].

Theoretical experiments with nitrostarch attracted the attention of technologists. Uchatius [19] worked out a commercial method of nitrostarch manufacture in 1861 and proposed the use of nitrostarch as a propellant.

Patents were granted in 1889–90 to Schücker [20] for smokeless powder consisting of nitrostarch and oxidizing substances as saltpetre or potassium chlorate, while a patent for manufacturing nitrostarch was granted to Dynamit A.G., Alfred Nobel, in 1891 [21]. This proposed the nitration of starch by dissolution in a tenfold amount of nitric acid, followed by precipitation of the product by means of spent acid from nitroglycerine manufacture. Subsequent operations comprised washing with water, aqueous sodium carbonate, and aqueous aniline. According to Snelling [22] the production of nitrostarch started in the U.S.A. in about 1888, under the name "Volney's powder".

Initially nitrostarch could not be used in practice due to its inadequate chemical stability, but by the beginning of the present century nitrostarch had found practical application in the U.S.A., where it was introduced by a British chemist, Hugh [24] who in 1900 and 1903 constructed and set in operation two nitrostarch factories: one near Asburg Park, New Jersey, and the other near Wharton. Hugh advertized "non-freezing Hugh's Powder" as a substitute for dynamite. It has been proved to be pure nitrostarch.

To nitrate starch, Hugh treated it with an anhydrous mixture of nitric acid, sulphuric acid and oleum to obtain a product that very probably contained 13.3–13.5% N. Hugh's plant was destroyed as the result of an explosion, and the manufacture and application of Hugh's powder was abandoned. Further development of nitrostarch was then taken up by du Pont [25]. In 1905 this company introduced a low-freezing explosive "Nyalite". A similar low-freezing explosive material "Arctic", introduced by the same firm in 1907, was manufactured for the next decade. Both contained nitrostarch.

Another corporation engaged in the same manufacture of nitrostarch for commercial mining purposes was the Trojan Powder Co. [25], which remained for many years the largest and most important producer of nitrostarch.

Another major manufacturer was the Eastern Dynamite Corporation, at Wilmington, Delaware, which developed the patents of Holmes [26]. The starch was nitrated by means of mixed nitric–sulphuric acid and then stabilized by prolonged boiling with water in the presence of calcium carbonate, for 75–100 hr. In later patents the addition of ammonium salts to the water was recommended.

Sadtler [27] lays particular stress on the purification of the starch prior to nitration.

In the period after World War I the efforts of the Trojan Powder Co. to improve the chemical stability of nitrostarch were continued, and a series of patents was granted (Waller [28]).

Special care was devoted to the manufacture, stabilization and application of nitrostarch in the Trojan Powder Co. under the direction of Snelling. His work during the period from 1918 to 1945 is embodied in a large number of patents [29].

Further, a noteworthy patent describing the nitration of starch in the form of flakes was obtained by Norman of the Hercules Powder Co., in 1933 [30].

Towards the end of World War I some 25,000 tons of nitrostarch per annum were manufactured in the U.S.A. It was used mainly in the form of two explosive materials: Grenite and Trojan Explosive. The composition of these explosives is given in Vol. III.

In the period between the two World Wars the production of nitrostarch on an industrial scale also started in Hungary and Poland.

At the beginning of World War II nitrostarch explosives were used for filling bombs, but this practice ceased when the output of trinitrotoluene reached adequate volume. Serious interest was roused, on the other hand, in Trojan's Nitrostarch Demolition Explosive. Its composition is reported in Vol. III.

In Hungary nitrostarch explosives were used during World War II for filling hand grenades.

An extensive review of the literature on nitrostarch was given by Caesar [23].

GENERAL CHARACTERISTICS OF STARCH

Starch is a plant product composed of polysaccharides having the general formula $(C_6H_{10}O_5)_n$. Usually starch is diffused in the form of granules, differing in shape and dimensions according to the particular plants in which the starch occurs. Despite such morphological and physical differences (i.e. in the molecular size) the chemical properties of starches of different origin are the same in principle.

A basic characteristic, common for all kinds of starch, is its aptitude to undergo hydrolysis. Because of this property it is one of the fundamental elements of the diet.

In all types of starch small amounts of phosphorus are present owing to the part played by phosphoric compounds in the enzymatic processes of starch formation. Disregarding a few exceptions, starch consists of two fundamental components:

amylose and *amylopectin*. The separation of these components can be achieved roughly by means of hot water (70°C) which dissolves amylose (10–20%) but is incapable of dissolving amylopectin (80–90%). As a result of hydrolysis these substances yield *maltose*, resulting from an enzymatic breakdown, or *glucose*. The components of starch can be distinguished by means of the iodine test; amylose in the presence of iodine is coloured blue, whereas with amylopectin the colour is violet to red-violet. In comparison with amylose, amylopectin is more resistant to the action of enzymes. Thus in the presence of β-amylase, the amylose is completely hydrolysed to maltose, whilst amylopectin undergoes hydrolysis only to the extent of some 60%.

From osmotic pressure measurements, the molecular weight of amylose has been determined as approximately 10,000–50,000. This value is well in line with the value estimated from the determination of the terminal functional groups.

The molecular weight of amylopectin is appreciably higher, since according to osmotic pressure determinations it is 50,000–1,000,000.

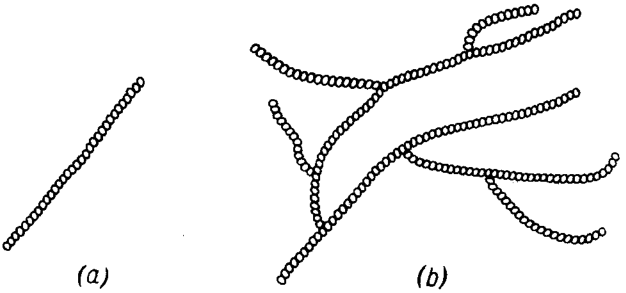
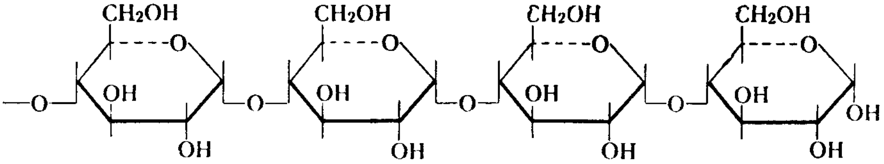


FIG. 166. Structure of amylose and amylopectin: *a*—amylose, *b*—amylopectin.

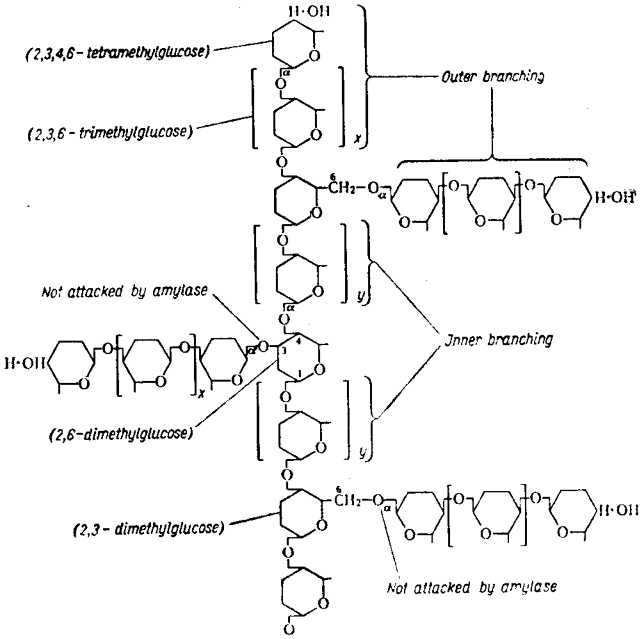
From the determination of the end groups, the long-chain molecules of amylopectin seem to be composed of 24–30 glucose units, from which it is concluded that the substance is a branched-chain carbohydrate.

On the basis of researches devoted to the products of partial or total hydrolytic breakdown of methylated starch, the chain of α-D-anhydroglucose is thought to constitute the main element of the amylose and amylopectin molecules. These units are combined as in maltose, i.e. by means of α-glucosidic linkages formed between the carbon atoms 1 and 4:



As a result of hydrolysing methylated starch, in addition to the main product, which is 2,3,6-trimethylglucose, a small amount of 2,3,4,6-tetramethylglucose is formed from the end rings.

Similarly, the hydrolysis of methylated amylopectin yields small quantities of 2,3-dimethylglucose and its isomeric ether, probably 2,6-dimethylglucose. The presence of the last two compounds confirms the branching of the chains (Fig. 166) at carbon atom 6, and perhaps 3. Staudinger [31] has therefore proposed the following formula for amylopectin (reproduced according to L. F. Fieser and M. Fieser [73]):



PHYSICAL PROPERTIES OF NITROSTARCH

According to Hackel and T. Urbański [18] the solubility of nitrostarch is dependent on its nitrogen content.

Nitrostarch containing 8.0–12.8% N dissolves completely in ether–alcohol, but products with a nitrogen content of over 12.8% N are only partially soluble. In the instance of 13.1% N the solubility amounts to about 78%.

Nitrostarch characterized by a nitrogen content below 8.0% is scarcely soluble in ether–alcohol. Thus the solubility of a 6.4% N-product is only 8.4%.

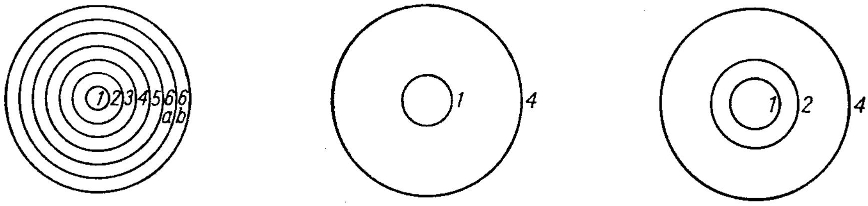
Nitrostarch dissolves in alcohol more easily than nitrocellulose, and at a nitrogen content of 10.0–11.5% is wholly soluble in ethyl alcohol. Incomplete dissolution indicates nitrostarch of higher or lower nitrogen percentage. A product containing 12.1% N has a solubility of 32.5%.

As shown by the experiments of Hackel and T. Urbański, all nitrostarch containing 6.4% of N or more dissolves entirely in acetone.

Kołaczkowska and T. Urbański [32] on the basis of X-ray investigations attempted to explain the crystallographic transformations suffered by starch as result of nitration. They used nitrated potato starch and soluble starch in this investigation.

In the X-ray diagram of potato starch, a series of rings was discovered. Using the nomenclature of Katz [33] these are typical of the "B-spectrum" (Fig. 167a). The spectrum of soluble starch resembles the spectra of amorphous substances (Fig. 167b).

It has been proved that nitrostarch produced by the nitration of potato starch, and the product of nitrating soluble starch, gave exactly the same picture shown in Fig. 167c for which Kołaczkowska and Urbański suggested the name of "N-spectrum".



(a) (b) (c)

FIG. 167. X-Ray diagrams of natural potato starch (a), soluble starch (b), nitrostarch (c).

From these experiments the authors concluded that the nitration of raw starch entailed a decrease in its structure regularity. Amorphous starch, on the contrary, acquired a more regular stucture as the result of nitration.

These experiments also suggest that nitration of starch passes through the stage of hydrolysis to soluble starch before being nitrated:

$$\text{Starch} \xrightarrow{HNO_3} \text{soluble starch} \longrightarrow \text{nitrostarch}$$

This is supported by the examination of the viscosity of nitrostarch which indicates strong degradation of the starch molecule in the course of nitration.

The viscosity of nitrostarch solutions is appreciably lower than the viscosity of the corresponding nitrocellulose solutions. Taking the viscosity of water as 100, the viscosity of 1% nitrostarch solutions varies within the relative values of 45 and 70. Due to such low viscosity and non-oriented crystal structure, nitrostarch solutions leave very fragile film after evaporation. Hence nitrostarch is valueless for varnish production, and for smokeless powder making.

In principle the viscosity of nitrostarch is affected by the same factors which cause a change of viscosity in nitrocellulose. Thus a high nitrogen content in the product, an elevated nitration temperature, or an intensive stabilization boiling of the nitrated product lowers the viscosity of the nitrated substance. However, in the case of nitrostarch the changes in viscosity under the influence of these factors are insignificant.

The data collected below illustrate the behaviour of nitrostarch obtained by treatment with nitric acid alone, without any admixture of sulphuric acid (Table 104).

There is no doubt that starch is strongly degraded during nitration owing

TABLE 104

THE RELATIONSHIP BETWEEN THE NITRATING CONDITIONS AND THE PROPERTIES OF NITROSTARCH

Temperature of nitration °C	Nitrogen content of nitrostarch %	Relative viscosity (water = 100)	Solubility in alcohol %
20	12.13	58.4	32.5
	11.09	52.7	100
	10.28	50.7	78.2
	9.51	50.3	41.8
0	13.19	71.6	
10	13.08	68.3	
20	12.76	61.7	
30	12.57	57.3	

to the hydrolytic action of nitric acid. This is demonstrated by the rapid decrease in viscosity of a 10% starch solution in 97.3% nitric acid, at a temperature of 20°C, as reported by Hackel and T. Urbański [18]:

after the lapse of:	relative viscosity (water = 100)
45 min	4730
75 min	3530
2 hr	2720
3 hr	1925
6 $\frac{1}{4}$ hr	1040
12 hr	625
24 hr	415

On account of such strong degradation, the viscosity of nitrostarch solutions is low whatever the preparative method applied. Likewise large differences in the viscosities of starch before nitration exert practically no influence on the viscosity of the nitrated product. Experiments carried out by T. Urbański and Gołofit [34] provided the data needed to determine the viscosity of starch (in Parlow degrees) and the viscosity of nitrostarch obtained by nitration with nitric acid, sp. gr. 1.50, followed by precipitation with water. The results are collected in Table 105.

The degradation of nitrostarch is also considerable, if starch is nitrated by means of a mixed acid composed of nitric and sulphuric acid. On the contrary, application of nitrating mixture consisting of nitric acid and ortho-phosphoric acid makes it possible to obtain a product nearly twice as viscous as that obtained by treatment with a mixture of nitric and sulphuric acid (T. Urbański and Kapuściński [36]). This shows that the mixture of nitric and phosphoric acid causes less degradation of starch than nitric acid alone or mixed with sulphuric acid. Previously, Berl and Kunze [37] had come to the same conclusion. They found the product of

TABLE 105

COMPARISON OF THE VISCOSITIES OF STARCH AND NITROSTARCH (AFTER T. URBAŃSKI AND GOŁOFIT [34])

Type	Starch		Nitrostarch	
	Viscosity in Parlow degrees	Relative viscosity (water = 100)	Nitrogen content %	Relative viscosity (water = 100)
1	224	1415	13.3	138
2	165	707	13.2	136
3	151	560	13.1	134
4	144	471	13.3	131
5	122	319	13.2	132
6	99	232	13.2	131
soluble	14	103	13.3	124

nitration with a mixture of nitric and phosphoric acid to be of significantly higher viscosity. Later it was confirmed by Kunz *et al.* [37a). They determined the mean molecular weight of starch nitrated with nitric acid–phosphoric acid–water (64/26/10) and nitric acid–sulphuric acid–water (70/20/10) mixtures and found the relative figures 100 and 21–43, respectively.

The nitration product of starch is a non-homogeneous substance. Nitrostarch may be divided into fractions by adding water to its solution in acetone as demonstrated by T. Urbański and Cieślak [38]. The individual fractions vary slightly in respect of nitrogen content, whereas their viscosity is almost identical.

Ashford, Cook and Hibbert [39] have found that it is possible to divide nitrostarch into a soluble fraction of low nitrogen content, and an insoluble fraction containing up to 13.9% N by boiling nitrostarch in alcohol.

A further factor that causes the non-homogeneity of nitrostarch is the presence of the two components, amylose and amylopectin in starch. It has been demonstrated by nitrating each of these starch components separately that the nitration products differ from one another. Berl and Kunze [37] detected that amylopectin yields a product of a considerably higher viscosity than that resulting from the nitration of amylose. This effect may be attributable to the higher molecular weight of amylopectin.

However, T. Urbański and Berłowski [40] have not confirmed this observation and in fact they report that either of these substances give products of more or less the same viscosity. This could occur in consequence of extensive hydrolysis during nitration.

The solubility of the amylose nitration product in ether–alcohol was reported (Ashford, Cook and Hibbert [39]) to be lower, e.g. 20%, than that of the nitration product of amylopectin, which is 86–87%. Such behaviour is explicable in terms of the branched structure of the latter, on the general principle that the solubility of all branched-chain polymers, *except space-network polymers,* is higher than that of straight-chain ones. According to Ashford *et al.* nitroamylose is more stable than amylopectin.

THERMOCHEMICAL AND EXPLOSIVE PROPERTIES OF NITROSTARCH

D. Smoleński and Strzondała [41] determined the heat of combustion of nitrostarch of various nitrogen percentage and hence estimated the heat of formation of nitrostarch, for nitrostarch obtained both by nitration in mixed acid (Table 106) or in nitric acid alone (Table 107).

TABLE 106

NITROSTARCH PRODUCED BY MEANS OF MIXED ACID

Nitrogen content %	Heat of combustion cal/g	Heat of formation cal/g
10.52	2575.8	702.4
11.02	2510.6	668.3
12.87	2276.7	555.5
13.24	2217.9	541.0

TABLE 107

NITROSTARCH PRODUCED BY MEANS OF NITRIC ACID ALONE

Nitrogen content %	Heat of combustion cal/g	Heat of formation cal/g
10.52	2580.7	696.5
12.20	2378.4	576.3
12.87	2309.0	523.3
13.34	2273.3	504.5

The differences in values between the two kinds of nitrostarch are regarded by the authors as related to the presence of sulphuric esters in the nitrostarches prepared by means of mixed acids.

Nitrostarch when ignited burns readily in a way similar to nitrocellulose.

Data characterizing the explosive properties of nitrostarch have been published by Hackel and T. Urbański [42] for nitrogen contents from 7.7% to 13.4% N.

Le Roux [42a] examined explosive properties of nitrostarch of 13.52% N. At a density of 0.90, a charge of 30 mm dia. in a cardboard tube detonated at the rate of 4970 m/sec. The relative lead block expansion was 117 (picric acid = 100), i.e. much the same as for nitrocellulose of 13.40% N.

TABLE 108

EXPLOSIVE PROPERTIES OF NITROSTARCH (AFTER HACKEL AND T. URBAŃSKI [42])

No.	Nitrogen content %	Rate of detonation (in a pipe of diameter 34/28 mm), $d = 0.88$, initiation by No. 8 detonator	Rate of detonation, initiation by 10 g of picric acid	Lead block test cm³	Sensitiveness to shock; 8% explosions caused by a 5-kg weight falling from a height of cm
1	13.4	6190	—	430	21
2	13.1	5740	—	395	23
3	12.8	5300	—	375	—
4	12.4	4950	—	360	36
5	12.1	4480	—	320	38
6	11.6	3880	—	300	70
7	11.0	3020	—	260	100
8	10.5	2880	—	230	100
9	9.4	1500	3200	160	100
10	8.9	1000	3000	125	100
11	7.7	does not detonate		35	does not explode

NITRATION OF STARCH

A fundamental difference between starch and cellulose is shown by their behaviour in the presence of nitric acid. Starch brought into contact with nitric acid of over 76% concentration swells and eventually dissolves, whereas cellulose swells only insignificantly and generally does not dissolve (as described already it can only be dissolved in nitric acid of *ca.* 80% HNO_3).

When a nitrostarch solution in nitric acid is poured into water, sulphuric acid or phosphoric acid, the nitrostarch is precipitated as an amorphous powder.

Hackel and T. Urbański [18] reported that a solution of starch in 10 times its weight of nitric acid (97.3% HNO_3) poured after 6 hr at 20°C into 20 times its weight of water yielded a nitrostarch of 11.7–11.9% N almost completely soluble in alcohol and ether–alcohol. The method has not come into practical use as the dilution of nitric acid with water is not economic.

Nitrostarch of 12.6% N can be prepared, if starch dissolved in ten-fold quantity of nitric acid is poured into 40 times its volume of 94% sulphuric acid, at a temperature not exceeding 20°C. Such nitrostarch includes 11.4% of substance soluble in alcohol, and 95.7% of substance soluble in ether–alcohol.

Starch exposed to the action of nitric acid for a period shorter than 6 hr is converted into nitrostarch of lower nitrogen content, e.g. 12.2% N, after 4 hr.

The main reason why this procedure has not been developed commercially is that during the precipitation of nitrostarch by means of sulphuric acid a sticky intermediate product separates. This is difficult to mix, hence it is not easy to keep its temperature constant and correct, and its composition uniform. In consequence of local overheating, local denitration often takes place so that the product always has a lower nitrogen content than one nitrated directly in a mixture of nitric and sulphuric acid.

Nitration in a mixture of nitric and sulphuric acid results in a more homogeneous product. The maximum nitrogen content is attained after 1–2 hr. As in the case of nitrocellulose, the nitrogen content depends on the final composition of the nitrating acid, i.e. on two factors:

(1) the composition of the mixed acid,

(2) the ratio of mixed acid to starch.

In order to determine the relationship between the nitrogen content of nitrostarch and the composition of the nitrating mixture, Hackel and T. Urbański [18] examined the nitration of starch by means of over a hundred mixed acids of different composition. The starch was nitrated for 1 hr in 50 times as much nitrating acid at 10–12°C. The results obtained can be depicted in a triangular diagram HNO_3–H_2SO_4–H_2O. The composition of the acid is given both in mole per cent, and in weight per cent (Figs. 168a, b).

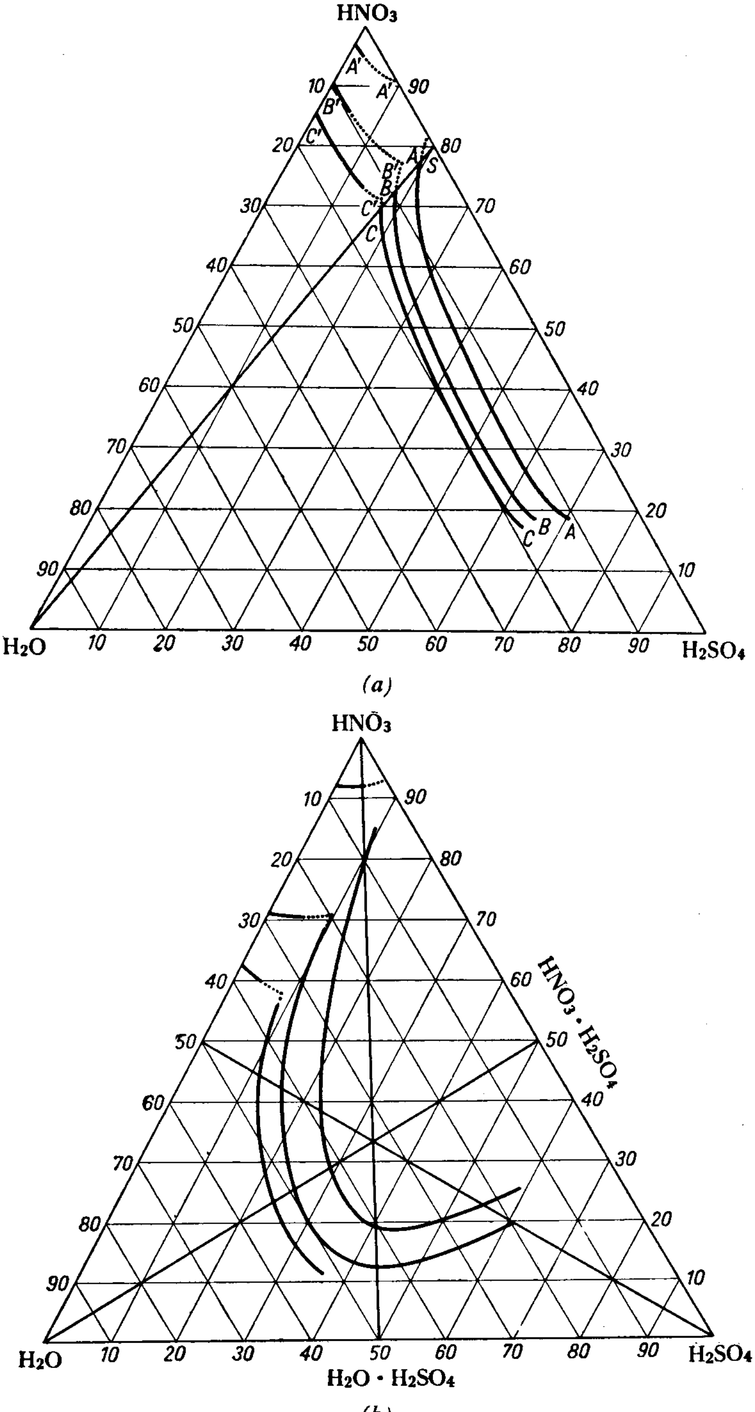
The region of mixtures between the curve *AAA'A'* and axis HNO_3–H_2SO_4 corresponds with nitration to a nitrogen content of more than 12.75% N. In the area limited by *AA–BB* and *A'A'–B'B'* respectively, there are values that correlate with mixed acids yielding products of 11.1–12.75% N. Between *BB–CC* and *B'B'–C'C'* respectively, products of 9.15–11.1% N are obtained. To the left of the line *CC* lies an area corresponding to nitrating acids that give non-homogeneous, low-grade nitrated, oxidized or hydrolysed products. The outlines of the curves *AA*, *BB*, *CC*, resemble those for nitrocellulose (Fig. 121) and also those for nitronium ion $NO_2^{\oplus}$ concentrations.

Comparison of the Sapozhnikov graph for nitrocellulose with the graph by Hackel and T. Urbański shows that in the latter the curve has a minimum which corresponds approximately with a mixed acid where the nitric acid to sulphuric acid weight ratio is about 6 (mole ratio is about 9).

All mixed acids made up with a $HNO_3:H_2SO_4$ weight ratio exceeding 6, i.e. poorer in sulphuric acid, favour the production of nitrostarch of higher nitrogen percentage. This can be demonstrated by the slope of the lines *A'A'*, *B'B'*, *C'C'*, and is explained by the fact that mixtures confined to those areas dissolve the starch during nitration, which therefore proceeds not as a two-phase system as with most mixtures, but in a single phase, so that the nitrating action of these mixtures is more intense. Only towards the end of the nitration process a certain amount of nitrostarch is precipitated from certain mixed acids.

Further, the hydrolysis of starch nitrate in acids containing little or no sulphuric acid does not proceed to such a large extent as is usual when starch is treated with mixtures of high sulphuric acid content.

In all experiments with nitrating acid prepared by mixing nitric and sulphuric acid at a weight ratio higher than 6, the nitrostarch was separated by drowning the whole in water.



(a)

(b)

FIG. 168. Triangular diagram of nitration of starch, according to Hackel and T. Urbański [18]: (a) in mole %, (b) in weight %.

By nitrating different types of starch by means of mixed acid Staudinger and Eilers [43] obtained a product containing 12.5% of nitrogen. Staudinger and Husemann [44] followed the degradation of starch during its nitration.

An interesting nitration method according to which starch was nitrated in two stages at 5°C for 30 min by means of a nitrating mixture including 75–90% of nitric acid, was worked out in the Hungarian factory "Nitrokemia" [45]. Nitration was carried out in two stages. The patents claim that this improves the chemical stability of the product.

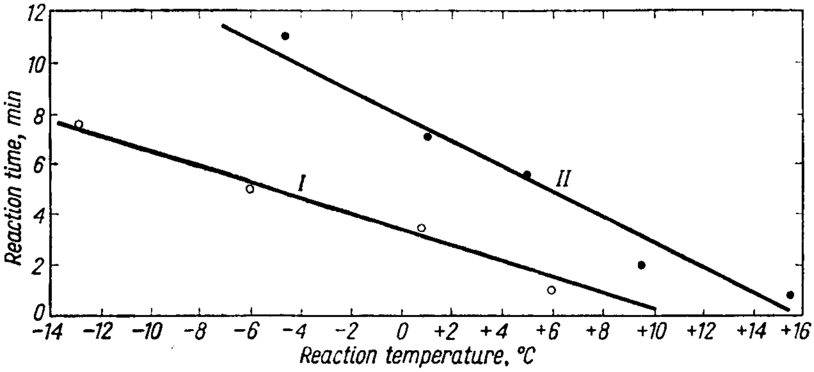


FIG. 169. Reaction time of nitration of starch as a function of temperature, according to Kunz and Tóth [46].

Recently extensive investigations on the nitration of starch, mainly by using mixed nitric and sulphuric acid have been carried out by Kunz and Tóth [46]. Their object was to determine the effect of the ratio of the components in the nitrating mixture and the activity of nitric acid in the mixtures on the nitrogen content of the nitrostarch, the heat of esterification, and the relation between the nitration temperature and the viscosity of the product. Their observations concerning the time of reaction are of special interest. This varies as a linear function of the nitration temperature. In the graph (Fig. 169) the relationship is shown for two mixed acids:

(I) 35.0% HNO_3, 57.5% H_2SO_4, 7.5% H_2O,
(II) 33.4% HNO_3, 60.75% H_2SO_4, 5.81% H_2O.

At temperatures of +14°C and over a product nitrated to the maximum nitrogen content is obtained almost immediately.

T. Urbański and Kapuściński [36] investigated the nitration of starch in a mixture consisting of nitric acid and phosphoric acid, and found that mixed acids containing *ca.* 10% of water or more caused the starch to swell so that nitration proceeded unevenly. Using an anhydrous mixed acid, for instance composed of 20% of HNO_3 and 80% of H_3PO_4, nitrostarch containing 13.0–13.1% of nitrogen was obtained. This is compatible with the results of earlier experiments by Berl and Kunze (37].

It has been demonstrated (T. Urbański and Janiszewski [47]) that it is possible to nitrate starch by means of nitric anhydride vapour in a stream of air or with nitrogen pentoxide dissolved in nitric acid. By nitration for 1 hr starting with 30 min at 10°C, and finishing at 16°C, a product containing as much as 13.86% of nitrogen, characterized by a high chemical stability, was prepared.

During World War II the nitration of starch by means of nitrogen pentoxide was investigated by Caesar *et al.* [48]. They used N_2O_5 dissolved in chloroform. In the course of the reaction nitric acid was formed, which partially dissolved the nitrostarch. In order to counteract this disadvantage the authors added sodium fluoride, which bound the nitric acid by a hydrogen bond to form a complex compound $Na{-}F\cdots HO{-}NO_2$. In this way they succeeded in achieving practically complete substitution of the hydroxyl groups and thus obtained starch trinitrate of low degradation. Its nitrogen content was 13.92–14.03%. No sulphuric esters being present, the stabilization of this product did not present any difficulties.

Later these results were confirmed by Vollmert [49].

According to Izraelashvili [50] nitration conditions favourable for yielding an ester of high nitrogen percentage occur if the concentration of nitronium ions $NO_2^{\oplus}$ in the nitrating agent is high.

Hackel and T. Urbański [18] examined starch derived from different plants (maize, wheat, rice, tapioca and potato) and on reaction with mixtures of nitric and sulphuric acid they obtained nitric esters of practically identical properties (i.e. of the same nitrogen content, solubility, and viscosity) providing the degree of purity of the starch was the same.

COMMERCIAL METHODS OF NITROSTARCH MANUFACTURE

The methods of manufacturing nitrostarch on an industrial scale are not reported in any detail in the technical literature, since for most of them are kept secret.

A solitary description of a commercial method in use in the U.S.A. was published by Davis [51]. To prepare starch for nitration it is first freed from oils and pectic acids by washing in a dilute solution of sodium or ammonium hydroxide, and then rinsing with water. The starch is then dried to a moisture content of below 0.5%, and nitrated.

As the nitrating agent, mixed acid composed of

38%	HNO_3
62%	H_2SO_4

is used.

A charge of about 90 kg of starch is nitrated in one operation. It is immersed in some 360 kg of acid warmed to 32°C. The nitrator is equipped with stirrer. During the operation the temperature is kept within the limits 38–40°C. At the end of nitration the contents of the nitrator are drowned into a tank with water, and the separated product is filtered from the acid.

The nitration product is purified by washing in cold water, without boiling. In order to neutralize acid, in the first stage of washing ammonia is added. Timely application of ammonia is very important for stabilization, since ammonia is readily absorbed by the grains of nitrostarch. The product is dried at a temperature of 35–40°C. Its nitrogen content is 12.75%.

There are many questionable points in this description. To begin with, the dilution of the batch by plunging into water is uneconomic. This can also easily cause denitration of the product owing to local overheating. A stabilization method that omits boiling does not, in general, yield a product of satisfactory stability.

STABILIZATION OF NITROSTARCH

The problem of how to stabilize nitrostarch has been solved by different means, but the majority of stabilization processes remain obscure as patent secrets. None the less, from certain observation some general conclusions can be made. It was early observed by Béchamp [13] that nitrostarch obtained by nitration in nitric acid alone is more stable than one obtained by means of nitric acid mixed with sulphuric acid. This has been confirmed experimentally by Hackel and T. Urbański [18], and seems likely to be explained by the formation of starch sulphates or mixed nitric and sulphuric esters of starch.

One of the nitrostarch stabilization methods worked out by Hackel and T. Urbański (unpublished) consisted in giving the nitrostarch a very finely divided form so as to make it possible for water to invade the interior of the nitrostarch granules. It is, in fact, a method very similar in principle to the process of stabilizing nitrocellulose, since the fundamental operation in the latter consists in cutting the nitrocotton fibres into shorter pieces so as to open the interior of the fibres and permit water to penetrate.

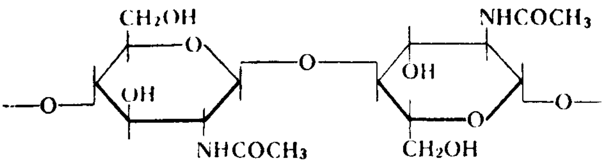
The other principal operation in the stabilization of nitrostarch is prolonged boiling, initially in acid water, and finally in alkaline water. As in the stabilization of nitrocellulose premature alkalization of the stabilizing medium is not recommended as this hinders the hydrolysis of sulphuric esters. Nevertheless in some American contributions (as mentioned above) early addition of ammonia for washing nitrostarch is reported to favour the formation of a stable product.

In patents granted to the Hungarian plant "Nitrokemia", at Füzfö [52] the addition during stabilization boiling of substances capable of swelling nitrostarch is suggested in order to facilitate penetration of the stabilizing liquor into the grains of nitrostarch. Such compounds as epichlorohydrin can act as swelling agents.

For laboratory purposes nitrostarch may be stabilized by boiling with ethyl alcohol. The insoluble part containing 13.4–13.9% N is characterized by considerably higher chemical stability than the raw product before boiling (Ashford, Cook and Hibbert [39]).

NITROCHITIN

Chitin is a long-chain polymer (similar to cellulose) composed of β-N-acetyl glucosamine unit (Meyer and Mark [53]). Every unit contains two OH groups and one NH–$COCH_3$ group:



Nitration of chitin was carried out for the first time by Fürth and Scholl [54]. They tried to produce degradation of the chitin by acting with fuming nitric acid (*d* 1.525). They obtained two products: one insoluble in the common organic solvents, the other soluble in polar solvents. Most likely they were nitrochitin and the oxidation product, respectively. The authors pointed out a similarity between nitrochitin and nitrocellulose. Later on, Schmidt [55] examined the birefringence of chitin and nitrochitin.

The most extensive experiment on nitrochitin preparation and properties were reported by Shorygin and Khait [56]. Shorygin and Khait found that the ordinary nitrating mixture cannot be used to nitrate chitin, as decomposition occurred when the nitrating mixture contained sulphuric acid. They prepared nitrochitin by dissolving chitin in fuming nitric acid (*d* 1.50). After 1–2 hr the solution was poured into large volume of water. The nitrochitin was precipitated in the form of white flakes. The nitrogen content of the ONO_2 groups was 7.5% N, which corresponds to 1.5 ONO_2 groups in every glucosamine unit.

Shorygin and Khait described the properties of nitrochitin. It burns readily when ignited. The ignition temperature is about 163°C. It withstands the heat test at 65°C for 3–8 hr (no change of the colour of starch–potassium iodide paper).

Nitrochitin is partly soluble in formic acid and can be fractionated into two parts by means of this solvent. It can be precipitated with water from the solution in formic acid. The two fractions differ very little with respect to the nitrogen content, but very probably they differ in molecular weight. Nitrochitin swells in benzene, tetralin, nitrobenzene, aniline, phenol, pyridine and furfural.

NITRO-DERIVATIVES OF LIGNIN

An appreciable part of the lignin molecule is aromatic in character. Hence it would be expected to take part readily in the reaction of nitration. It has been found, however, that the capacity of lignin to undergo oxidation predominates especially in the presence of dilute nitric acid. This can be explained by the fact that the aromatic part of the lignin molecule derives from pyrocatechol. The reaction of lignin with nitric acid forms the basis of a method of separating cellulose from wood pulp, that consists in treating this mass with dilute nitric acid (3–10%).

The reaction may be applied in analysis or as an industrial process. Thus Krais [57] obtained patents for producing cellulose from wood pulp by means of 3–6% nitric acid.

The earliest experiments devoted to the nitration of lignin, previously isolated from wood pulp by means of hydrochloric acid, were carried out by Hägglund [58]. Lignin mixed with fuming nitric acid was heated on a water bath until the lignin was completely dissolved, whereupon the nitration product was precipitated by diluting the solution with water. In the aqueous solution oxalic acid was the main product. Hägglund did not investigate more closely the nitrolignin obtained in this way.

Several authors have examined the effect on lignin of nitric acid or its mixture with sulphuric acid.

Detailed investigations were carried out by Fischer and Schrader [59] who nitrated lignin by treating it with 31.5% nitric acid at room temperature, completing the operation with moderate heating. Only 4.3% of nitrogen was found in the product, to which the formula $C_{39}H_{29}O_{21}N_3(OCH_3)_3$ was assigned on the basis of analysis. At the same time König [60] nitrated lignin at a low temperature in a mixture of nitric acid to obtain a product containing 3% of nitrogen.

Powell and Whittaker [61] nitrated lignin with mixed nitric and sulphuric acid at —5°C. The nitration product was isolated by precipitation with water and ice.

The nitrolignin prepared by these workers was a red powder, with the empirical composition:

$$C_{42}H_{39}O_{13}(NO_2)_3$$

The most extensive investigations devoted to the preparation of nitrolignin by direct nitration of wood pulp were those of Kürschner *et al.* [62]. A solution of nitric acid (*d* 1.40) in ethyl alcohol was used at the temperature of boiling ethanol. Under these conditions cellulose remained unchanged. Lignin, on the other hand, was nitrated and dissolved in the alcoholic solution. Nitrolignin was then separated from the solution by means of water, in the form of an amorphous yellow powder. The yield of nitrolignin was 15–17% of the weight of wood pulp. According to the type of wood used to prepare the lignin the nitrogen content of the fully nitrated product varied from 3.0–4.5%.

On the basis of his own experiments, Kürschner suggested the following functional composition of nitrolignin:

$$C_{18}H_{13}O_2(COOH)(OH)_2(OCH_3)(NO_2)$$

In order to separate lignin from carbohydrates stronger reagents were used in the experiments of Friese *et al.* [63] for the nitration of wood pulp, namely normal mixed acids. In this way nitrolignin with a higher nitrogen content was obtained.

When nitric acid and sulphuric acid mixed in a 1:2 ratio were used a product containing 8.45% N was obtained with a yield of 55%. O-nitro groups make up 7.1% N whereas the contribution of C-nitro groups was only 1.35%. An approximately equal relationship between the C-nitro and O-nitro groups was reported by these investigators on nitrating by means of mixtures consisting of nitric and phosphoric acid or nitric acid, acetic acid and acetic anhydride.

A property of the nitration product of lignin which attracted attention was its failure to form detectable amino groups on reduction. The product of reduction could not be diazotized. The reason for this phenomenon is still a matter for controversy. However, Kürschner's view [62] that the amino groups produced in consequence of reduction enter into reaction with the carboxyl group to form a lactam ring seems feasible.

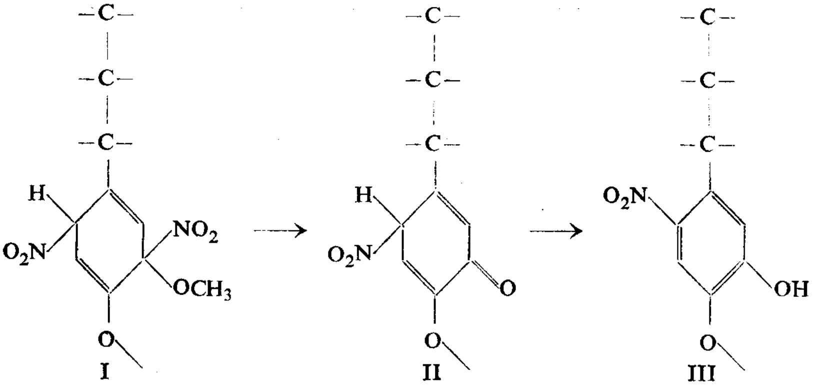
In the course of treating lignin with nitric acid, especially with dilute acid, hydrocyanic acid is evolved. This is explained by the formation of nitrosophenols that undergo a tautomeric conversion into quinone oximes, the latter then being oxidized and hydrolysed. During these reactions HCN is split off in a manner resembling that reported by Seyewetz [64] (compare Vol. I).

In spite of the aromatic character of lignin the experiments described indicate that it is unsuitable for manufacturing nitro compounds likely to be of practical value as explosives.

Nevertheless these experiments have helped to clarify the chemical character of lignin. From this point of view the researches of Freudenberg *et al.* [65], who acted on lignin with nitrogen dioxide or with nitric anhydride are also of importance.

The most noteworthy experiments were these in which nitrogen pentoxide was used in chloroform solution. Thus Freudenberg obtained a product containing 4.7% of nitrogen that corresponds to 0.9 nitro group for a unit comprising one aromatic ring. Freudenberg considered that partial removal of the methoxy groups occurred during nitration. Hence methyl alcohol or methyl nitrite were present among the reaction products.

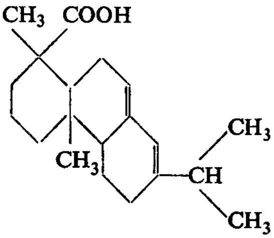
To explain this fact Freudenberg proposed the following reaction scheme:



in which the formula (I) represents the original product of nitration of lignin, while (II) is a semiquinone which is transformed into a nitrophenol (III).

NITRO-DERIVATIVES OF ABIETIC ACID

It is known that the solid residue of distillation of essential oils (turpentine) of coniferous tress—rosin or colophony—is composed mainly of abietic acid:



Nitration of abietic acid was reported in 1904 [66]. Johansson [67] was the first to describe a crystalline nitro-derivative which he considered to be dinitroabietic acid of the formula $C_{19}H_{27}(NO_2)_2COOH$, m.p. 178–184°C (see also [68]). Later reports by Dubourg [69], Goldblatt *et al.* [70] described the nitration in nitric acid ($d = 1.42$) in presence of acetic acid to form dinitroabietic acid $C_{18}H_{25}(NO_2)_2COOH$ of m.p. 171°C (yield 33%).

Fieser and Campbell [71] nitrated dehydroabietic acid with nitric–sulphuric acid mixtures and obtained a product $C_{19}H_{25}(NO_2)_2COOH$, decomposition 178–185°C, identical with this described by Johansson. This was 6,8-dinitro-dehydroabietic acid. It seems to be identical with one of the non-identified products with three (?) NO_2 groups of Dubourg [69].

A trinitroabietic acid, $C_{15}H_{16}(NO_2)_3COOH$, m. p. 156–158°C, was also obtained by Dubourg. He also prepared polynitroabietic acid by nitration of abietic acid with hot anhydrous nitric acid.

An ethyl ester of dinitroabietic acid (m.p. 157.5–158°C) was also described by Goldblatt *et al.* [70].

Nitro-derivatives of abietic acid did not find any practical application, although a few patents were issued [72].

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CHAPTER XVII

SUGAR NITRATES ("NITROSUGARS")

HISTORICAL

LONG ago, such widely occurring and readily available carbohydrates as glucose, lactose, galactose, and saccharose attracted the attention of chemists, who examined these substances to find out whether they were suitable raw materials for manufacturing explosives, in the form of nitric esters.

However, as the result of investigations carried out during different periods of the nineteenth century it became clear that the nitration of sugars was a very delicate operation. The formation of resinous products can occur with the greatest ease. The residues of the nitrating acid are removable only with difficulty and no economic purification process was available. In consequence the product was unstable and it readily suffered decomposition. It was shown, however, by the extensive studies of Will and Lenze [1], that it is possible to obtain crystalline products from the majority of the sugars examined. The following is a general method of O-nitration of sugars. Sugar is dissolved in nitric acid at a temperature below 0°C, and the solution is then poured into well stirred sulphuric acid, the temperature being kept below 0°C. The corresponding sugar nitrate is precipitated. After being separated from acid by filtration, the product is washed with water and ice and then crystallized, most frequently from alcohol. There exist certain sugar nitrates that have no distinct melting point despite being crystalline merely softening within rather wide temperature limits.

Recently a chromatographic method of purifying sugar nitric esters on aluminium oxide has been described (Ansell and Honeyman [2], Honeyman and Morgan [3]).

The nitration of sugars was also studied by: Hlasiewetz and Pfaundler [4], Lea [5], Colley [6], Elliott [7], Gé [8], E. J. Hoffman and Hawse [9], Pictet *et al.* [10, 11], and a number of authors whose studies are mentioned later. The most noteworthy of the earlier results, mainly those of Will and Lenze [1], are collected in Table 109.

An excellent review on sugar nitrates was given by Honeyman and Morgan [3].

TABLE 109

THE RESULTS OF NITRATING DIFFERENT SUGARS

Type of sugar	Formula and nitration degree	Crystallization solvent	Melting point °C	Stability	
				Loss of weight at 50°C	Temperature of decomposition °C
Monoses					
L-Arabinose	$C_5H_6O(ONO_2)_4$		85	40% after 40 days	120
D-Xylose	$C_5H_6O(ONO_2)_4$		liquid	—	—
D-Xylose	$C_5H_7O_2(ONO_2)_3$		141	—	—
L-Ramnose	$C_6H_8O_2(ONO_2)_4$		135	1.2% after 30 days	—
L-Ramnose	$C_6H_9O_3(ONO_2)_3$		*ca.* 100	—	—
D-Galactose	$C_6H_7O(ONO_2)_5$	ethyl alcohol	α 115–116	42% after 1 day	125
			β 72–73	46% after 1 day	125
D-Glucose	$C_6H_7O(ONO_2)_5$		liquid	38% after 1 day	135
D-Mannose	$C_6H_7O(ONO_2)_5$		81–82	46% after 1 day	124
α-D-Glucoheptose	$C_7H_8O(ONO_2)_6$	ethyl alcohol	100		
Bioses					
Maltose	$C_{12}H_{14}O_3(ONO_2)_8$	methyl alcohol	164–165	23% after 43 days	170–180
Lactose	$C_{12}H_{14}O_3(ONO_2)_8$	methyl or	145–146	40% after 40 days	135
Lactose	$C_{12}H_{16}O_5(ONO_2)_6$	ethyl alcohol	70	—	—
Saccharose	$C_{12}H_{14}O_3(ONO_2)_8$	,,	85	11% after 3 days	135
Trehalose	$C_{12}H_{14}O_3(ONO_2)_8$	methyl or ethyl alcohol	124	—	136
Trioses					
Raffinose	$C_{18}H_{21}O_5(ONO_2)_{11}$		55–65		136

PREPARATION

According to the recent experiments of Fleury, Brissaud and Lhoste [12], the nitration of sugars can be carried out at a temperature of about 0°C by means of a mixture prepared from 2 parts anhydrous nitric acid, 1 part acetic anhydride and 1 part acetic acid. A quantitive yield is thus achieved. Further, crystallization of the products is achieved more easily than with esters obtained by nitration with nitric and sulphuric acid.

The following products were prepared by these authors:

	Melting point, °C	Ignition temperature, °C
(1) D-α-anhydroglucose pentanitrate	53.5	200
(2) D-β-anhydroglucose pentanitrate	111	257
(3) D-α-xylopyranose tetranitrate	73.5	250
(4) β-cellobiose octanitrate	140	287

It is possible to crystallize the majority of these esters from hydrated or anhydrous alcohol. These compounds are not stable. Their weight decreases on heating at 100°C, as follows:

compound (1)	60 parts within 10 hr
compound (2)	60 parts within 6 hr
compound (3)	60 parts within 10 hr
compound (4)	35 parts within 20 hr

Monasterski [13] has carried out experiments on nitration of saccharose by means of a mixture of anhydrous nitric acid and oleum 17%, in the presence of urea nitrate, at a temperature not above +2°C. After washing in water, in sodium carbonate solution, and in water again, the product was crystallized from ether–alcohol. Maltose was also nitrated in the same way.

Will and Lenze [1] reported that monoses, in contact with mixed acid at 0–15°C for a period of two days, yield pentosan and hexosan nitric esters. This probably takes place in consequence of the dehydrating action of such mixture on the monoses. In this way they obtained:

from D-xylose:	xylan dinitrate $C_5H_6O_2(ONO_2)_2$ (m.p. 75–80°C);
D-galactose:	galactosan trinitrate, $C_6H_7O_2(ONO_2)_3$;
D-glucose:	glucosan trinitrate, $C_6H_7O_2(ONO_2)_3$ (m.p. about 80°C);
D-fructose:	fructosan trinitrate $C_6H_7O_2(ONO_2)_3$, in two crystalline forms: α (m.p. 139–140°C, temp. of decomposition 145°C), β (m.p. 48–52°C, temperature of decomposition 135°C)
D-sorbose:	sorbosan trinitrate, $C_6H_7O_3(ONO_2)_3$ (m.p. 40–54°C).

Methylglucosides were also nitrated by Will and Lenze [1]. From methyl-α-D-glucoside they obtained the tetranitrate, $C_7H_{10}O_2(ONO_2)_4$, melting at 40–50°C. This is considerably more stable than glucose pentanitrate, its loss of weight after 5 days at 50°C being barely 0.7%. Its decomposition temperature is 135°C.

From methyl-α-D-mannoside a similar product, $C_7H_{10}O_2(ONO_2)_4$, was obtained in the form of needles, melting at 36°C, rather unstable at 50°C.

Fleury, Brissaud and Lhoste [12] also prepared alkyl glucoside esters, using the nitrating mixture described above, composed of nitric acid, acetic anhydride and acetic acid:

(1) methyl-α-D-glucopyranoside tetranitrate (m.p. 48°C) (also Brissaud, Leclercq and Roussin [14]); (2) methyl-β-D-glucopyranoside tetranitrate (m.p. 116.5°C); (3) ethyl-D-xylopyranoside trinitrate, that transforms on crystallization into (4) ethylxyloside trinitrate (m.p. 95.5°C); (5) methyl-β-cellobioside heptanitrate (m.p. 134°C).

The stability of the above compounds is indicated by the following figures that show the loss of weight on keeping the specimen at a temperature of 100°C:

for (1) — the loss is 3% within 20 hr
(2) — the loss is 5% within 20 hr
(4) — the loss is 3% within 20 hr
(5) — the loss is less than 1% during 20 hr.

Besides these investigations which were undertaken to determine whether sugar nitrates were of any practical value as explosives, a series of papers devoted to the theoretical problems of the sugar chemistry have been published. It has been found possible to remove nitrate groups selectively from determined positions by means of methods outlined below, and also to bring about complete denitration by means of reduction processes. These techniques were successfully employed, for instance, in synthesizing a range of new D-glucose, D-galactose, and D-fructose methyl ethers.

The applications mentioned are well illustrated by the following example. Methyl-β-D-glucopyranoside 2,3-dinitrate was converted in the presence of methyl iodide and silver oxide into the 4,6-dimethyl ether of the above nitrate, whereupon it was treated with trityl chloride and acetic anhydride in pyridine eventually yield methyl 4-O-acetyl-6-O-trityl-β-D-glucoside 2,3-dinitrate (Bell and Synge [15]).

Experiments have been made with more moderate nitrating reagents both in order to achieve a more easily controlled reaction than that resulting from the use of a mixed nitric and sulphuric acid, and also with the view to obtaining less impure products. Thus Königs and Knorr [16] used a solution of nitric acid in chloroform to nitrate β-D-glucopyranose penta-acetate, obtaining 2,3,4,6-tetra-O-acetyl-α-D-glucosyl nitrate. Only the acetyl group attached to the C atom was substituted by the nitro group.

Use was also made of a nitric acid solution in chloroform containing phosphorus pentoxide (Oldham [17]). In this way Oldham nitrated trimethyl glucose ether and triacetyl-1,6-anhydroglucopyranose and obtained the crystalline substances: 2,3,5-trimethyl-α-D-glucose 1,6-dinitrate (m.p. 86°C), triacetyl-α-D-glucose 1,6-dinitrate (m.p. 132–135°C).

Nitrogen pentoxide dissolved in chloroform is an excellent O-nitrating agent (Oldham [17]). Montgomery and Clark [18] obtained 1,2,4,5-di-O-isopropylidene-D-fructose 3-nitrate in that way. According to Bell and Synge [15] below 0°C methyl-4,6-O-ethylidene-β-D-glucoside was transformed mainly into 2,3-dinitrate within about 5 min.

With nitric acid, methyl β-D-glucoside 2,3,4,6-tetranitrate is the chief product, probably due to the stronger hydrolysing power of nitric acid, which causes the labile acetal system to break down.

Methyl 4,4-O-benzylidene-α-D-glucoside was converted by Honeyman and Morgan [3] into its 2,3-dinitrate; neither its acetal system nor the aromatic ring was nitrated.

By treating 2,3,4,6-tetra-O-acetyl-α-D-glucosyl chloride in ether solution with silver nitrate (Schlubach, Stadtler, Wolf [19]) 2,3,4,6-O-acetyl-α-D-glucosyl nitrate was obtained.

Leibowitz and Silmann [26] have nitrated the degradation products of polyamylose, namely "di-, tri-, and tetra-amylose". Following in principle the nitration method introduced by Will and Lenze, Leibowitz and Silmann obtained a series of compounds, which they named:

α-diamylose hexanitrate, $[C_6H_7O_2(ONO_2)_3]_2$, m.p. 206°C, crystallized from acetic acid;
β-triamylose hexanitrate, $[C_6H_8O_3(ONO_2)_2]_3$, m.p. 203°C, crystallized from ethanol;
β-triamylose nonanitrate, $[C_6H_7O_2(ONO_2)_3]_3$, m.p. 198°C, crystallized from acetic acid;
α-tetra-amylose octanitrate $[C_6H_8O_3(ONO_2)_2]_4$, m.p. 204°C, crystallized from acetic acid.

All the products were unstable, as within several months of storing in a desiccator, a loss of weight of some 75% was noted.

CHEMICAL PROPERTIES

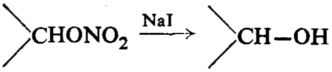
Fehling's solution is reduced at an elevated temperature by all sugar esters including esters of bioses and trioses.

Sugar nitric acid esters are also subject to reductive denitration (see p. 9) and to the chemical reactions typical of sugar nitrates.

One of these consists in the substitution of iodine for the ester group attached to the primary carbon atom as the result of prolonged heating with sodium iodide in acetone solution (Finkelstein's reagent (20]). The reaction appears likely to consist in breaking the C—O linkage:

$$-CH_2-ONO_2 + NaI \longrightarrow -CH_2I + NaNO_2 \qquad (1)$$

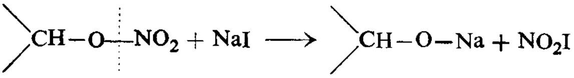
Finkelstein's reagent was first brought into use for this purpose by Oldham [17]. The secondary ester radical does not undergo this chemical reaction, but it may suffer hydrolysis followed by the formation of an OH group:



(2)

Such a reaction takes place more or less readily depending on the position of the atom to which the hydroxyl group is attached. Thus, Oldham and Rutherford [21] kept methyl-2,3-di-O-methyl-β-D-glucoside and sodium iodide in acetone at 100°C for 20 hr and obtained methyl 6-desoxy-6-iodo-2,3-di-O-methyl-β-D-glucoside, accompanied by a small amount of 4-nitrate. As for the β-D-gluco-pyranoside tetranitrate, it seems that the nitrate group attached to the C_4-carbon atom is more reactive than the C_3-nitrate. Thus, Honeyman and Morgan [3] reported that methyl 4,6-O-ethylidene-β-D-glucoside 2,3-dinitrate, exposed to heating with NaI under the same conditions as above (20 hr at 100°C) produced the 3-nitrate with a good yield.

The reaction mechanism seems likely to be different when secondary ester is hydrolysed by means of sodium iodide. It appears to consist in breakage of the O—N bond:



(3)

$$NO_2I + NaI \longrightarrow NaNO_2 + I_2 \qquad (4)$$

Among other characteristic chemical reactions of the sugar nitrates, the reaction with sodium nitrite ethanol solution deserves attention. It is used to remove an NO_2 group from a secondary ester. Thus methyl-4,6-O-ethylidene-α-D-glucoside and 4,6-O-benzylidene-α-D-glucosyl 2,3-dinitrate are converted after about 12 hr of boiling into the corresponding 3-nitrate. The primary ester groups undergo this interchange only in particular cases.

Pyridine and hydroxylamine separately exert only a weak influence on the high-nitrated sugar esters of nitric acid, whereas when they are used together they bring about somewhat violent chemical reaction, as demonstrated by Hayward and Purves [21a].

In this way, from methyl-α-D-glucopyranoside tetranitrate a mixture composed of lower nitrated esters, mainly 2,3,6-trinitrate (28% yield), and 3,6-dinitrate (17% yield) is formed. This is also the best way of any to remove the nitrate group attached to the C_4-carbon atom.

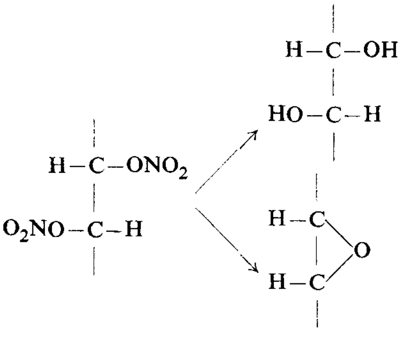
The alkaline hydrolysis of nitric esters can furnish a complicated mixture o products as formerly described (p. 7).

Owing to the ability of alkalis to attack carbonyl compounds, however, clearly the products obtained by the hydrolysis of sugars are more complicated than those obtained from simple nitric esters. This was described in detail by Honeyman and Morgan [3]. It should be pointed out that relatively mild alkaline agents, such as barium carbonate in boiling methanol can also be used to hydrolyse the nitrate groups, e.g. 2,3,4-tri-O-methyl-α-D-glucose 1,6-dinitrate is converted into the corresponding tri-O-methyl-α-D-glucopyranoside.

A high yield of methyl 3,6-anhydro-α-D-glucopyranoside was obtained on treating methyl α-D-glucopyranoside-6-nitrate with alkali (Gladding and Purves [22]).

Investigations by Honeyman [3] have shown that two modes of heterolytic fission of 2,3-nitrate groups can occur under the action of sodium methoxide in methanol on 4,6-O-benzylidene-α-D-glucoside 2,3-nitrate.

A small yield of 7.5% of 2,3-anhydro-α-D-alloside-3-nitrate, and methyl 4,6-O-benzylidene-α-D-glucoside was obtained. The formation of two last products could be explained by the diagram:



(5a)

(5b)

2,3-anhydro-α-D-alloside

Anbar, Dostrovsky, Samuel and Yoffe [23] confirmed the existence of these two modes of fission by the use of a solution of alkali in water containing ^{18}O.

EXPLOSIVE PROPERTIES

The explosive properties of nitrosugars have been examined by Monasterski [13]. This author reported that saccharose octanitrate developed a heat of explosion of 950 kcal/kg, and produced in the lead block an expansion of about 300 cm^3. In the drop test it exploded from the impact of a 2-kg weight falling from a height of at least 20 cm. Maltose octanitrate, in the lead block, caused a net expansion of some 260 cm^3.

Médard [23a] examined the explosive properties of methyl-α-D-glucopyranoside tetranitrate prepared according to Fleury *et al.* [12]. The product requires a relatively weak initiator, e.g. 0.25 g of mercury fulminate suffised to detonate a sample of the substance of density 1.10. Only the cast product (density 1.65) requires a strong detonator (over 1.5 g fulminate).

The sensitiveness to impact is expressed by the data: 50% explosions were obtained by the impact of 1 kg from the height of *ca.* 105 cm. The data are similar to those of cyclonite.

The relative lead block expansion was found to be 130 (picric acid = 100), and the rates of detonation of charges of 30 mm dia. in cardboard tubes were:

density 1.10	5630 m/sec
density 1.50	6970 m/sec
density 1.60	7560 m/sec.

Cast charges (density 1.65) of 20 mm dia. gave the rate of 7830 m/sec.

Médard concluded that methyl-α-D-glucopyranoside tetranitrate is only slightly inferior to cyclonite with regard to its explosive power. Médard also examined mixtures of the substance with dinitrotoluene or ammonium nitrate.

Practical application has been achieved only in the U.S.A. where a mixture of nitrated saccharose with nitroglycerine has found some use. In order to produce such an explosive, a mixture containing 20–25% of saccharose and 75–80% of glycerine is nitrated to produce an oily nitration product [24]. This material was used for the manufacture of dynamite instead of pure nitroglycerine. A mixture of this kind was commercially produced in U.S.A. on economic grounds, namely saccharose was cheaper than glycerine [25].

The product of nitrating saccharose mixed with glycerine marketed under the trade name *Nitrohydrene*, has an appreciably higher viscosity than nitroglycerine itself, hence its stabilization washing is considerably more difficult. Nitrohydrene is particularly inclined to form a water emulsion. To cause it to separate more completely from water after being washed in sodium carbonate solution Nitrohydrene is treated with a sodium chloride solution. The composition of Nitrohydrene differs slightly from that of the original mixture. Nitrohydrene 80/20 obtained by nitrating a mixture consisting of 80% of glycerine and 20% of saccharose contains 86% of nitroglycerine and 14% of nitrosaccharose. In Nitrohydrene 75/25, 82% of nitroglycerine and 18% of nitrosaccharose are present.

The stability of Nitrohydrene is significantly worse than that of nitroglycerine.

The higher the nitrosaccharose percentage in the mixture, the lower its stability. According to Naoúm [25] wood meal admixed with dynamite may act as a stabilizer, because it absorbs the impurities or the decomposition products and can enter into reaction with these compounds, thus removing them. With the aim of improving storage life, 0.1–0.2% of diphenylamine is also added to act as a stabilizer. A mixture prepared in this way can be kept for 75 days at 55°C or for 8 years at 20°C with no sign of decomposition.

Naoúm [25] has determined the values of the lead block expansion as follows:

Nitroglycerine	550 cm^3
Nitrohydrene 80/20	530 cm^3
Nitrohydrene 75/25	515 cm^3

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CHAPTER XVIII

ESTERS OF OXY-ACIDS OF CHLORINE

ESTERS of hypochlorous, chloric and perchloric acid possess explosive properties, but due to their extraordinary sensitiveness to friction, to impact or even to shaking, they have not found any practical application.

Ethyl hypochlorite, C_2H_5OCl, is a substance that is decomposed with explosion when irradiated by sun-light or brought into contact with copper dust. Methyl hypochlorite, boiling at 12°C, also exhibits similar properties.

Ethyl hypochlorite is a yellow liquid, the boiling point of which is 36°C (Sandmeyer [1]). It was prepared by introducing chlorine gas into a cooled mixture composed of 1 part of sodium hydroxide, 1 part of ethanol and 9 parts of water.

Ethyl perchlorate, $C_2H_5OClO_3$, was first prepared by Hare and Boyle [2] as early as 1841. These authors drew attention to the highly explosive character of the substance and the danger of handling it. It is an oil liable to explode even when it is poured from one vessel into another. They obtained it by digesting barium ethyl sulphate with barium perchlorate. Later it was prepared by Roscoe [3] by acting with silver perchlorate on ethyl iodide.

Methyl perchlorate exhibits similar properties.

The explosive properties of these two substances were examined by Berthelot [4]. He found that methyl perchlorate is endothermic substance, with a heat of formation $-\Delta H_f$ of 4 kcal/mole.

The explosive decomposition of methyl perchlorate approximately follows the equation:

$$CH_3ClO_4 \longrightarrow CO_2 + H_2O + HCl + \tfrac{1}{2}O_2 + 1529 \text{ kcal/kg}$$

the volume of gases produced (V_o) is 713 l./kg. These data approximate closely to the corresponding values for nitroglycerine.

It has been found possible (K. A. Hofmann and Zedtwitz [5]) to obtain the esters of perchloric acid by treating alcohols with nitrosyl perchlorate, $NO{\cdot}ClO_4{\cdot}H_2O$. Nitrosyl perchlorate is a stable, crystalline substance that reacts explosively on contact with aromatic amines. In the presence of alcohol the perchlorate and alkyl nitrite are produced.

J. Meyer and Spormann [6] prepared methyl, ethyl and propyl perchlorates from barium ethyl sulphate and barium perchlorate. Their products were oily liquids very sensitive to heat, impact and friction. They determined the boiling points of methyl and ethyl esters as *ca.* 52 and *ca.* 89°C, respectively.

They also found that methyl perchlorate can be formed by the action of diazomethane on perchloric acid. The esters can be hydrolysed by water. The ease of hydrolysis increases from the propyl to the methyl derivative.

Recently, Radell, Connolly and Raymond [7] prepared normal pentyl, hexyl, heptyl and octyl perchlorates from the corresponding alkyl iodide and silver perchlorate. The oily esters were purified as urea inclusion compounds.
Their boiling points were:

n-$C_5H_{11}OClO_3$	51.5°C (11 mm Hg)
n-$C_6H_{13}OClO_3$	52.0°C (4.5 mm Hg)
n-$C_7H_{15}OClO_3$	49–51°C (2.5 mm Hg)
n-$C_8H_{17}OClO_3$	55–60°C (1.5 mm Hg)

The authors examined the infra-red spectra and found a number of characteristic bands:

Cl—O asymmetric stretching 1260, 1230 cm^{-1}
Cl—O symmetric stretching 1035 cm^{-1}
Cl—O stretching 1125–1080, 709–704 cm^{-1}.

Their sensitiveness to impact varies from 5 to 12.7 cm (5-kg weight) and decreases with an increase of the molecular weight. The ignition temperature varies from 150°C (n-pentyl perchlorate) to 350°C (n-octyl perchlorate).

K. A. Hofmann, Zedtwitz and Wagner [8] also obtained the esters listed below:
diethylene glycol monoperchlorate, $ClO_4{\cdot}C_2H_4OC_2H_4OH$ (I)
chlorohydrin monoperchlorate, $ClO_4{\cdot}CH{\cdot}_2CHOH{\cdot}CH_2Cl$ (II)

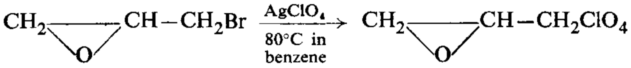
The substance (I) was obtained by treating ethylene oxide with 60% perchloric acid, and the compound (II) by acting with 60% perchloric acid on epichlorohydrin.

The physical state of both esters is that of an oil immiscible with water. According to these investigators, the compounds are strong explosives producing an explosive effect larger than nitroglycerine. Under the influence of water at the room temperature or directly in the presence of atmospheric moisture, the perchlorates are readily hydrolysed, hence their importance in practice is negligible. The stability of the compound (I) is considerably higher than that of (II). Even so it is insufficient to make it practicable to use substance commercially.

Zinovyev *et al.* [9] prepared partial or complete esters with ethylene glycol, glycerine and pentaerythritol by setpwise addition of the alcohol to be nitrated to anhydrous perchloric acid at —75 to —78°C, followed by heating to 60 to 80°C. The reaction mixtures could not be diluted with water since even a few drops of water caused violent explosion. Dilution was effected by adding the constant boiling mixture of perchloric acid and water after which water was added to separate the heavy esters. The esters were extracted with ether. Separation of the ether layer could not be carried out in ordinary funnels as an explosion can occur when the solution enters a ground glass stop-cock. All the products were oily liquids, except the pentaerythritol esters, which were solids. All the perchlorates were very sensitive to impact and friction, and exploded even on careful pouring from one container to another.

A number of alkaryl perchlorates were also prepared for analytical purposes [10].

An interesting attempt to prepare a perchlorate polymer was made by Radell and Connolly [11]. They prepared epiperchloratohydrin (I) from epibromohydrin:



I

The product (I) polymerized on standing to yield a viscous, sirupy mass. It was unstable and exploded at a temperature as low as 25°C after the solvent was removed.

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CHAPTER XIX

SALTS OF NITRIC ACID

THE salts of nitric acid can be divided into two groups: explosive and non-explosive. Metallic salts, e.g. sodium nitrate, potassium nitrate are not explosives themselvest None the less use is made of them in many explosive mixtures, as components tha act as readily available oxygen carriers.

There are also salts of nitric acid that demonstrate explosive properties. This group consists both of inorganic nitrates such as ammonium nitrate, and of organic nitrates. Despite their marked explosive properties these substances are usually used only as ingredients of explosive mixtures.

AMMONIUM NITRATE

Ammonium nitrate is the most readily available and cheapest salt of nitric acid, now manufactured wholly from synthetic ammonia and from nitric acid obtained by oxidation of ammonia. Ammonium nitrate was prepared for the first time as early as in 1659 by Glauber. The original experiments with it as a component of explosive mixtures began in the second half of the nineteenth century. Ammonium nitrate is the most widely used oxygen carrier, since it is an ingredient of the commonest group of high explosives. The reasons for this are to be seen in its properties and those of its explosive mixtures: appreciable chemical stability, and low sensitiveness to friction and to shock.

The disadvantage of ammonium nitrate, which limits its application, is its hygroscopicity.

PHYSICAL PROPERTIES

Ammonium nitrate exists in the form of crystals, melting at 169.6°C. It occurs under five crystalline modifications distinguished by the transition temperatures:

$$\underset{\alpha\ (\mathrm{V})}{\text{Tetragonal}} \xrightleftharpoons{-18^{\circ}\mathrm{C}} \underset{\beta\ (\mathrm{IV})}{\text{Orthorhombic}} \xrightleftharpoons{+32.1^{\circ}} \underset{\gamma\ (\mathrm{III})}{\text{Orthorhombic}} \xrightleftharpoons{84.2^{\circ}\mathrm{C}}$$

$$\rightleftarrows \underset{\delta\ (\mathrm{II})}{\text{Tetragonal}} \xrightleftharpoons{125.2^{\circ}\mathrm{C}} \underset{\varepsilon\ (\mathrm{I})}{\text{Cubic}} \xrightleftharpoons{169.6^{\circ}\mathrm{C}} \text{Liquid}$$

Attention was first drawn to the existence of several crystalline variations of ammonium nitrate by Frankenheim in 1854 [1].

At temperatures above 169°C, under pressures exceeding 9000 kg/cm^2, Bridgman [2] has established the existence of one more form (VI).

The experiments of Volfkovich, Rubinchik and Kozhin [3] indicated that only three transformations are observed when melted ammonium nitrate is cooled quickly at 2°C per minute:

$$\text{Liquid state} \xrightarrow{169^\circ\text{C}} \text{(I)} \xrightarrow{125^\circ\text{C}} \text{(II)} \xrightarrow{50^\circ\text{C}} \text{(IV)}$$

Owing to rapid cooling, form (II) changes directly to form (IV) at 50°C, omitting the transitions that would take place at 84.2 and 32.1°C. An indispensable condition for this behaviour consists in cooling the liquid phase. The phenomenon has not been observed on cooling ammonium nitrate previously heated to 125°C, because the formation of the form (III) is clearly noticeable here. Likewise the transformation at 50°C does not occur when the variation (IV) is heated, as in this case forms (III) and (IV) develop in turn.

The same authors also detected that cooling the form (V) below —170°C causes further transformation to a modification which the authors suggest should be designated as (VII).

The transition at the temperature of 32.1°C, or according to some authors at 32.3°C, from the orthorhombic β-form into the γ-form is accompanied by a volume increase of the crystals of *ca.* 3%. Simultaneously the crystals are split into smaller ones. When the γ-form is cooled, its smaller crystals tend to agglomerate (to "cake"). If moisture is present in the salt, lumps are formed. Both the phenomenon itself and methods of preventing it are discussed more widely later.

The specific gravity of the orthorhombic β-modification is 1.72, and that of the γ-form is 1.66. On heating the substance above 84.2°C a convertion into the δ-variation, followed by an increase of the sp. gr. up to 1.69, occurs.

A negative thermal effect accompanies the transformations of the ammonium nitrate crystal form with rising temperature, whereas during cooling the process is of course exothermic (Table 110).

The transformations, particularly at the temperatures of 32.1 and 84.2°C, are very important with reference to the manufacture and application of ammonium nitrate explosives. In the manufacture of mining explosives containing ammonium nitrate care should be taken that the cartridges are filled with material cooled below 32.1°C. Likewise the temperature inside the various storage rooms in transit during production as well as in the storehouse of finished explosives, should not be allowed to rise above 30°C. Neglecting to observe these conditions may cause the cartridges to harden (see Vol. III). Further, it should be taken into consideration that as the result of loading shells with hot amatols or with any other explosive material containing ammonium nitrate, the loading density will change not only in consequence of cooling but also owing to the transformations of the ammonium nitrate crystal forms.

TABLE 110

THE EFFECTS OF TRANSFORMATION BETWEEN AMMONIUM NITRATE CRYSTALLINE MODIFICATIONS (AFTER HENDRICKS, POSNJAK, KRACEK; [3a])

Crystalline form of ammonium nitrate	Temperature °C	Change of volume cm^3/g	Thermal effect cal/g
I → II	125.2	−0.013	+11.9
II → III	84.2	+0.008	+5.3
III → IV	32.1	−0.002	+5.0
IV → V	−18	+0.016	+1.6

C. C. Stephenson, Bentz and D. A. Stevenson [4] have estimated the specific heat of ammonium nitrate at different temperatures from 15 to 315°K. A selection of figures determined by these authors is collected in the table below:

	T, °K	C_p,cal/mole °K
form (V)	15.12	0.43
	33.08	3.39
	73.62	10.74
	132.78	18.01
	175.58	22.55
	216.70	27.00
	250.69	30.62
	252.78	30.91
	254.30	31.13
form (IV)	256.80	31.46
	260.27	30.03
	267.70	30.76
	274.91	31.40
	278.92	31.88
	280.35	31.87
	289.53	32.58
	300.85	33.47
	302.83	33.65
form (III)	308.9	28.63
	311.24	28.78
	313.52	28.85
	314.06	28.87

The changes in specific heat brought about by the conversion from one crystal form into another, particularly by the transition of the form (IV) into the variation (III), are worth noting.

The solubility of ammonium nitrate in water is very high, as shown in Table 111.

TABLE 111

SOLUBILITY OF AMMONIUM NITRATE IN WATER

Temperature °C	Solubility %	Temperature °C	Solubility %
20	66.1	100	91.0
40	73.3	120	94.7
60	80.2	140	97.4
80	85.9	160	99.4

Ammonium nitrate is also soluble in methyl alcohol and ethyl alcohol. In methyl alcohol 14% of ammonium nitrate is dissolved at 18.5°C.

Ammonium nitrate is also miscible with fused salts of nitric acid. The composition of the eutectics and the fusion temperatures of mixtures with sodium, potassium, and calcium nitrate are considered in future chapters (Vol. III). Data concerning the properties of mixtures with guanidine nitrate, nitroguanidine, ethylene diamine dinitrate, are also reported in Vol. III.

Ammonium nitrate is highly hygroscopic: it becomes liquid in moist air.

According to the relative humidity and the temperature, transformation processes changing the crystallographic form of ammonium nitrate or of its mixtures take place, as a result of which the salt may agglomerate into a stiff mass. This is very undesirable and troublesome. Attempts to break up the caked ammonium nitrate by detonation with explosives have caused accident for which the "caking" was indirectly responsible (p. 454). Numerous experiments have been carried out in search of a method to protect ammonium nitrate against caking during storage. Here are the most important proposals which have been made:

(1) Protection of ammonium nitrate against moisture by storage under completely dry conditions, e.g. by means of suitable water-proof packaging, e.g. waxed paper.

(2) Addition of water-absorbing substances, e.g. anhydrous salts that readily form hydrates, such as anhydrous copper sulphate.

The addition of fine-powdered "inert coating" substances which are adhering to the surface of the ammonium nitrate crystals or granules and are simultaneously capable of absorbing moisture, e.g. powdered kaolin, chalk, kieselguhr, silica gel, zinc carbonate or zinc oxide, in amounts from 0.1 to 5%. This method seems to be accepted in many countries.

In France 1% of calcium stearate is added. It is believed to endow ammonium nitrate with a higher resistance against moisture.

Another method was suggested by J. Taylor and Sillitto [5]. It consists in adding of 0.2–1.5% carboxymethylcellulose and calcium stearate to ammonium nitrate. The mechanism of the action of these compounds is based on the fact that carboxymethylcellulose gels rapidly when it comes into contact with water, forming a barrier to the further penetration of water into the composition. Calcium stearate is a substance very difficult to wet with water and so helps water proofing by slowing down the initial wetting. Subsequently it requires more time for the sodium carboxymethyl-cellulose to swell.

(3) Addition of 2–10% fuel oils, generally 4–6%. However, it should to be pointed out that the presence of a relatively large quantity of a combustible material increases the ability of ammonium nitrate to detonate. This is discussed later (p. 461).

(4) Manufacturing granulated ammonium nitrate with granules as uniform in size as possible, in order to prevent the product from containing any powder which would absorb moisture more readily. A fall in humidity owing to the influence of a higher temperature could cause the fine-crushed product to agglomerate. The same result can be obtained by producing ammonium nitrate in the form of minute balls or pellets ("prilled" ammonium nitrate). This shape minimizes the contact surface of the granules whereas any saturated solution of salt is spread over a larger surface, due to surface tension (Dubovitskii [6]).

Adding "inert coating" and fuel oil to ammonium nitrate is more efficient when the latter is in granulated, prilled or flaked form.

(5) Adding to ammonium nitrate small quantities of Acid Magenta, a trisulpho-triamine-methyl-triphenylmethane dyestuff*. According to Butchart and Whetstone [7] 0.1% of this dyestuff admixed with a saturated ammonium nitrate solution or 0.03% of the dye added to the crystals forms an effective layer that prevents ammonium nitrate from caking within the temperature range −18 to 32°C.

The presence of such a small quantity of an organic substance in ammonium nitrate does not increase its sensitiveness to initiators, hence the danger of storing, or transporting these materials is not increased.

(6) In order to prevent caking some authors have suggested avoiding drying at elevated temperatures. Thus Perelman and Klevke [8] suggested drying ammonium nitrate under reduced pressure at temperatures below 0°C.

(7) According to investigations by Jaenecke *et al.* [9] addition of potassium nitrate to ammonium nitrate prevented the transition from modification (IV) into (III) and the change of volume of the ammonium nitrate crystals. Accordingly, it was suggested at the time of World War II that addition of potassium nitrate

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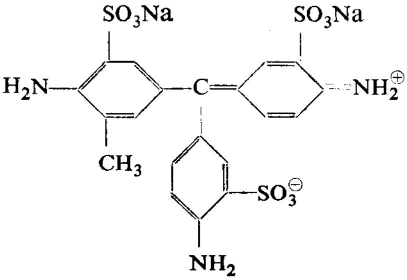


should counteract cracking of compressed or cast charges and agglomeration of powdered ones containing ammonium nitrate.

CHEMICAL AND EXPLOSIVE PROPERTIES

Attention was paid to the explosive properties of ammonium nitrate as early as 1883 by Berthelot [10] who first formulated the equation of decomposition, and gave the numerical data for the heat of explosion, heat of formation, the volume of gases evolved and the temperature of explosion.

Complete detonation of ammonium nitrate is defined by the eqn. (1). Formulae (2), (3), and (4) correspond with incomplete explosion. In a more recent publication Saunders [11] reports that the decomposition of ammonium nitrate at the time of explosion proceeds in accordance with the eqn. (5).

$$NH_4NO_3 \longrightarrow N_2 + 2H_2O + \tfrac{1}{2}O_2 + 346.5 \text{ kcal/kg} \qquad (1)$$

$$4NH_4NO_3 \longrightarrow 3N_2 + 2NO_2 + 8H_2O + 300 \text{ kcal/kg} \qquad (2)$$

$$NH_4NO_3 \longrightarrow \tfrac{1}{2}N_2 + NO + 2H_2O + 140 \text{ kcal/kg} \qquad (3)$$

$$NH_4NO_3 \longrightarrow N_2O + 2H_2O + 133.6 \text{ kcal/kg} \qquad (4)$$

$$8NH_4NO_3 \longrightarrow 5N_2 + 4NO + 2NO_2 + 16H_2O + 132.6 \text{ kcal/kg} \qquad (5)$$

Other formulae of decomposition are also possible. Heat of formation $-\Delta H_f$ is 88,6 kcal/mole.

Thermal decomposition. According to A. J. B. Robertson [12] a very high activation energy, $E = 40.5$ kcal/mole, characterizes the thermal decomposition of ammonium nitrate.

Wood and Wise [13] examined the rate of decomposition of ammonium nitrate enclosed in sealed ampoules and kept at temperatures between 200 and 300°C. They found the energy of activation $E = 31.4$ kcal/mole.

Cook and A. Taylor [14] as well as Guiochon and L. Jacqué [15] used a thermogravimetric method to study the decomposition of ammonium nitrate between the temperatures: 217–267 and 180–280°C respectively. They found the energy of activation was 38.3 and 36.5 kcal/mole respectively.

Using the numerical data of Shah and Oza [16], Guiochon [17] also calculated the energy of activation $E = 39.0$ kcal/mole, thus approaching the data of A. J. B. Robertson, Cook and A. Taylor, Guiochon and L. Jacqué. Moreover, all these authors agree that the reaction of thermal decomposition ("thermolysis" according to Guiochon and L. Jacqué) of ammonium nitrate is of the first order (under the conditions studied).

However, Feick and Hainer [18] consider most of the above figures of the energy of activation are not very accurate as in the period prior to explosion a considerable quantity of ammonium nitrate is evaporated. The authors suggest the following equations for ammonium nitrate thermal decomposition:

$$\text{at } 170°\text{C}, \ NH_4NO_3 \rightleftarrows NH_3 + HNO_3, \ \Delta H = 35.4 \text{ kcal/mole} \qquad (6)$$

$$\text{at } 290°\text{C}, \ NH_4NO_3 \rightleftarrows N_2O + 2H_2O, \ \Delta H = -16.4 \text{ kcal/mole} \qquad (4)$$

Decomposition accompanied by the development of nitrous oxide compatible with the scheme (4) only starts above 170° C. Marked decomposition together with the evolution of nitrogen, nitric oxide and water, corresponding with the reaction (3), begins at a temperature of about 220°C [11].

Kummer [19], Friedman and Biegeleisen [20] studied the decomposition of ammonium nitrate labelled with ^{15}N: $[^{15}N]H_4$ $[^{14}N]O_3$. The completely anhydrous salt did not decompose until 300°C. Only sublimation took place. But a trace of water initiated decomposition at 180°C. The main products of the reaction were N_2O and water (according to the eqn. (4)) and with the labelled salt, nitrous oxide $[^{14}N]$ $[^{15}N]O$ was produced showing that the gas was formed by the interaction of the two ions in the molecule. They also showed that with ordinary ammonium nitrate and $H_2{}^{18}O$, no $N_2{}^{18}O$ was formed, indicating that the water had a purely catalytic effect.

According to Guiochon [17] the experiments with labelled nitrogen atoms seem to support an earlier suggestion of Davis and Abrams [21] that the decomposition of ammonium nitrate may pass through the intermediate formation of nitramide through dehydration of ammonium nitrate in the first stage (7):

$$NH_4NO_3 \longrightarrow NH_2NO_2 + H_2O \tag{7}$$

$$NH_2NO_2 \longrightarrow N_2O + H_2O \tag{8}$$

The reaction (8) would be very rapid and the reaction (7) is the rate determining step.

A number of authors also examined the influence of addition of various compounds on the thermolysis of NH_4NO_3. Saunders [11], Tramm and Velde [22], Keenan [23] were among those who investigated the influence of the presence of ammonium chloride. The widest experiments on this line were carried out by Guiochon and L. Jacqué [24, 17]. Using the thermogravimetric method, they examined decomposition of ammonium nitrate with ammonium fluoride, chloride, bromide, iodide and sodium chloride between 160 and 250°C. Figure 170 shows the change in weight of the samples of ammonium nitrate — pure and with ammonium chloride: at 200 and 250°C with 5% NH_4Cl and with 0.01, 0.2, 1.0 and 5.0% NH_4Cl respectively.

The authors drew attention to the induction period noticeable in both types of samples: of pure ammonium nitrate and those with ammonium chloride. The time, length and character of the induction period does not seem to depend on the concentration of ammonium chloride in the samples. After the induction period the decomposition of ammonium nitrate with ammonium chloride becomes faster than that of the pure substance. Guiochon and L. Jacqué found that the samples became acid during the induction period. Free nitric acid, and in the samples with ammonium chloride free hydrochloric acid (and subsequently chlorine) are formed. By adding nitric acid or chlorine to the samples, a considerable reduction or suppression of the induction period was achieved.

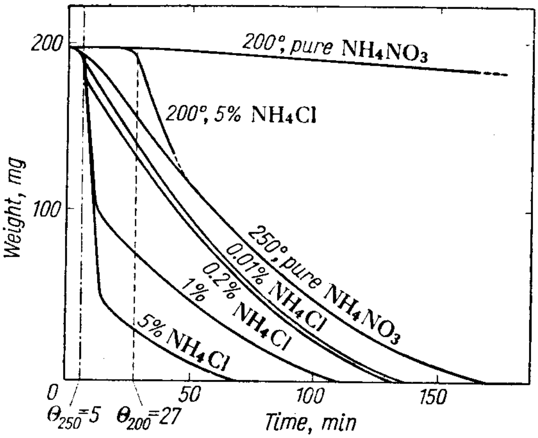


FIG. 170. Thermal decomposition of ammonium nitrate (pure and with varying quantities of ammonium chloride) at 200°C (broken line) and 250°C. Θ—induction period in min, according to Guiochon and Jacqué.

Several authors noticed that the addition of chromium salts to ammonium nitrate increases the rate of its decomposition: Audrieth and M. T. Schmidt [25], Blinov [26], J. Taylor and Sillitto [5], J. Taylor and Whetstone [27], A. J. B. Robertson [12], Shidlovskii [28], Shirai and Ishibashi [29].

J. Taylor and Sillitto found that ammonium nitrate mixed with 3% of potassium chromate or bichromate undergoes spontaneous decomposition ("burning") on being heated to about 400°C. J. Taylor *et al.* [5, 27] suggest utilizing mixtures made from ammonium nitrate and potassium chromate as the main component of rocket solid fuels. This is described in more detail in Vol. III.

The most extensive investigation was carried out by Guiochon and L. Jacqué [30] and Guiochon [17, 31]. They used the same thermogravimetric method as in their former experiments, and examined the influence of chromium oxide (0.3–8%), potassium bichromate (0.1–3%), chromium nitrate (1–5%) and also pure chromium (0.033–5.5%) [30].

The increase in the rate of decomposition under the influence of added Cr_2O_3 and $K_2Cr_2O_7$ is shown on Figs. 171 and 172 respectively. It has been found that an increase of the rate occurred only at temperatures near to the melting point of the samples. Guiochon [17] also found that cobalt salts increase the rate of thermolysis of ammonium nitrate. Other mineral salts (of manganese, nickel and copper) have a similar but much weaker action. A large number of salts of other metals are without any noticeable action.

Thermal decomposition of ammonium nitrate can also be facilitated by adding organic compounds. Thus, ammonium nitrate mixed with cellulose begins to decompose at 100°C and decomposition becomes distinctly perceptible at 120°C. Also salts of some organic bases (e.g. pyridine nitrate) considerably lower the temperature of decomposition of ammonium nitrate.

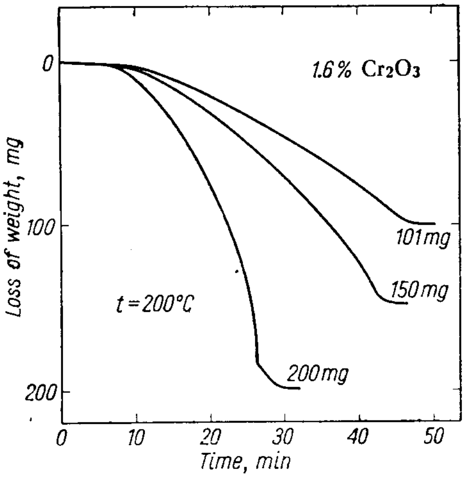


FIG. 171. Decomposition of ammonium nitrate with 1.6% Cr_2O_3 added, according to Guiochon and Jacqué.

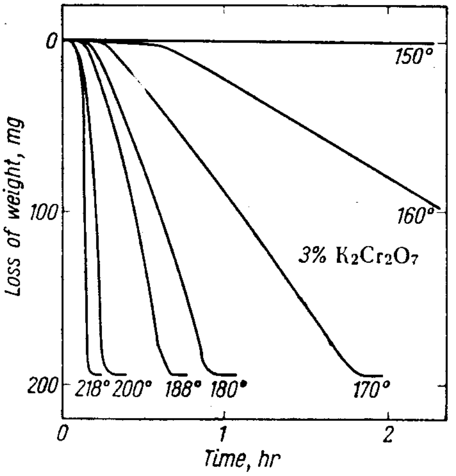


FIG. 172. Decomposition of ammonium nitrate with 3.0% $K_2Cr_2O_7$, according to Guiochon and Jacqué.

Explosive decomposition and stability. The following data are reported to be correlated with the decomposition according to eqn. (1):

volume of gases, V_0	980 l.
temperature,	$t = 1500°C$ (Muraour and Aunis [32] found a temperature of 1125°C)
"force",	$f = 6570$ m

It has long been realized that ammonium nitrate is one of the most difficult explosive materials to detonate. Moreover, it was generally accepted that it would be impossible to cause the substance to detonate even by means of exceptionally strong initiation, provided no admixtures of other explosives were present. This view led to the belief that ammonium nitrate was so safe to handle that it was subjected to operations normally permitted only for non-explosive substances. This resulted in several great catastrophes noteworthy in the history of ammonium nitrate manufacture.

In Upper Silesia, in the summer of 1921, while unloading caked ammonium nitrate from a railway car in order to make the work easier shot holes were bored in the material, and charged with an ammonium nitrate explosive, whereupon the charges were exploded. The detonation of these charges was followed by the detonation of ammonium nitrate contained in the car. The detonation was transmitted to ammonium nitrate in the neighbouring car. This accident claimed numerous victims and was accompanied by appreciable material damage.

The largest catastrophe in the history of the chemical industry took place in September, 1921, at Oppau, where a partial detonation of about 4000 tons of a double salt, composed of more or less equal amounts of ammonium nitrate and ammonium sulphate occurred. The cause of this explosion has never been fully explained. Most likely it was brought about by attempts to break up the agglomerated double salt by means of an explosive. Approximately 1000 men were killed in the Oppau explosion.

These catastrophic accidents showed that ammonium nitrate even diluted by another ammonium salt, is an explosive capable of detonating under a sufficiently powerful explosive stimulus [33].

Ammonium nitrate is stable at room temperature, though on storage a little ammonia is evolved, in accordance with the reaction (6a) (see also eqn. (6), p. 455):

$$NH_4NO_3 \longrightarrow NH_3 + HNO_3\,(\text{gas}) - 521\ \text{kcal/kg} \tag{6a}$$

This is an endothermic reaction of non-explosive character. It is evident from reaction (6a) why ammonium nitrate becomes acid during storage. Owing to the presence of free nitric acid in ammonium nitrate, its admixture with nitroglycerine may cause the latter to decompose in the course of time. Hence a little calcium carbonate, e.g. 0.3%, is very often added to ammonium nitrate destined for the manufacture of explosives including nitroglycerine.

At any temperature below the melting point, that is below 160°C, no chemical reactions occur except (6a) as mentioned already.

Pure ammonium nitrate when hermetically confined can be made to explode by rapid heating to a temperature above 200°C. Thus, for example Herguet [34] reports that ammonium nitrate confined hermetically undergoes an explosive decomposition on being heated to a temperature of 260–280°C. On the other hand attempts to bring about an explosion of ammonium nitrate that was not perfectly confined failed. Sherrick [35] has established that ammonium nitrate non-hermetically confined does not decompose explosively due to a thermal reaction, but will do so if brought in contact with molten iron.

The ease of detonation of ammonium nitrate is greatly influenced by its density. This was studied in detail by Fukuyama [36]. He prepared porous ammonium nitrate. The porous state appears at the transition points of 125 and 84°C when cooled. After the transition, the salt reserves its normal, less porous state. By rapid cooling the porous state can be preserved.

Table 112 gives the sensitiveness to initiation of low density and ordinary ammonium nitrate according to Fukuyama. Samples were loaded in a steel pipe of 12.5/16.5 mm dia. 50 mm length.

TABLE 112*

	Ammonium nitrate								
	of low-density						ordinary		
Loading density, g/cm^3	0.5	0.6	0.7	0.8	0.9	1.0	0.8	0.9	1.0
Weight of initiator (mercury fulminate–chlorate mixture)									
0.3 g	*I*	*I*	*N*						
0.4	*E*	*E*	*I*						
0.5			*E*	*N*	*N*	*N*			
0.75				*I*	*I*	*N*			
1.0				*E*	*E*	*E*	*N*	*N*	
1.4							*E*	*E*	*I*
No. 6 detonator and 2 g TNT									*I*
No. 6 detonator and 4 g TNT									*E*

* Abbreviations: *N* – no explosion, *I* – incomplete explosion, *E* – explosion or detonation.

The rate of detonation of low-density ammonium nitrate was also determined by Fukuyama [36] (Table 113) at different temperatures in steel pipes of 35/40.4 mm dia. The initiation was by a No. 6 detonator.

In steel tubes of smaller diameter at room temperature, at the loading density 0.5 g/cm^3, the rates of detonation were:

in 12.5/16.5 mm dia.	1520–1550 m/sec
in 27/32 mm dia.	1690–1740 m/sec

Fukuyama also studied the sensitiveness and the rate of detonation of ammonium nitrate containing water.

He found that ammonium nitrate containing 5–8% of water at a loading density 0.5 can be brought to detonation by a very strong initiator such as a No. 6 detonator with 15 g of TNT. With a 60 g TNT detonator, ammonium nitrate of even 10% water content can detonate in a 35/40.4 mm steel tube at a rate of 1900 m/sec.

TABLE 113*

Temperature °C	Loading density g/cm³	Rate of detonation m/sec	Loading density g/cm³	Rate of detonation m/sec
20	0.67	1760	1.0	*N*
50	0.67	1900	1.0	*N*
70	0.60	1900	1.0	*N*
90	0.60	1900	0.93	*I*
100	0.65	2170	0.93	*I*
110	0.65	2170	0.90	*I*
120	0.60	2000	0.84	1250
130	—	—	0.79	1530
140	0.65	2170	0.74	1570

* Abbreviations: *N* — no explosion, *I* — incomplete explosion.

The sensitiveness of ammonium nitrate to impact is relatively low: explosion takes place when a 10 kg weight is dropped from a height of 20 cm. The sensitiveness to shock increases with increasing of temperature, as shown in Table 114, published by Rinkenbach [42]:

TABLE 114

THE EFFECT OF THE TEMPERATURE ON THE SENSITIVENESS TO SHOCK OF AMMONIUM NITRATE

Temperature, °C	25	75	100	150	175 fused
height of fall a 2-kg weight, cm	79	71	69	69	50

The sensitiveness of fused ammonium nitrate is distinctly higher, and approximates to that of TNT. Ammonium nitrate does not take fire from the hot flame produced by a safety fuse.

The rate of detonation of ammonium nitrate depends to a large extent on the degree of fineness, the initiator, the density, and the confinement of the charge. It varies within wide limits, from 1100 to 2700 m/sec.

The net expansion in the lead block, as reported by different authors, varies between 180 and 220 cm³.

Many years' experience indicates that pure ammonium nitrate containing no organic substances detonates with greater difficulty than one containing organic substances. The well known explosion on the ship "Texas City" in April, 1947, was originated by the inflammation of an ammonium nitrate made in U.S.A. that contained 1% of mineral oil and 5% of kaolin. In order to prevent the propagation of fire both the ventilation channels and the doors in the partitions separating the store rooms were shut. This resulted in an increase of pressure within the storage holds which ended by an explosion.

This accident caused a re-investigation of the explosive properties of ammonium nitrate mixed with fuel oil. A considerable amount of work was done by several authors particularly in the Explosives Research Laboratories, U.S. Bureau of Mines.

Cook and Talbot [37] found that the highest sensitiveness of ammonium nitrate to initiation by detonation exists when ammonium nitrate contains 0.75–1.5% of paraffin oil. It can be detonated by a No. 6 detonator.

Brinkley and Gordon [38] have shown that some compositions can be brought to detonation with considerable ease, and the maximum sensitiveness is at *ca.* 2–4% of oil content.

This was confirmed by Van Dolah [39]. The latter also determined the rate of detonation of paper cartridges of prilled ammonium nitrate with 4% fuel oil at a density of 0.95:

in 1.25 in. dia.	2980 m/sec (No. 8 detonator)
in 1.87 in. dia.	3750–3760 m/sec (No. 6 and 8 detonators)

Also according to Van Dolah ammonium nitrate–oil mixtures offer a certain dust explosion hazard and any electric equipment (switches controls, motors, lights) located in the plant should conform to the safety requirements or should be installed outside the plant. In order not to increase the dust explosion hazard no liquid hydrocarbon fuel with higher volatility than No. 2 Diesel fuel (minimum flash point of 145°F, ASTM closed-cup procedure) should be used as an admixture to ammonium nitrate. More volatile fuels, such as gasoline, kerosine or No. 1 Diesel fuel cannot be recommended according to Van Dolah, as they would seriously increase the hazard of a vapour explosion.

It has been suggested by Lee and Akre [40] that fertilizer grade ammonium nitrate containing "inert-coating" and fuel oil can be used as a blasting explosive. Indeed it became a useful explosive in open pit blasting. This is described in detail in Vol. III.

Tournay, Murphy, Damon and Van Dolah [41] examined the fumes produced by the detonation of ammonium nitrate–fuel mixtures. They came to the conclusion that carbon monoxide formation is within the allowed limits. However, the concentration of nitric oxide and nitrogen dioxide is much higher than in typical dynamite compositions. On the ground of these experiments they expressed the view that ammonium nitrate–fuel compositions should not be recommended for underground blasting.

An unconfirmed hypothesis was also formulated that ammonium nitrate in the presence of sulphuric acid undergoes dehydration to the formation of nitramine (Vol. III) which is a strong and unstable explosive compound.

A double salt of ammonium nitrate and sulphate, defined by the formula $2NH_4NO_3 \cdot (NH_4)_2SO_4$, is capable of detonating with a rate of 1000–1400 m/sec provided an exceptionally strong initiator and completely hermetic confinement are used (Kast [33, 43]). However, the detonation train of this double salt has a tendency to break up after travelling a short distance (see also Blinov [43a]).

It has been suggested (Cornet and Boodberg [44]) that the explosive properties of ammonium nitrate might be utilized for improving the ignition of the fuel in Diesel motors. For this purpose concentrated ammonium nitrate solution was added to the fuel containing 0.25% of emulsifier, thus producing an emulsion of aqueous ammonium nitrate in the fuel. Adding 4% of ammonium nitrate solution of 20% concentration, to a self-igniting fuel that ignites at 215°C reduced the self-ignition temperature to 207°C. The same amount of water without ammonium nitrate added to the fuel increased the self-ignition temperature to 220°C.

COMMERCIAL PRODUCT

Ammonium nitrate for explosive manufacture should conform with the following purity requirements in accordance with the Soviet standard (GOST 2–40):

colour	white or yellowish
ammonium nitrate content	99.5%
maximum moisture percentage	0.5% type A (fine crystals) 0.8% type B (larger crystals)
reaction	neutral
non-volatile mineral content	max. 0.15%
water-insoluble material	max. 0.08%
salts of sulphuric acid calculated as $NH_4(SO_4)_2$	max. 0.15%
organic substances (oxidizable)	traces

According to the U.S. Standards ammonium nitrate for production of military explosives should contain: 99.0% of NH_4NO_3, no more than 0.02% free nitric acid, 0.18% of water-insoluble material, 0.50% of ammonium sulphate and 0.5% of ammonium chloride. The product should be free from alkalis and metal nitrates. A substance of similar purity is used for the manufacture of mining explosives.

In the U.S.A. ammonium nitrate is available commercially in different forms. There are prilled, flaked and granular forms.

Various brands of ammonium nitrate uncoated or coated with clay or kieselguhr, and with other inorganic or organic substances, such as fuel oil are produced.

Methods of manufacture ammonium nitrate are described in specialist books on inorganic technology and technology of nitric acid and ammonium salts. However, the method of manufacture of low density prilled ammonium nitrate merits special attention as it can be used to manufacture low density coal mine explosives.

Prilled ammonium nitrate is prepared essentially by methods involving the following steps:

The ammonium nitrate solution (from the neutralizer) is evaporated to *ca.* 96% concentration in the steam heated vacuum evaporator. The concentrated solution is sprayed into the top of the prilling tower, where it falls through an upward flow of air supplied by blowers at the base of the tower. During its fall it is cooled and solidifies to round pellets or "prills" of the desired size.

The prills are drawn off continuously from the hopper bottom of the tower by means of a conveyer and fed to the pre-drier, then to the drier and cooler. From the cooler the prills are elevated to a double deck screen. Oversize and undersize are dissolved in water and returned to the neutralizer or used for producing "nitrogen solutions".

The intermediate size is dusted with a small amount of coating material (diatomaceous earth or kaolin) in a rotary coating drum.

Fertilizer grade ammonium nitrate prilled with fuel oil is generally used in the U.S.A. for making explosives other than permitted types (see Vol. III).

Ammonium nitrate prepared from ammonia obtained by the dry distillation of coal should not be used as component of any explosive material because of the ammonium thiocyanate and pyridine present in it (the latter as nitrate). When the ammonia liquor from dry distillation of coal was the sole source af ammonia and ammonium nitrate, decomposition of mixtures containing ammonium nitrate with TNT (amatols), was brought about: at the melting point TNT reacted with ammonium thiocyanate or with pyridine nitrate and evolved gaseous products. Minute traces of these impurities were sufficient to cause abundant gas evolution to develop during the fusion, pouring, and cooling of amatol.

HYDRAZINE NITRATE

Hydrazine nitrate, $NH_2\cdot\overset{\oplus}{N}H_3\cdot\overset{\ominus}{NO_3}$, exists in two crystalline forms of different melting temparatures: the stable form melts at 70.7°C, while the labile melts at 62.1°C. In contact with water hydrazine nitrate dissolves with great ease to form a strongly acid solution. In the fused state it reacts rapidly with several metals, such as zinc and copper. Hodgkinson [45] explains this behaviour as due to the formation of azides under these conditions. In the presence of nitrites, hydrazine nitrate forms salts of hydrazoic acid.

According to Kast [46] hydrazine nitrate is practically stable at 75°C, since after 9 months of heating it lost barely 0.7% of the weight. It does not explode on heating to 360°C. The substance is sensitive to friction and to impact, resembling tetryl, and according to Médard [47] resembling cyclonite. Compressed under a pressure of 3000 kg/cm^2 it has the density 1.64 g/cm^3.

Médard [47] established that hydrazine nitrate is an explosive that is readily detonated by an initiating cap, even when the density achieved by loading the product in the molten state is high (1.62 g/cm^3). The rate of detonation of a cartridge, 30 mm dia., placed in a cardboard paper case is:

density, g/cm³	rate, m/sec
1.00	3900
1.20	5200
1.25	5640
1.30	5440
1.45	5000
1.57	3250

The expansion in the lead block is 20% larger than with picric acid. According to Kast [46] it is 320 cm^3. Hydrazine nitrate is slightly less hygroscopic than ammonium nitrate. It is stable at temperatures within the range 110–120°C. Since its melting point is low hydrazine nitrate is valuable for preparing fusible mixtures with ammonium nitrate. An admixture of about 10% of hydrazine to ammonium nitrate significantly decreases the difficulty of provoking detonation of the latter compound.

Hydrazine dinitrate is an unstable substance, hence it is of no practical value.

FLUORINE NITRATE

Moissan [48] observed that explosions took place when fluorine was introduced into concentrated nitric acid. Afterwards it was found that more dilute nitric acid, e.g. 4*N* HNO_3, reacts with fluorine to form an explosive product. The reaction product was isolated by Cady [49] who has also determined that both the chemical composition and the molecular weight of the product are well in line with the formula $NO_3—F$.

Fluorine nitrate, under normal conditions, is a colourless gas with an irritant smell that is condensed at a temperature of about —42°C. It combines with potassium iodide and with potassium hydroxide as shown in the equations:

$$NO_3F + 3I^{\ominus} \longrightarrow I_3^{\ominus} + F^{\ominus} + NO_3^{\ominus} \quad (9)$$

$$NO_3F + 2OH^{\ominus} \longrightarrow \tfrac{1}{2}O_2 + F^{\ominus} + NO_3^{\ominus} + H_2O \quad (10)$$

According to Yost and Beerbower [50] fluorine nitrate explodes when heated within the temperature limits of 200 and 300°C. Sometimes the liquid or solid substance explodes without any obvious cause.

METHYLAMINE NITRATE

Naoúm [51] proposed the use of methylamine nitrate as an ingredient of fusible explosives. During World War II it was employed in Germany, under the name Man-Salz as one of components of a fusible explosive blend used for filling missiles, along with sodium nitrate and cyclonite.

Methylamine nitrate was obtained by treating methylamine with concentrated nitric acid (66%). The explosive strength of methylamine nitrate exceeds that of TNT. Its hygroscopicity, which is even higher than that of ammonium nitrate, is a disadvantage.

On experimental grounds Le Roux [52] reports that the tendency of methylamine nitrate to detonation is not high. At a density of 0.9 g/cm^3 it is completely decomposed by a 2-g detonating cap along a short space only. A much stronger detonator, containing up to 40 g of PETN, is necessary to cause the detonation to propagate on a larger area. Likewise the substance is scarcely sensitive to shock.

The heat of explosion of methylamine nitrate is 1200 kcal/kg, the volume of gases produced being $V_0 = 834$ l./kg. When initiated by 40 g pentaerythritol tetranitrate (PETN) it detonates in steel pipes of 30/33 mm diameter, with the following rates:

density, g/cm³	rate of detonation, m/sec
0.90	3140
1.10	3280
1.20	2860
1.30	does not detonate

It produces a net expansions of 325 cm³ in the lead block.

Methylamine nitrate is a stable compound. Marked thermal decomposition starts at 195°C, and on raising the temperature to 235°C, oxides of nitrogen are developed. A sample of the substance thrown into a test-tube heated to 375–390°C explodes in 7 sec.

Le Roux found that methylamine nitrate forms the following eutectics:

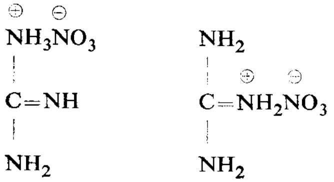
methylamine nitrate	67%	m.p. 55.5°C
ammonium nitrate	33%	
methylamine nitrate	92%	m.p. 84°C
sodium nitrate	8%	

TETRAMETHYLAMMONIUM NITRATE, $(CH_3)_4\overset{\oplus}{N}\overset{\ominus}{NO_3}$

According to le Roux [53] tetramethylammonium nitrate has no explosive properties: it did not detonate even when initiated by a strong charge of PETN. Attempts to provoke explosive decomposition by impact failed. Le Roux suggested that the compound might be used as an ingredient of explosive mixtures, for instance blended with cyclonite or incorporated in a fusible mixture with ammonium nitrate (see Vol. III).

Tetramethylammonium nitrate has the form of white crystals, soluble in water, m.p. 410°C. Its density is 1.25 g/cm³. Compressed under 3400 kg/cm² it has a density of 1.22 g/cm³.

GUANIDINE NITRATE



$$\begin{array}{c} \overset{\oplus}{N}H_3\overset{\ominus}{NO_3} \\ | \\ C{=}NH \\ | \\ NH_2 \end{array} \qquad \begin{array}{l} NH_2 \\ | \\ C{=}\overset{\oplus}{N}H_2\overset{\ominus}{NO_3} \\ | \\ NH_2 \end{array}$$

Guanidine nitrate exists as crystals melting at 215–216°C, soluble in water (4.64 g in 100 ml of water) and in alcohol. It may be recrystallized from the either of these solvents.

PROPERTIES

Guanidine nitrate has found application as a component of fusible explosive mixtures containing ammonium nitrate (see Vol. III). Further, it represents the most important intermediate product for the commercial manufacture of both nitroguanidine and aminoguanidine. Gaensa [54] proposed the use of guanidine nitrate as an ingredient of propellants, while Gérard [55] suggested using it as a component of fusible mixtures containing ammonium nitrate.

T. Urbański and Skrzynecki [57] investigated the ammonium nitrate–guanidine nitrate system, and established that the substances form an ordinary eutectic containing 26 parts of guanidine nitrate melting at 127.7°C. The formation of the eutectic composed of guanidine nitrate and nitroguanidine, and of the ternary eutectic with ammonium nitrate and nitroguanidine, will be discussed in Vol. III. The most important chemical property of guanidine nitrate is its ability to be converted into nitroguanidine in the presence of dehydrating agents, for instance sulphuric acid (Vol. III).

Guanidine nitrate, being a rather weak explosive, can be detonated only with difficulty.

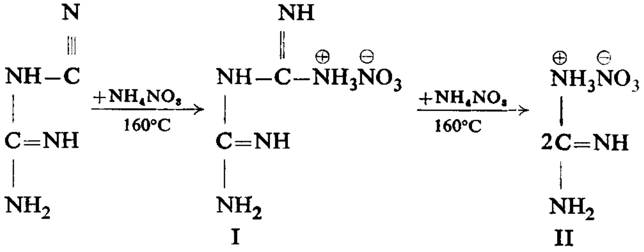
Patart [58] determined experimentally that the "force" f of guanidine nitrate is 5834 m and hence he calculated the temperature of explosion $t = 930°C$. This low explosion temperature is probably a consequence of incomplete detonation due to the compound's poor aptitude to detonation.

T. Urbański, Kapuściński and Wojciechowski [59] reported that guanidine nitrate produced a net expansion in the lead block amounting to only 140 cm^3 (Kast [46] reported 110 cm^3). The rate of detonation was not determined, since the substance could only undergo a partial detonation. Even the addition of 4% of TNT did not bring about a total detonation. According to Médard [59a] guanidine nitrate can be brought to detonation at a density 1.0 in a steel tube 36/42 mm by using 50 g of NP. Mn 95/5 (a mixture of 95% PETN and 5% nitronaphthalene) as a primer. He found the rate to be 3700 m/sec.

MANUFACTURE

A. W. Hofmann [56] was the first to prepare guanidine nitrate from guanidine hydrochloride which he obtained by treating chloropicrin with an alcoholic solution of ammonia at 100°C. In 1908 the method of manufacturing guanidine salts by way of fusing or heating dicyandiamide with ammonium salts was worked out by Stickstoffwerke at Spandau, Germany. On the development of the synthetic ammonia industry, the raw materials for making guanidine nitrate became readily available.

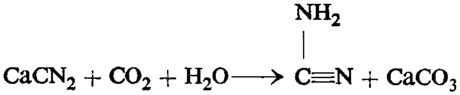
The most widely used method for manufacturing guanidine nitrate was described in detail by Davis [60]. Its basic principle is heating dicyandiamide with two equivalents of ammonium nitrate at 160°C. Originally the mixture was fused to form biguanide nitrate (guanylguanidine nitrate, (I)). On being heated in the presence of another mole of ammonium nitrate this salt is gradually converted into guanidine nitrate (II):



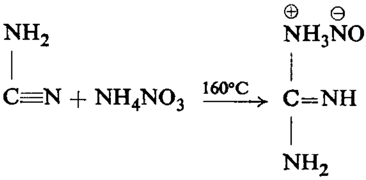
$$\begin{array}{l}\mathrm{N}\\ \ \ |||\\ \mathrm{NH-C}\\ |\\ \mathrm{C{=}NH}\\ |\\ \mathrm{NH_2}\end{array} \xrightarrow[160^\circ\mathrm{C}]{+\mathrm{NH_4NO_3}} \begin{array}{l}\qquad\ \ \mathrm{NH}\\ \qquad\ \ \|\\ \mathrm{NH-C-\overset{\oplus}{N}H_3\overset{\ominus}{N}O_3}\\ |\\ \mathrm{C{=}NH}\\ |\\ \mathrm{NH_2}\\ \ \mathrm{I}\end{array} \xrightarrow[160^\circ\mathrm{C}]{+\mathrm{NH_4NO_3}} \begin{array}{l}\mathrm{\overset{\oplus}{N}H_3\overset{\ominus}{N}O_3}\\ \quad |\\ \mathrm{2C{=}NH}\\ \quad |\\ \mathrm{NH_2}\\ \ \ \mathrm{II}\end{array}$$

Biguanide is a strong base, hence it brings about the decomposition of ammonium nitrate, accompanied by evolution of free ammonia. In order to avoid the loss of ammonium nitrate, the latter should be used in excess. For a long time this method was the most widely used for the production of guanidine nitrate, and nitroguanidine. Another process used for manufacturing nitroguanidine from dicyandiamide is described in Vol. III.

A slightly different method of guanidine nitrate manufacture was introduced in German plants during World War II. It consists in the chemical combination of ammonium nitrate and cyanamide as defined by eqns. (12) and (13).



$$\mathrm{CaCN_2 + CO_2 + H_2O \longrightarrow \overset{\displaystyle NH_2 \atop |}{C{\equiv}N} + CaCO_3} \qquad (12)$$



$$\begin{array}{l}\mathrm{NH_2}\\ |\\ \mathrm{C{\equiv}N}\end{array} \mathrm{+\ NH_4NO_3} \xrightarrow{160^\circ\mathrm{C}} \begin{array}{l}\mathrm{\overset{\oplus}{N}H_3\overset{\ominus}{N}O_3}\\ |\\ \mathrm{C{=}NH}\\ |\\ \mathrm{NH_2}\end{array} \qquad (13)$$

Both reactions are carried out in the same reactor. A diagrammatic outline of the plant for guanidine nitrate manufacture is illustrated by Fig. 173 [61].

An autoclave (*1*) is supplied with an aqueous solution that contains 600 g of ammonium nitrate and 40 g of ammonia per litre. Calcium cyanamide in the ratio of 500 g $CaCN_2$ to every litre of solution is then added from container (*2*) after being weighed at (*3*). The autoclave is closed, carbon dioxide is introduced, while the contents are cooled with water so that the temperature does not exceed 100°C. When no more carbon dioxide is absorbed, the supply is stopped, and so is the inflow of cooling water. The reaction mixture is now steam heated to 160°C. Afterwards a communicating valve joining the autoclave (*1*) with a second autoclave (*15*) is opened. The other vessel (*15*) is filled with ammonium nitrate solution prepared for the next charge. In this way the major part of the ammonia passes from autoclave (*1*) over to autoclave (*15*). After the reaction is finished the mixture is raised from the auto-

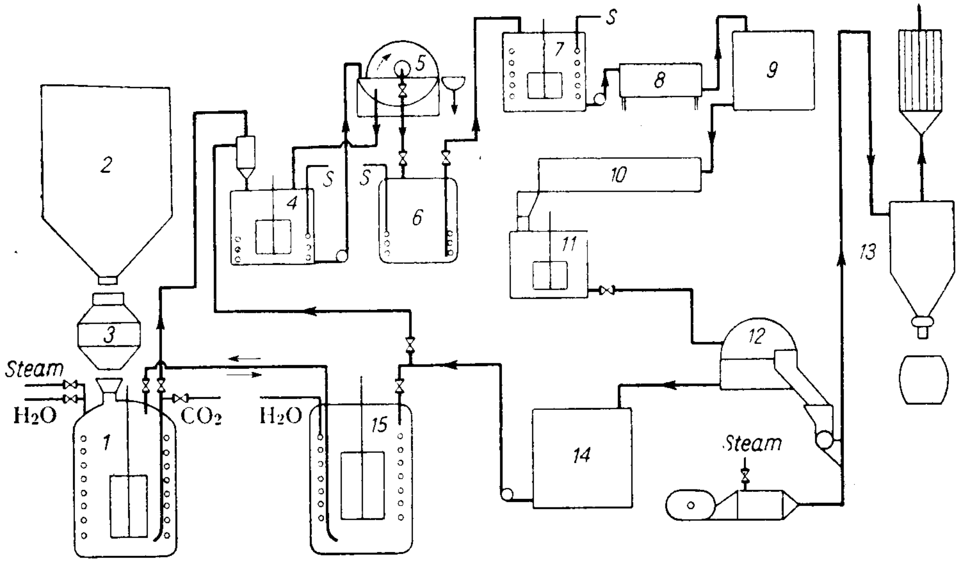
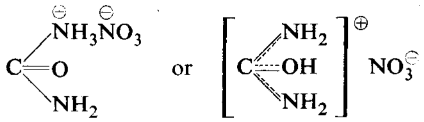


FIG. 173. Flow-sheet of the manufacture of guanidine nitrate [61].

clave to the tank (*4*) and then to a rotating filter (*5*). In the tank (*4*) calcium carbonate suspended in guanidine nitrate solution is diluted with the mother liquor from a tank (*14*) in the ratio 1:1, and the calcium carbonate is separated on the filter (*5*), and rinsed with water. The guanidine nitrate solution, together with the washings from rinsing the precipitate, is passed over the receiver (*6*) to the evaporator (*7*), where the whole solution is evaporated to a concentration of 300 g guanidine nitrate per litre. This solution is filtered hot in a filter press (*8*). The hot liquor collected in the tank (*9*) flows down to a crystallizer (*10*). In the crystallizer the solution is held until it cools to 20–25°C. Thereafter the crystallized guanidine nitrate together with its mother liquor is passed to the centrifuge (*12*), where the separation of crystals takes place. The product is then transported to the drier (*13*), and the mother liquor goes to the tank (*14*) from which it is pumped over to the autoclave. There sufficient ammonium nitrate is added to adjust its concentration to the initial 600 g/l. Then ammonia evolved in the preceding operation in the autoclave (*1*) is introduced so as to saturate the solution with 40 g NH_3 per litre. The yield of guanidine nitrate is 50–55% of theoretical.

UREA NITRATE



[61a]

m.p. 163°C

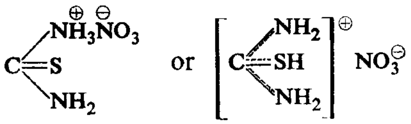
Urea nitrate is prepared by treating urea with dilute nitric acid, e.g. 34%. Choisy [62] proposed using it as an explosive. However, the manufacture of cheap urea nitrate was only possible after the Bazarov–Fichter reaction (i.e. the synthesis of urea from carbon dioxide and ammonia) was developed on an industrial scale. Under action of dehydrating agents (e.g. sulphuric acid) it yields nitro urea (Vol. III).

Urea nitrate has not found practical application, since it is not stable enough, although according to Kast [46] the loss of weight after 14 days at 75°C was only 0.2%. Decomposition into carbon dioxide, nitrous oxide, ammonium nitrate and urea takes place even at 140°C, and at 180°C decomposition is rather violent. Nevertheless a small sample of the substance does not explode.

Urea nitrate is insensitive to friction and to impact. The density of the substance subjected to a pressure of 1500 kg/cm^3 is 1.59 g/cm^3. In the lead block test it caused an expansion of 260 (Kast) or 270 cm^3 (T. Urbański, Kapuściński, Wojciechowski [59]). It detonates somewhat better than ammonium nitrate and guanidine nitrate, but a No. 8 detonator did not provoke complete detonation. Médard [59a] reported that urea nitrate gives a relative figure of the lead block expansion 79.6 (picric acid = 100) and the rate of detonation of 30 mm dia. charges is:

density 0.85 (in paper tube) 3400 m/sec
density 1.20 (in steel tube) 4700 m/sec.

THIOUREA NITRATE



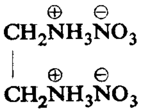
m. p. 130–134°C

Thiourea nitrate was prepared by Palamo Coll [62a] by the action of dilute nitric acid ($d = 1.33$) on thiourea at 5–10°C. The same author prepared nitrothiourea by the action of thiourea nitrate with acetic anhydride (Vol. III).

Its decomposition temperature on a hot copper plate (induction period $\tau = ca.$ 0.5 sec) is 410°C, as determined by T. Urbański and Kurcewicz [62b].

The same authors found that thiourea nitrate is a weak explosive giving a lead block expansion of 150 cm^3.

ETHYLENEDIAMINE DINITRATE



$$\begin{array}{l}\mathrm{CH_2}\overset{\oplus}{\mathrm{NH_3}}\overset{\ominus}{\mathrm{NO_3}}\\ |\\ \mathrm{CH_2}\overset{\oplus}{\mathrm{NH_3}}\overset{\ominus}{\mathrm{NO_3}}\end{array}$$

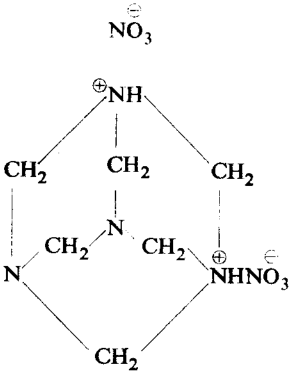
m.p. 185–187°C

This substance was suggested as a component of explosive materials by Stähler [63]. It was introduced in Germany during World War II, where it was used as an ingredient of fusible mixtures containing ammonium nitrate (see Vol. III) under the name PH-Salz. The drawback of ethylenediamine dinitrate lies in its hygroscopicity.

Le Roux [64] reports that ethylenediamine dinitrate forms an eutectic with ammonium nitrate 50/50, the fusion temperature of which is above 100°C. He suggested using a mixture composed of 50% of ammonium nitrate and 50% of ethylenediamine dinitrate instead of amatol 50/50.

Ethylenediamine dinitrate is a chemically stable compound. After being kept for 14 days at 75°C it lost only 0.38% of its original weight. It does not explode on heating up to 350°C. Its explosive strength is greater than that of TNT or picric acid, but slightly lower than tetryl. The density of ethylenediamine dinitrate pelleted under a pressure of 1500 kg/cm^2 was 1.49 g/cm^3 according to Kast [46]. Its expansion in the lead block amounts to 345 cm^3. The rate of detonation can reach 6800 m/sec (30 mm dia. cardboard tube) according to Le Roux.

HEXAMETHYLENETETRAMINE DINITRATE



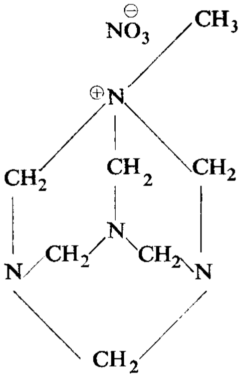
I (m.p. 160°C)

Hexamethylenetetramine dinitrate ("hexamine" dinitrate) itself is of no importance as an explosive. However, it plays a considerable part in the production of cyclonite by one of the methods described in Vol. III. Hexamine dinitrate is prepared from hexamine by treating it with 50–70% nitric acid, at a temperature not above —15°C.

Foss, Hirst, Jones, Springall, A. T. Thomas and T. Urbański [65] have established that boiling an aqueous solution of hexamine dinitrate causes the substance to transform into methylhexamethylene mononitrate (II).

The base of the nitrate (II) has proved to be identical with Knudsen's base for which an incorrect formula was given by Knudsen [66], and identical with the product (II) of interaction of methyl nitrate with hexamine described by Hahn and Walter [67].

Observations also made by Foss *et al.* [65] showed that a certain amount of the nitrate (II) is produced during prolonged storage of hexamine dinitrate owing to partial decomposition followed by the reduction of formaldehyde to a methyl radical.



II (m.p. 192°C)

This is of practical importance, for the presence of the substance (II) in (I) may reduce the purity of cyclonite.

NITRATES OF ETHANOLAMINE NITRIC ESTERS

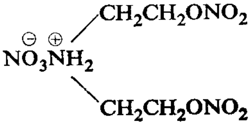
Naoúm [68] has drawn attention to the nitric acid salts of ethanolamine nitric esters (O-nitrated ethanolamines), i.e. mono-, di- and triethanolamine nitrate salts, as substances suitable for explosives. Nitration of a mixture of all three ethanolamines furnishes an oil-like, insufficiently stable product, readily decomposed with the evolution of oxides of nitrogen. The individual substances are crystal products soluble in water, in which they are hydrolysed.

Ethanolamine nitric ester nitrate (ethanolamine dinitrate) $\overset{\ominus}{NO_3}\overset{\oplus}{NH_3}CH_2CH_2ONO_2$ is a solid melting at 103°C. According to Naoúm this compound can be prepared by nitrating ethanolamine [68]. Aubry [69] has reported that a yield of 90–96% can be achieved in this reaction. This method of preparation has not been confirmed by some authors. Serious disadvantages of the substance include its inclination to absorb moisture, and the readiness with which it loses nitric acid owing to the weakly basic properties of the amine [70].

The nitric acid produced causes decomposition, hence the product has a low chemical stability.

Ethanolamine dinitrate is a strong explosive, since its expansion in the lead block test, as determined by Naoúm, is 430 cm^3. It has a remarkably low sensitiveness to impact. Nevertheless its tendency to dissociate and to form free nitric acid and its low stability prevent any practical application.

Diethanolamine dinitric ester nitrate (diethanolamine trinitrate)

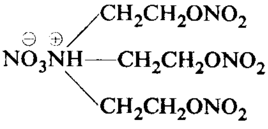


$\overset{\ominus}{NO_3}\overset{\oplus}{NH_2}(CH_2CH_2ONO_2)_2$

This compound has the same drawbacks and advantages as that described above. Médard [71] has published the relevent physical data. The melting point of diethanolamine trinitrate is 123.8°C (previously values of 116 and 120.5°C were published). The pure substance is non-hygroscopic. Its sensitiveness to shock is insignificant: a 10-kg weight dropped from the height of 1.0 m caused 34% explosions. The rate of detonation at a density of 1.0 g/cm^3 amounts to 5560 m/sec, whilst at a density of 1.40 g/cm^3 it is 6510 m/sec. The lead block test figure is some 30% higher than that of picric acid. The most serious disadvantage of this explosive is that its stability is not high enough: a specimen kept at 130°C deflagrates after 8 min whilst at 85°C an explosive decomposition takes place within 5 hr.

However, it is not unimportant as it is an intermediate product in the manufacture of diethanolnitramine dinitrate (DINA, see Vol. III).

Triethanolamine trinitric ester nitrate (triethanolamine tetranitrate)



(m.p. 62°C)

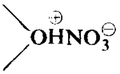
Its properties resemble those of the preceding substance. One molecule of nitric acid is readily lost by the compound, which is then transformed into triethanolamine trinitrate. The latter is also unstable and inclined to undergo decomposition. Diphosphoric salt of the trinitric ester was claimed to be an effective remedy against *angina pectoris*, instead of nitroglycerine.

OXONIUM NITRATES

Oxonium nitrates have been known since 1835 [72]. They were originally described as addition compounds of aldehydes and ketones with nitric acid [72, 73]. Reddelien [74], who carried out particularly extensive studies, represented the structure of the compounds diagrammatically as $>C=O\cdots HONO_2$. Recently, Hofman, Stefaniak and T. Urbański [75] produced evidence of the oxonium structure of the additive compounds, on the basis of infra-red absorption spectra:

$$C=\overset{\oplus}{O}HNO_3^{\ominus}$$

The products of addition of nitric acid to ethers also possess the same oxonium structure:



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CHAPTER XX

SALTS OF OXY-ACIDS OF CHLORINE

SALTS OF CHLORIC ACID

PURE sodium and potassium chlorates do not possess explosive properties, but in earlier times were important components of the most widely used explosive mixtures (Vol. III). Also some complex salts of chloric acid possess initiating properties (Vol. III). Chlorates of nitrogen bases are explosives and deserve some attention. In particular, ammonium chlorate should be mentioned owing to the part it has played in the history of explosives.

AMMONIUM CHLORATE

Ammonium chlorate, NH_4ClO_3, is a substance that undergoes explosive decomposition according to the equation:

$$2NH_4ClO_3 \longrightarrow N_2 + 3H_2O + 2HCl + \tfrac{1}{2}O_2 + 459\ \text{kcal/kg} \tag{1}$$

The rate of detonation of ammonium chlorate of density 0.9 g/cm^3 is 3300 m/sec, and its expansion in the lead block test is about 250 cm^3. Ammonium chlorate is sensitive to impact: it explodes if a 2-kg weight is dropped on it from a height of 15–20 cm. It takes fire from the flame produced by a safety fuse, and if confined the flame causes it to explode.

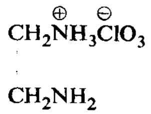
Ammonium chlorate is non-hygroscopic, but dissolves readily in water. It decomposes with ease on keeping at room temperature, and very promptly at slightly higher temperatures. Galhaar [1] has stated that in 7 weeks it lost 80% of its weight. Explosion occured at 40°C after 11 hr, and at 70°C after only 45 min.

Due to its low stability, the use of ammonium chlorate in explosive mixtures is out of the question. Furthermore it is not permissible to mix ammonium salts together with salts of chloric acid (e.g. ammonium nitrate with potassium chlorate, see Vol. III) [2].

HYDRAZINE CHLORATE, $NH_2\overset{\oplus}{N}H_3\overset{\ominus}{C}lO_3$

Salvadori [3] studied the properties of hydrazine chlorate and established that it melts at 80°C, simultaneously exploding violently.

ETHYLENEDIAMINE CHLORATE



$$\begin{array}{c}\mathrm{CH_2}\overset{\oplus}{\mathrm{N}}\mathrm{H_3}\overset{\ominus}{\mathrm{Cl}}\mathrm{O_3}\\ | \\ \mathrm{CH_2NH_2}\end{array}$$

Suggestion that ethylenediamine chlorate might be used in explosive manufacture was made by Stähler [4] who reported the substance to be a very strong explosive, sensitive to impact. So far it has not found commercial application.

CHLORINE DIOXIDE

Having considered the explosive chlorates, the explosive properties of chlorine dioxide, ClO_2 should also be mentioned. Chlorine dioxide is a mixed chlorous–chloric anhydride

$$2ClO_2 + H_2O \longrightarrow HClO_2 + HClO_3 \qquad (2)$$

There are several methods of manufacturing is on a commercial scale, for instance the calcination of oxalic acid blended with potassium chloride, treatment of sodium chlorite with chlorine, or of sodium chlorate with sulphur dioxide in the presence of concentrated sulphuric acid. Chlorine dioxide is utilized as a strong bleaching agent for cellulose, paper, flour, oils and such like, as well as a solvent for removing lignin from wood pulp.

Under normal condition it exists as a gas that it condensed at +10°C, and freezes at —76°C. In the condensed or solid state, chlorine dioxide explodes even while being poured from one vessel into another. The expansion produced in the lead block is 200 cm^3. It was recently suggested as a component in liquid propellants for rockets.

SALTS OF PERCHLORIC ACID

The explosive salts of perchloric acid are considerably more interesting than the explosive chlorates, since these are more stable and safer to handle. A few of them, for instance ammonium perchlorate, rank as components of explosive mixtures and rocket propellants. Some salts of perchloric acid possess initiating properties (Vol. III).

Others, for instance guanidine perchlorate, pyridine perchlorate, are among the strongest explosives.

Potassium perchlorate, a non-explosive compound, is an important ingredient in many mixed explosives. An excellent monograph on perchlorates was written by Schumacher [54].

AMMONIUM PERCHLORATE

There exist two crystalline modifications of ammonium perchlorate, NH_4ClO_4: an orthorhombic form below 240°C, and a cubic form above this point. An addition of small amount of some dyestuffs inhibits change of the crystalline forms [52].

The explosive properties of ammonium perchlorate are more marked than those of ammonium nitrate.

Ammonium perchlorate is used as a component of perchlorate high explosives. Lately it has been brought into prominence as a constituent of solid rocket fuels, the combustible components of which include such polymers as thiokol and methyl polymethacrylate (Vol. III). Hence a considerable interest has recently been taken in ammonium perchlorate.

Thermal decomposition

A study of the kinetics of the decomposition of ammonium perchlorate has been made by Bircumshaw and Newman [5]. The gaseous products, up to a temperature of 300°C, were found to be oxygen, chlorine, chlorine dioxide, nitrous oxide, nitrogen tetroxide, chlorine dioxide, hydrochloric acid, perchloric acid and water. The total volume of oxygen and nitrogen produced by unit weight of the solid showed practically no variation up to about 300°C.

The course of the reaction in the range 200–300°C was followed gasometrically by two methods: (1) by heating the salt *in vacuo*, condensing out all the gaseous products other than oxygen and nitrogen, and measuring the rate of increase of pressure with time in a constant volume apparatus, (2) by measuring the "build up" of pressure during 30 or 60 sec at fixed intervals of time.

Experiments were made on single crystals heated for varying lengths of time. It was shown by photo-micrographs that decomposition started at points on the surface and then spread inward and over surface (Fig. 174). The cross-section of a crystal heated for a period to produce about half decomposition showed that the reaction spreads inwards, and demonstrated the presence of a definite interface between the decomposed and "undecomposed" material (Fig. 175).

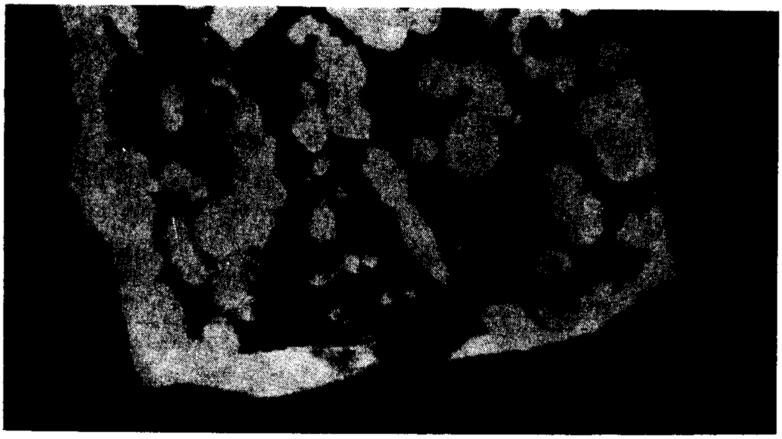


FIG. 174. Nuclei formed in crystals of ammonium perchlorate (Bircumshaw and Newman [5]).

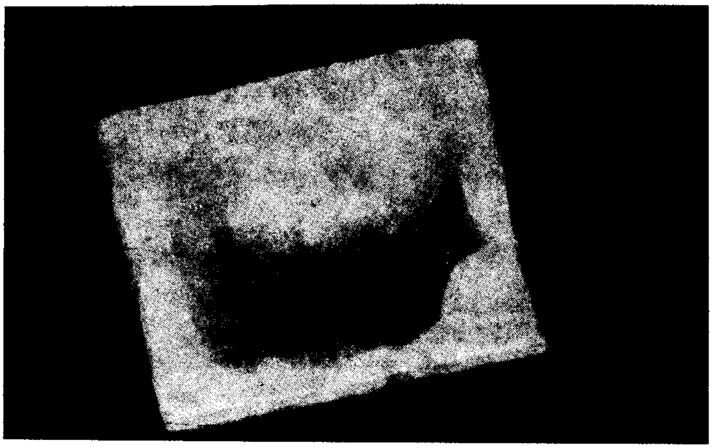


FIG. 175. Interface between the decomposed and undecomposed ammonium perchlorate (Bircumshaw and Newman [5]).

A most interesting and unexpected result was found in the lower temperature range (220–300°C). Only 30% by weight of the salt would decompose in spite of the fact that in plotting pressure as a function of time the usual sigmoid curve was obtained. The residue, which has a different physical appearance ("zeolytic") from the original crystalline salt, was found to be pure ammonium perchlorate with a trace of $H^{\oplus}$ and perhaps $NO_3^{\ominus}$ ions. It could be "rejuvenated" by exposure to a water vapour (after two days the salt again decomposed to the extent of 30% of its weight) and to the vapour of other liquids in which the salt was soluble. The extent of the rejuvenation depended on the solubility and the time of exposure. Experiments were made in which the original salt, both before and after a small amount of decomposition had occurred, was exposed to the gaseous products of decomposition. This was found to have no effect, so it was concluded that stoppage of decomposition was not due to poisoning of the reaction centres. The rejuvenation may be due to the same type of interface recrystallization.

The perchlorate was found to sublime *in vacuo* to some extent at all temperatures. A small pressure of inert gas was found to reduce the sublimation. The sublimate was found to be ammonium perchlorate with traces of $H^{\oplus}$ and $NO_3^{\ominus}$ ions. It decomposed with a reduced induction period at a slightly higher rate. It was found that sublimation continued after decomposition had stopped. It is curious that the vapour, which may or may not be dissociated, is not decomposed at these temperatures.

The variation in maximum rate (build up curves) with temperature is shown in Fig. 176. A rapid increase in the rate above 240°C might have been expected since the salt is then in the cubic form with both ions rotating, but evidently the cubic is the more stable form. The occurrence of the minimum could be due to the cubic form possessing the maximum stability at this temperature. Alternatively,

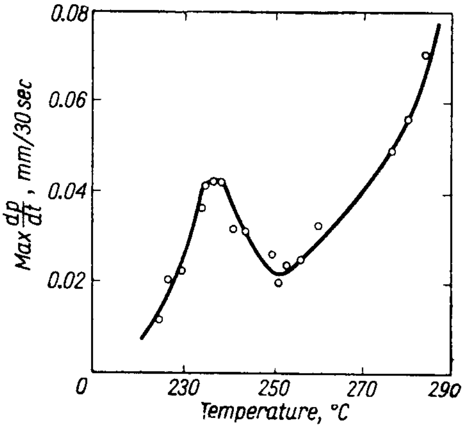


FIG. 176. Rate of decomposition of ammonium perchlorate. Variation with temperature according to Bircumshaw and Newman [5].

assuming that the cubic is more stable than the orthorhombic form, the fall in rate between 240 and 250°C might be due to the presence of a mixture of the two forms (allowing for transition time). The more thermally stable form is present in increasing quantity as the temperature approaches 250°C.

Experiments were made to determine the influence of the surface area on the rate of decomposition. Five fractions were obtained and the effect of the surface area was determined from the rate curves at a temperature of 230°C. By plotting the maximum rate as a function of the total surface area it was found the rate rose steeply to a maximum at a certain size as the particle size decreased, and then decreased again. Mampel [6] predicted that a decrease in the rate would occur at a particular particle size. The period of acceleration will come to an end just after the expanding reaction zones begin to interfere with one another, and this will happen sooner with small than large particles. On decreasing the size, the effect of increasing the area first comes into play, but after a certain size, the above effect begins to operate and the rate decreases again.

The recent experiments by Galwey and Jacobs [7a] were mainly dedicated to examining the thermal decomposition of ammonium perchlorate above *ca.* 350°C. They found the decomposition differs in several respects from that below this temperature, complete decomposition occurs, whereas at low temperatures a residue of ammonium perchlorate always remains as described above.

They suggest that the rate determining step for the high temperature thermal decomposition is a proton-transfer on the surface of the solid followed by oxidation of the ammonia gas by radicals resulting from the decomposition of perchloric acid. It seems probable that perchloric acid should undergo fast decomposition at these temperatures, generating oxygen atoms which oxidize the ammonia:

$$2HClO_4 \longrightarrow H_2O + Cl_2O_7$$

$$Cl_2O_7 \longrightarrow 2Cl_2 + 7O_2$$
$$4NH_3 + 5O_2 \longrightarrow 6H_2O + 4NO$$

The scheme accounts for the major products found by Dodé [8] who represented the overall reaction as follows:

$$2NH_4ClO_4 \longrightarrow 4H_2O + 2NO + O_2 + Cl_2$$

A few experiments made by Bircumshaw and Newman [5] at a temperature of 400°C in a spiral gauge apparatus agreed with the conclusion that the decomposition was quite different from that at the lower temperatures. There was no induction period, the whole of the reaction was a decelerating one, and decomposition went to completion. The reaction appeared to follow a simple power law, $p = kt^n$, where n varied with temperature and was always less than unity.

Although no solid products are produced in this decomposition, nevertheless the reaction type must be

$$\underset{\text{solid}}{A} \longrightarrow \underset{\text{solid}}{B} + \underset{\text{gas}}{C} + \underset{\text{gas}}{D} \ldots$$

the undecomposable residue functioning as the solid B and providing the interface at which the reaction takes place. The sigmoid curves obtained were explicable, in the accelerating phase in terms of the Prout–Tompkins [10] accelerating equation,

$$\log \frac{p}{p_f - p} = k_1 t + \text{constant}$$

where p is the pressure at time t, p_f the final pressure, i.e. the pressure at $\simeq$ 30% decomposition; on the basis of the power expression, $p = kt^n$, $n \cong 6.0$. In the decelerating phase, the Prout–Tompkins equation,

$$\log \frac{p}{p_f - p} = k_2 t + \text{constant}$$

and the unimolecular decay law both gave straight lines.

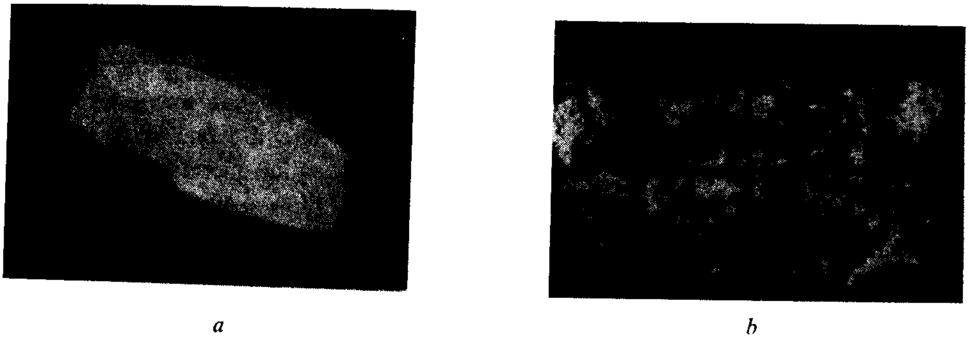
From the rate constants obtained, the activation energy was found to be 27.8 and 18.9 kcal/mole for the orthorhombic and cubic forms respectively.

According to Glasner and Makovky [13] the activation energy of decomposition of ammonium perchlorate is 31.0 kcal/mole in the temperature range 440–478°C.

Recently Freeman, Anderson and Campisi [11] examined the effects of X-rays on the chemical reactivity of ammonium perchlorate in the solid state. They found that pre-exposure of ammonium perchlorate to high energy radiation greatly affects the way it decomposes thermally.

In unirradiated ammonium perchlorate crystals decompose at preferential regions that occur along intermosaic boundries where crystal structure imperfections occur (Fig. 177a). The reaction sites in X-ray irradiated samples occur in a homogeneous-like manner throughout the crystal. Nuclei for reaction are distributed uniformly throughout the crystal (Fig. 177b).

An electron spin resonance study by Hyde and Freeman [12] revealed that ammonia radical ion $NH_3^{\oplus}$ form when ammonium perchlorate is exposed to X-rays. This radical ion was found to be stable in the ammonium perchlorate lattice up to 120°C. It is not formed during thermal decomposition and is not present in ammonium perchlorate sublimate.



a b

FIG. 177. Microphotographs of ammonium perchlorate in transmitted light: (a) unirradiated crystal, (b) X-ray irradiated crystal (Freeman, Anderson and Campisi [11]).

The activation energy of decomposition of both irradiated and unirradiated ammonium perchlorate in the orthorhombic form below 240°C is *ca.* 18.0 kcal/mole according to Freeman. This seems to indicate that irradiation of ammonium perchlorate does not change the decomposition mechanism but provides many more nucleation sites.

The authors have also found that chlorate ion is present after irradiation. The chlorate ion may provide intermediate species which act as catalysts.

The introduction of silver ions which act as electron traps enhances the radiation-induced changes in the thermal decomposition of ammonium perchlorate. Irradiated samples containing silver show thermal decomposition similar to samples without silver, but which received a considerably greater radiation dose.

The influence of a number of catalysts on the decomposition of NH_4ClO_4 has been investigated [9]. Salt crystallized out from solutions containing traces of free perchloric acid decomposed with a much shorter induction period. Ammonia had the reverse effect. Mixing the salt with a number of oxides was also tried. Calcium oxide slowed down the reaction. Aluminium oxide had no effect. Ferric oxide had a marked catalytic effect, but the greatest effect was observed with manganese dioxide. It gave complete decomposition at 230°C without sublimation, unlike the other cases. Galwey and Jacobs [7a] investigated the thermal decomposition of ammonium perchlorate with MnO_2 at 137–212°C. They found that the reaction proceeds in two stages: the first being the catalysed decomposition of NH_4ClO_4 (activation energy 32 kcal/mole) and the second the decomposition of NH_4ClO_4 which is not influenced by the presence of MnO_2. See also Makovky and Salmon [55].

The same authors [7b] examined the thermal decomposition of ammonium perchlorate with charcoal (see also Vol. III). At temperatures below 240°C the activation energy was 32.1 kcal/mole, above 240°C there was a non-isothermal decomposition following a power law (activation energy 40.1 kcal/mole). Above 260°C the reaction accelerated rapidly and resulted in a mild explosion. Absorption of ammonia by charcoal was found to be an important factor: it increased the overall rate of decomposition.

Explosive properties

Explosive decomposition of ammonium perchlorate was estimated by Naoúm and Aufschläger [14] to proceed according to the equation:

$$2NH_4ClO_4 \longrightarrow N_2 + 3H_2O + 2HCl + \tfrac{5}{2}O_2 + 266 \text{ kcal/kg} \qquad (3)$$

The volume of gases (V_0) amounts 810 l./kg
the explosion temperature $t = 1200°C$
"force" $f = 4600$ m

The heat of formation $-\Delta H_f$ is 79.7 kcal/mole.

Ammonium perchlorate explodes under the impact of a 10-kg weight dropped from a height of 15 cm. According to Kast [15] the rate of detonation of a sample of density 1.17 g/cm^3, in an iron pipe 35 mm dia. was 2500 m/sec, the net expansion in the lead block being 220 cm^3.

HYDRAZINE PERCHLORATE

Hydrazine perchlorate, $\overset{\oplus}{NH_2NH_3}\overset{\ominus}{ClO_4}$, m.p. 137–138°C, was obtained by Salvadori [3] from hydrazine and perchloric acid. The substance is as strong an explosive as tetryl, being significantly more sensitive to shock approximating in this regard to mercury fulminate [16].

From aqueous solutions its semihydrate, $(N_2H_5ClO_4)_2{\cdot}H_2O$, melting at 85°C is formed. This compound is less sensitive to impact.

FLUORINE PERCHLORATE, ClO_4F

Fluorine perchlorate (b.p. —15.9°C, m.p. —167.5°C) is a gaseous explosive compound prepared for the first time by Fichter and Brunner [17] by the action of fluorine on perchloric acid solution. Rohrback and Cady [18] improved the method of preparing it by using 72% perchloric acid in a platinum vessel.

It possesses properties similar to fluorine nitrate (p. 465). It explodes in contact with organic materials. It is readily decomposed in an alkaline medium:

$$4OH^{\ominus} + 2ClO_4F \longrightarrow O_2 + 2ClO_4^{\ominus} + 2F^{\ominus} + 2H_2O \qquad (4)$$

The same reaction can occur with water but the rate of this reaction is low. It possesses strong oxidizing properties.

NITRYL PERCHLORATE (NITRONIUM PERCHLORATE, NITROXYL PERCHLORATE), NO_2ClO_4

This is a crystalline compound which decomposes on heating above 135°C giving off nitrogen dioxide.

Nitryl perchlorate was obtained by Gordon and Spinks [19] by mixing chlorine dioxide with ozone and nitrogen dioxide. Ingold [20] prepared it from nitrogen pentoxide and anhydrous perchloric acid by the reactions:

$$N_2O_5 + 3HClO_4 \longrightarrow 2NO_2^{\oplus} + ClO_4^{\ominus} + H_3O^{\oplus} + ClO_4^{\ominus}$$

$$H_3O^{\oplus} + ClO_4^{\ominus} + 2N_2O_5 \longrightarrow NO_2^{\oplus} + ClO_4^{\ominus} + 3HNO_3$$

Gordon and Spinks [19] also isolated the same product from the precipitate formed by mixing anhydrous nitric and perchloric acid, by fractional crystallization from methanol.

Earlier Hantzsch *et al.* [21] thought the precipitate in question was nitracidium and hydronitracidium perchlorates (p. 13, Vol. I). However Ingold *et al.* [22] showed that Hantzsch's product is a mixture of perchloric acid monohydrate and nitryl perchlorate.

Crystallographic examination [23] and Raman spectra [24] showed that the compound is composed of ions $NO_2^{\oplus}$ and $ClO_4^{\ominus}$. Gillespie [25] found that the following dissociation takes place in sulphuric acid:

$$NO_2ClO_4 + H_2SO_4 \longrightarrow NO_2^{\oplus} + HClO_4 + HSO_4^{\ominus}$$

The compound reacts rapidly with water to yield nitric and perchloric acid. It reacts violently with many organic compounds causing ignition or explosion.

When dissolved in nitromethane it can be used as a nitrating agent.

NITROSYL PERCHLORATE, $NOClO_4$

This is a crystalline compound of density 2.169 g/cm³, and low stability.

It was first prepared by K. A. Hofmann and Zedtwitz [26] by passing a mixture of nitric oxide and nitrogen dioxide into 72% perchloric acid. The acid was then evaporated to 140°C and on cooling the hydrate of nitrosyl perchlorate $NOClO_4 \cdot H_2O$ crystallized out. The product was dehydrated *in vacuo* over phosphorous pentoxide.

When heated below 100°C it decomposes [27] according to the equation:

$$2NOClO_4 \longrightarrow 2ClO_2 + N_2O_5 + \tfrac{1}{2}O_2$$

At higher temperature the decomposition follows a different course:

$$2NOClO_4 \longrightarrow Cl_2 + N_2O_4 + 3O_2$$

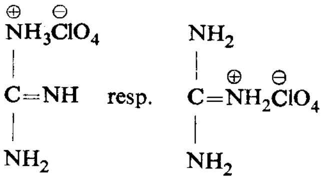
It is a strongly endothermic compound with a heat of formation $-\Delta H_f = 41.79 \pm 0.08$ kcal/mole [27].

It reacts with water with evolution of nitrogen oxides. Ethanol, acetone, dry ether and primary amines react violently with nitrosyl perchlorate causing ignition or explosion.

METHYLAMINE PERCHLORATE

Methylamine perchlorate, $CH_3\overset{\oplus}{N}H_3\overset{\ominus}{Cl}O_4$ (m.p. 210°C) [28], is a substance that resembles cyclonite and PETN in explosive strength. However, it is more sensitive to impact than these compounds.

GUANIDINE PERCHLORATE



$$\begin{array}{c} \overset{\oplus\ \ \ominus}{NH_3ClO_4} \\ | \\ C{=}NH \\ | \\ NH_2 \end{array} \quad \text{resp.} \quad \begin{array}{l} NH_2 \\ | \\ C{=}\overset{\oplus\ \ \ominus}{NH_2ClO_4} \\ | \\ NH_2 \end{array}$$

(m.p. 250°C)

Marckwald [29] proposed the use of guanidine perchlorate in explosives. It has the important advantages of being stable, non-hygroscopic and moderately sensitive to shock, and is capable of producing a violent explosion. Its preparation, by fusing dicyandiamide with ammonium perchlorate at 150–160°C, offers no significant difficulties.

Guanidine perchlorate heated to a temperature above 300°C undergoes explosive decomposition. Glasner and Makovky [13] studied the thermal decomposition of guanidine perchlorate, and concluded that the decomposition can be expressed by the following equations:

$$CH_5N_3 \cdot HClO_4 \rightleftarrows CN{-}NH_2 + NH_4ClO_4 \tag{5}$$

$$NH_4ClO_4 \rightleftarrows NH_3 + HClO_4 \tag{6}$$

$$3CN \cdot NH_2 \rightleftarrows C_3H_6N_6 \text{ (melamine)} \tag{7}$$

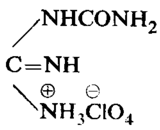
$$C_3H_6N_6 + HClO_4 \text{ (or } NH_4ClO_4) \longrightarrow HCl, CO, CO_2, N_2, NH_3, O_2, H_2O \tag{8}$$

Thus, in the first stage of reaction, ammonium perchlorate and cyanamide are produced. The latter furnishes melamine, which is decomposed in turn under the influence of ammonium perchlorate or the perchloric acid that is produced from the perchlorate.

The activation energy of the decomposition of guanidine perchlorate within the temperature range 390–440°C, quoted in the same contribution, is $E = 30.5$ kcal/mole. The decomposition is catalysed by metallic oxides such as Fe_2O_3, CuO and V_2O_5, and by platinum.

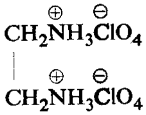
As for its explosive strength, guanidine perchlorate is similar to tetryl. Its sensitiveness to shock is comparable with that of picric acid. The rate of detonation is 6000 m/sec at a density of 1.15 and the net expansion in the lead block test is about 400 cm^3.

DICYANDIAMIDINE PERCHLORATE



Dicyandiamidine perchlorate [30] is an appreciably weaker explosive than guanidine perchlorate, hence it is of no practical importance.

ETHYLENEDIAMINE DIPERCHLORATE



$$\begin{array}{l} CH_2\overset{\oplus}{N}H_3\overset{\ominus}{Cl}O_4 \\ | \\ CH_2\overset{\oplus}{N}H_3\overset{\ominus}{Cl}O_4 \end{array}$$

This compound was suggested as an explosive by Stähler [4]. It is a stronger explosive than tetryl, but weaker than PETN. Its disadvantages are high sensitiveness to impact (greater that of PETN) and hygroscopicity. Mainly for this reason ethylenediamine diperchlorate has found no practical application.

According to the Chemisch-Technische Reichsanstalt [31]

the heat of formation $-\Delta H_f$ is	525 cal/g
the heat of detonation $-Q$	900 cal/g
gas volume	842 cm^3/g
expansion in lead block	410 cm^3
rate of detonation at $d = 1.67$ g/cm^3	7150 m/sec

Tetrazene perchlorate is used as an initiating explosive (see Vol. III).

AROMATIC AMINES PERCHLORATES

Spallino [32] has obtained aniline, *p*-nitraniline, *m*- and *p*-phenylenediamine perchlorates, by treating the corresponding amine sulphates with barium perchlorate

TABLE 115

THE PROPERTIES OF AROMATIC AMINES PERCHLORATES (T. URBAŃSKI AND KOWALSKI [34])

Perchlorate of	Melting point °C	Temperature of initiation–explosion within 1 sec at °C	Sensitiveness to shock — 10% of explosions from work of kg	Lead block expansion cm^3	Rate of detonation (glass tube 12 mm dia., density 1.1 g/cm^3) m/sec
Aniline	—	295	1.30	185	5980
o-Nitraniline	206	235	0.40	245	6600
m-Nitraniline	196	245	0.56	235	6825
p-Nitraniline	182	256	0.58	210	6445
m-Phenylenediamine	*	350	1.06	335	—
p-Phenylenediamine	*	326	1.08	235	7825
α-Naphthylamine	*	280	1.48	145	—
β-Naphthylamine	*	290	1.54	45	—
Picric acid (standard)			1.30		

* Melting is almost simultaneous with explosion.

in aqueous solution and evaporating the solution freed from barium sulphate. Lundsgaard [33] suggested using the perchlorates of toluidines, phenylenediamines, and benzidine as explosives.

T. Urbański and Kowalski [34] examined the properties of those perchlorates as well as a range of others, not previously described, to determine their sensitiveness, stability, and explosive strength (Table 115).

Only nitraniline perchlorates are fusible. The others explode without melting.

The investigations carried out by T. Urbański and Kowalski showed that the presence of a nitro group in the aromatic ring of the amine causes the sensitiveness to impact of the salt to increase appreciably, and contributes to its greater explosive strength. The presence of two molecules of perchloric acid combined with phenylenediamine significantly increases the explosive strength, without appreciably increasing the sensitiveness to impact. The initiation temperature of such diperchlorates is higher than that of monoperchlorates, probably as a result of higher melting points.

PERCHLORATES OF HETEROCYCLIC BASES

The very attractive characteristics of the perchlorates of heterocyclic bases were discovered with pyridine perchlorate which was first prepared by Cordier [35] and described by Arndt and Nachtwey [36]. The explosive properties of pyridine perchlorate were described by Muraour and Wohlgemuth [37].

T. Urbański and Kowalski [34] have studied the explosive properties of pyridine perchlorate as well as quinoline and its nitro derivative perchlorates. Due to the introduction of a nitro group the sensitiveness to shock of the quinoline perchlorate increased, but to a smaller extent than the authors had previously observed with primary aromatic amines. The introduced nitro group markedly favoured the increase of explosive strength of the perchlorates (Table 116).

TABLE 116

EXPLOSIVE PROPERTIES OF PERCHLORATES OF HETEROCYCLIC BASES (T. URBAŃSKI AND KOWALSKI [34])

Perchlorate of	Melting point °C	Temperature of initiation–explosion within 1 sec at °C	Sensitiveness to shock — 10% of explosions from work of kg	Lead block expansion cm³	Rate of detonation (glass tube 12 mm dia., density 1.1 g/cm³) m/sec
Pyridine	245	335	0.68	245	6650
Quinoline	130	291	0.94	195	—
8-Nitroquinoline	192	303	0.88	240	—
7-Nitroquinoline	172	290	0.84	240	—
6-Nitroquinoline	188	296	0.86	235	—
Picric acid (standard)			1.30		

Hexamethylenetetramine perchlorates (Hexamine perchlorates)

The following salts are known:

perchlorate	$(C_6H_2)_6N_3\overset{\oplus}{N}H\overset{\ominus}{ClO_4}$
diperchlorate	$(C_6H_2)_6N_2\overset{\oplus}{(NH)_2}\overset{\ominus}{(ClO_4)_2}$

Hexamine diperchlorates are strong explosives. In spite of this the compound has not come into commercial use because of its insufficient stability on storage.

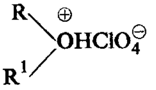
CARBONIUM AND OXONIUM PERCHLORATES

Gomberg in one of his papers on triphenylmethyl (Gomberg and Cone [38]) described carbonium perchlorates, e.g. triphenylcarbonium perchlorate

$$(C_6H_5)_3\overset{\oplus}{C}ClO_4^{\ominus} \text{ (m.p. 150°C)}$$

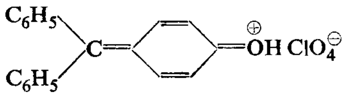
and a number of their derivatives.

Oxonium perchlorates of the general formula



have been obtained by K. A. Hofmann *et al.* and described in a series of papers [39]. They were prepared by acting with concentrated perchloric acid on aldehydes, ketones and ethers. They are extremely unstable crystalline compounds, and all are decomposed immediately by moisture.

Smeets [40] described dioxane perchlorate (m.p. 80–82°C) of the composition $C_4H_8O_2.HClO_4{\cdot}H_2O$. It was prepared from dioxane and 70% perchloric acid at 0°C. Pfeiffer *et al.* [41] described perchlorates of quinones, e.g. fuchson perchlorate



(m. p. 167°C)

PERCHLORYL COMPOUNDS

Perchloryl fluoride, ClO_3F

Perchloryl fluoride (b.p. − 47.5 ± 0.5°C, m.p.−146 ± 2°C) is a gaseous substance prepared for the first time by Bode and Klesper [42] by acting on potassium perchlorate with fluorine at −40 to −20°C. Engelbrecht and Atzwanger prepared the substance by electrolysis of sodium perchlorate in liquid hydrogen fluoride. Barth-Wehrenalp [43] described a new method of preparing it. This consists in heating potassium perchlorate with fluorosulphuric acid (HSO_3F).

It proved to be remarkably stable to high temperature (Engelbrecht and Atzwanger [44]).

It is not hydrolysed by water but reacts quantitatively with NaOH to yield sodium perchlorate and fluoride. It oxidizes iodides to iodine. Perchloryl fluoride reacts with ammonia to yield ammonium perchlorylamide NH_4NHClO_3 [45a]. It reacts with potassium and caesium hydroxide to yield crystalline precipitates of K_2NClO_3 and Cs_2NClO_3. It is isomorphous with metal sulphates, is explosive and very sensitive to flame, shock and friction.

It is quite safe to handle, but being a powerful oxidizing agent, it reacts violently with any oxidizable substance.

Details about the safety in handling perchloryl fluoride are described by Pennsalt Chemicals Corp. [45].

ORGANIC PERCHLORYL COMPOUNDS

This is a new class of compounds recently obtained and described by Inman, Oesterling and Tyczkowski [46]. They are characterized by the presence of the perchloryl group (ClO_3) and their general formula is $RClO_3$. So far only aromatic derivatives of this kind are known.

They are formed by a Friedel–Crafts type of reaction between perchloryl fluoride (ClO_3F) and aromatic compounds:

$$ClO_3F + AlCl_3 \longrightarrow ClO_3^{\oplus} + FAlCl_3^{\ominus}$$

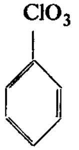
$$C_6H_6 + ClO_3^{\oplus} \longrightarrow C_6H_5ClO_3 + H^{\oplus}$$

$$H^{\oplus} + FAlCl_3^{\ominus} \longrightarrow AlCl_2F + HCl$$

A number of perchloryl compounds were prepared by this method with a good yield.

No data on their explosive properties are available, but they are reported to be sensitive to shock and high temperature.

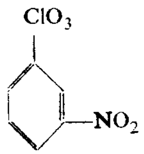
Perchloryl benzene



Perchloryl benzene is a liquid with a b.p. of 232°C and freezing point of −3°C. The density at 30°C is 1.185 g/cm³.

It can be hydrolysed with potassium hydroxide solution to yield potassium chlorate and phenol. When reduced with hydrogen on palladium it yielded benzene, HCl and water [53].

3-Nitroperchloryl benzene



This was obtained [46] by nitrating perchloryl benzene with a nitrating mixture of anhydrous nitric acid and sulphuric acid. It forms pale yellow needles with a m.p. of 49–50°C.

On reduction with stannous chloride it yielded 3-aminoperchloryl benzene, in the form of colourless needles, m.p. 30–31°C. By acetylation with acetic anhydride and acetic acid it yielded 3-perchlorylacetanilide (m.p. 136–137°C).

4-Fluoroperchloryl benzene

This was prepared by the reaction of fluorobenzene with perchloryl fluoride in presence of aluminium chloride. The compound melts at 28°C and has a b.p. of 53°C (0.25 mm Hg).

2,5-Dimethylperchloryl benzene

This was prepared by perchlorylation of *p*-xylene.

SALTS OF OTHER ACIDS

Among acids capable of forming explosive salts are included those with distinct marked oxidizing properties, e.g. chromic acid, permanganic acid.

Ammonium bichromate, $(NH_4)_2Cr_2O_7$, begins to undergo decomposition at a temperature over 100°C, and explodes at 240°C. Its explosive decomposition proceeds in accordance with the equation:

$$(NH_4)_2Cr_2O_7 \longrightarrow Cr_2O_3 + N_2 + 4H_2O + 310 \text{ kcal/kg} \qquad (9)$$

Initiated with a picric acid detonator, bichromate detonates with difficulty, and within a small space only. It does not take fire from a flame.

Noteworthy properties were discovered in ammonium "trichromate" $(NH_4)_3Cr_3O_{10}$, produced while crystallizing ammonium bichromate from nitric acid, $d = 1.39$ (Siewert [47]). At 190°C the compound undergoes explosive decomposition, evolving nitric oxide and nitrogen dioxide.

The kinetics of the ammonium chromate, bichromate and trichromate decomposition were investigated by Fischbeck and Spingler [48] who measured the increase of pressure with time in an evacuated vessel. The activation energy is 40.0, 49.0 and 34.0 kcal/mole, respectively.

Aliphatic amine chromates, for example methylamine chromate, manifest a more clearly defined explosive character. The properties of hexamethylenetetramine chromate are similar. The aliphatic amine chromates kindle from a flame to burn vigorously.

Ammonium permanganate, NH_4MnO_4, has distinct marked explosive properties, but it is unstable. Decomposition and alteration of the appearance of the compound can be discerned within 1–2 days, and within a few weeks its explosive properties are lost. This is probably due to the decomposition of ammonium permanganate, in accordance with the reaction:

$$2NH_4MnO_4 \longrightarrow NH_4NO_3 + 2H_2O + Mn_2O_3 \tag{10}$$

The temperature of initiation is reported by different authors to be 110–130°C. Bircumshaw and F. M. Taylor [49] have examined the thermal decomposition of ammonium permanganate between 96 and 117°C. The activation energy of this decomposition was estimated as 27.9 kcal/mole. Within the temperature range from 70 to 80°C the energy of activation was 26.0 kcal/mole. An explosive decomposition brought about by an initiator procedes according to the reaction:

$$NH_4MnO_4 \longrightarrow MnO_2 + 2H_2O + 0.5N_2 + 565 \text{ kcal/kg} \tag{11}$$

Ammonium permanganate detonates with a rate of 1700 m/sec. It causes an expansion of 100–125 cm^3 in the lead block test.

Ammonium permanganate is of no practical importance as an explosive. However, its spontaneous formation should be avoided, otherwise an explosion such as one that occurred in a German plant (Roburit Fabrik) at Witten, in 1906, may take place. 0.5% of potassium permanganate was added to an ammonium nitrate explosive, Roburit. Seven hours later self-ignition of the product occurred, followed by an explosion.

Ammonium nitrite, NH_4NO_2. Ammonium nitrite forms deliquescent crystals. On heating it begins to sublime at 32–33°C and decomposes explosively at 60–70°C. It cannot be stored under ordinary conditions as it decomposes at room temperature evolving N_2 and H_2O but the dry salt can be preserved for some time under an atmosphere of hydrogen.

It was prepared by Berzelius as early as 1812 [50] by treating lead nitrite with ammonium sulphate. Later M. Berthelot [50] obtained it by acting with barium nitrite on ammonium sulphate. Erdmann and Sörensen [50] prepared it by acting with dinitrogen tetroxide on coarsely ground ammonium carbonate near 0°C. Ammonium nitrite cannot be obtained from its aqueous solution, as it decomposes on evaporating.

Ammonium nitrite is explosive and very sensitive to heating. Explosive decomposition can occur even when an aqueous solution is heated to 60–70°C. Acidification of an aqueous solution with a drop of concentrated hydrochloric, sulphuric or nitric acid produces a spontaneous decomposition even at room temperature.

Kast [51] examined the explosive properties of ammonium nitrite. He found the heat of explosion to be 803 kcal/kg, temperature of explosion 2210°C, gas volume 1050 l./kg.

The rate of detonation was found to be *ca.* 4000 m/sec at the density of 1.0 and $f = 9865$ m.

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by

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CHAPTER VIII. THE MANUFACTURE OF SMOKELESS POWDER

PREFACE TO VOLUME III

THE manuscript of Volume III was submitted to the publishers in 1960. Owing to the rapid progress in the many branches of chemistry and chemical technology that form the scope of this volume, some paragraphs became obsolete and it has therefore been necessary to add some new items and to rewrite certain paragraphs.

The necessary information obtained from the current literature has been supplemented with data from a number of colleagues who kindly made available some less accessible material. It is my pleasant duty to express my thanks to Prof. S. Claesson (Uppsala), Prof. M. A. Cook (University of Utah, Salt Lake City), Prof. W. Cybulski (Mikołów, Poland), Dr. L. Deffet (Sterrebeck, Belgium), Dr. R. W. Van Dolah (Pittsburgh, Pa.), Dr. A. G. Grenier (Dow Chemical International, Midland, Michigan), Prof. J. Hackel (Warsaw), Prof. M. Kryszewski (Łódź), Dr. J. Meissner (Frankfurt a./M.), Prof. H. Sudo (Tokyo), Dr. A. Wetterholm (Gyttorp, Sweden) and to the firms: Draiswerke G.m.b.H., Maschinenfabrik (Mannheim-Waldhof), Olin Industries, Inc. (East Alton, Ill.), H. Orth G.m.b.H. Fachbüro für Verfahrenstechnik (Ludwigshafen-Oggersheim, Pfalz), Werner & Pfleiderer, Maschinenfabriken und Ofenbau (Stuttgart).

Some of the problems, such as safety in coal mines, merit a special monographic treatment which should go far beyond the scope of this volume. Therefore safety in coal mines was tackled only from the point of view of the composition of coal mine explosives.

Another rapidly developing branch of applied science is theory and practice of rocket propulsion. Only general information on composition of rocket propellants is given in the book. This is justified, as several special books on rocket fuel are now available.

My thanks are due to the translator, Mr. M. Jurecki and to Mrs. Sylvia Laverton, F.R.I.C. for tidying up the English text and to Mrs. A. Malawska, M.Sc. for her skilled editorial work.

AUTHOR

Part 1

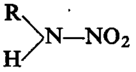
NITRAMINES

CHAPTER I

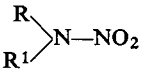
GENERAL INFORMATION

NITRAMINES are substances which contain a nitro group bonded to the nitrogen atom: $>N{-}NO_2$.

In formal terms all nitramines may be regarded as derivatives of the simplest inorganic nitramine, NH_2NO_2. If only one hydrogen is replaced by an alkyl or aryl group, the resulting substance is a primary nitramine, if two hydrogens are replaced, secondary nitramines are formed:



Primary nitramine



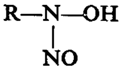
Secondary nitramine

Nitramines may also be said to include nitramides (primary and secondary) which differ from nitramines proper in that one of the groups (R) is acyl or sulphonyl.

STRUCTURE AND CHEMICAL PROPERTIES OF NITRAMINES

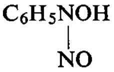
The existence of a bond in nitramines linking the nitrogen atom of the nitro group with that of the amino group is proved by the formation of hydrazine derivatives by the reduction of nitramines. Secondary nitramines give a particularly high yield of hydrazine derivatives.

There exists a group of compounds isomeric with primary nitramines, which also yield hydrazine derivatives when reduced. These compounds are nitrosohydroxylamine derivatives:



$$R{-}\underset{\displaystyle NO}{\underset{|}{N}}{-}OH$$

This structure was deduced from their mode of preparation: nitrosohydroxylamines are obtainable by nitrosation, nitramines by nitration. The physical properties of primary nitramines are entirely different from those of nitrosohydroxylamines, so that phenylnitramine $C_6H_5NHNO_2$, for example, differs radically from phenylnitrosohydroxylamine

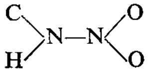


$$C_6H_5\underset{\displaystyle NO}{\underset{|}{N}}OH$$

Traube's "isonitramines", which are described later in this volume, are nitrosohydroxylamines.

The existence of an N—N bond in primary nitramines is also proved by the fact that these substances are obtained by the oxidation of diazo compounds. Additional evidence that nitramines contain a nitro and not a nitrite group and hence have a structure different from R—N—ONO is provided by the fact that nitramines are relatively resistant to alkali, whereas nitrous esters are highly unstable.

These inferences concerning the structure of nitramines, based on their chemical properties, are confirmed by the data obtained by X-ray analysis of the simple nitramines: dimethylnitramine and ethylenedinitramine. In particular, Costain and Cox [1], and Llewellyn and Whitmore [2], established that the grouping



is planar. Bond angles and interatomic distances are shown in Fig. 1.

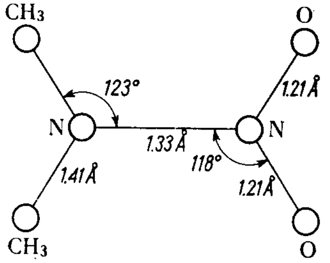


FIG. 1. Structure of the nitramino group, with dimethylnitramine as an example (not to scale).

Thus, in principle, the dimensions of the nitro group in both aromatic and aliphatic nitro compounds are identical.

Nitramines dissolved in water, alcohol or dioxane, give a broad ultra-violet absorption band, the maximum of which lies between 225 and 240 μ.

R. N. Jones and Thorn [3] adduce the two following typical absorption curves for nitramines: a primary — ethylenedinitramine — Fig. 2 and a secondary — 2,5-dinitro-2,5-diazahexane (according to R. N. Jones and Thorn) — Fig. 3. They have also been investigated by Baly and Desch [4], Franchimont and Backer [5], Carmack and Leavitt [6] and Corey, Dekker, Malmberg, Le Rosen, and Schroeder [7].

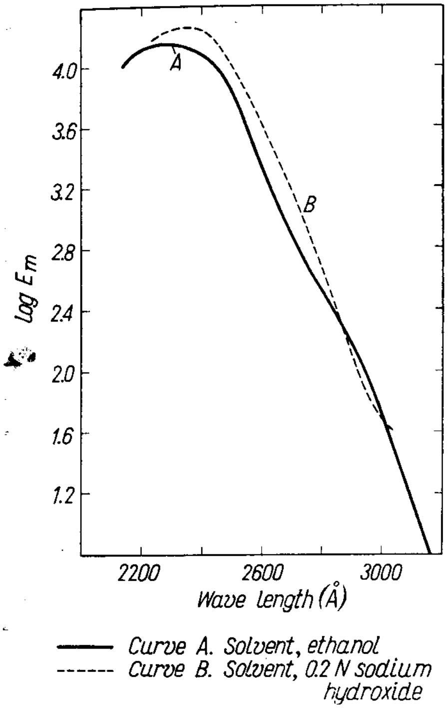


FIG. 2. Spectrum of typical primary nitramine (ethylenedinitramine), according to R. N. Jones and Thorn [3].

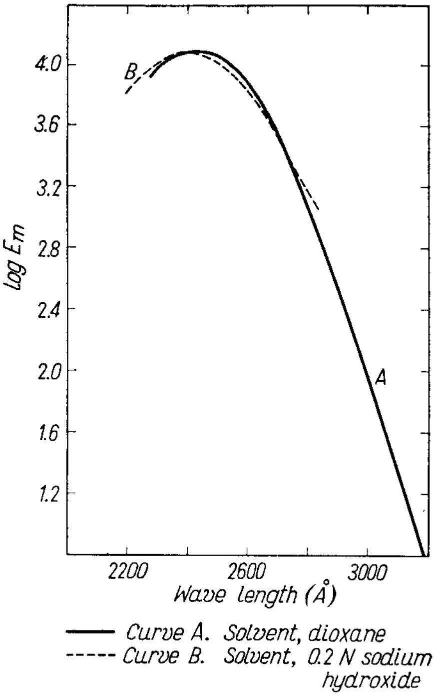


FIG. 3. Spectrum of typical secondary nitramine (2,5-dinitro-2,5-diazahexane), according to R. N. Jones and Thorn [3].

The ultra-violet absorption spectra of nearly 60 nitramines were examined by R. N. Jones and Thorn, who drew up an interesting rule about the coefficient of extinction for nitramines.

According to this rule, compounds which contain one primary nitramine group show a coefficient of extinction in the maximum of the absorption curve, ε_{max}, equal to approximately 7000. If the molecule contains n primary nitramine groups, ε_{max} increases in proportion to the number of nitramine groups, i.e. $\varepsilon_{max} = 7000\ n$. This empirical rule is valid for values of n ranging from 1 to 3. For secondary nitramines, $\varepsilon_{max} = 5500$. If the number of secondary nitramine groups is n, $\varepsilon_{max} = 5500\ n$. This rule is valid for values of n ranging from 1 to 4. If both primary and secondary nitramines occur together in a molecule, ε_{max} is the sum of the appropriate multiples of 7000 and 5500.

The infra-red spectra of nitramines show approximately the same frequencies as ordinary nitro compounds (Lieber, Levering and Patterson [8], Salyamon and Yaroslavskii [9], Salyamon and Bobovich [9] and Bellamy [10]).

On the basis of these authors' results, Bellamy states that the nitro group in nitramines has the following vibration frequencies:

asymmetric 1587–1530 cm^{-1}

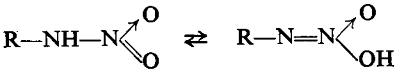
and symmetric 1292–1260 cm^{-1}.

According to Bellamy, these values may be considered as the average for all nitramines except nitroguanidine which, as the investigations of Lieber and his co-workers and of Kumler have shown, has a very high frequency of asymmetric vibration, i.e. ranging 1655–1620 cm^{-1}.

Similar deviations are shown by nitrourea. Presumably these are caused by the existence of tautomeric forms.

Nitramines show no basic properties whatever — indeed, primary nitramines have distinct acidic properties and can form salts with alkalis. Conversely, nitramides may be more strongly acidic than carboxylic acids, as, for example, nitrourethane, which is a stronger acid than formic acid.

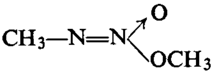
Primary amines react slowly with ammonia in a benzene medium, to form ammonium salts. Hence Hantzsch [11] assumed that primary nitramines (I), like primary and secondary nitroparaffins, are pseudoacids and react in a tautomeric aci-form (II)



$$\underset{\text{I}}{R{-}NH{-}N\begin{smallmatrix}\nearrow O\\ \searrow O\end{smallmatrix}} \rightleftarrows \underset{\text{II}}{R{-}N{=}N\begin{smallmatrix}\nearrow O\\ \searrow OH\end{smallmatrix}}$$

I II

This view was generally accepted. It was based, however, not so much on experimental evidence as on Hantzsch's personal authority. In point of fact Euler [12] found that the rate of formation of the ammonium salt is by no means as slow as Hantzsch believed and expressed doubt as to the existence of the supposed tautomerism. No further evidence confirming the existence of the aci-form was forthcoming until the O-alkyl derivatives, e.g. O-methyl-methylnitramine (III),

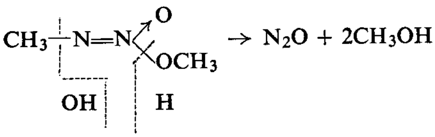


$$CH_3{-}N{=}N\begin{smallmatrix}\nearrow O\\ \searrow OCH_3\end{smallmatrix}$$

III

isomeric with dimethylnitramine (Gillibrand and Lamberton [13]), were obtained.

That the compound (III) actually has such a structure is proved by the fact that on hydrolysis with 40% sulphuric acid two molecules of methyl alcohol are formed:



$$\underset{OH}{CH_3}{-}N{=}N\begin{smallmatrix}\nearrow O\\ \searrow \underset{H}{OCH_3}\end{smallmatrix} \rightarrow N_2O + 2CH_3OH$$

One of the characteristics of nitramines is the ease with which they decompose in sulphuric acid. Primary nitramines undergo decomposition with particular ease; alcohol is formed and N_2O is evolved on boiling in dilute (2%) sulphuric acid (van Erp [14], Backer [15]):

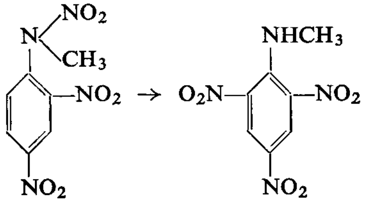
$$R{\cdot}NH{\cdot}NO_2 \rightarrow R{\cdot}OH + N_2O$$

Secondary nitramines are more stable towards sulphuric acid and decomposition rarely occurs until 40% or more sulphuric acid is used at a temperature of 100°C.

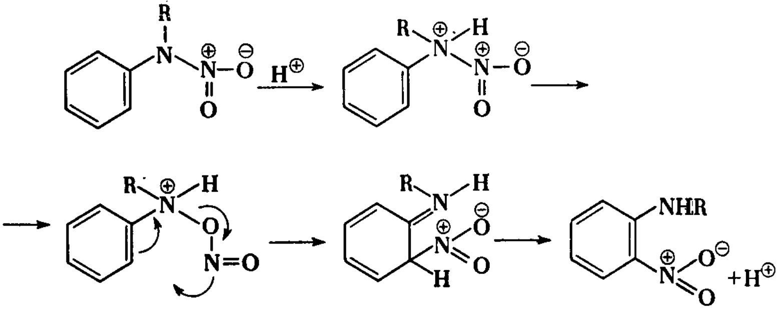
Concentrated nitric acid decomposes some primary nitramines; methylnitramine, for example, is decomposed by anhydrous nitric acid, even at a temperature below 0°C, to form methyl nitrate and N_2O (Franchimont [16]).

Rearrangement of primary and secondary aromatic nitramines occurs in an acid medium with the formation of C-substituted aniline derivatives (Bamberger and Landsteiner [17]).

Dinitrophenylmethylnitramine, for example, on treatment with nitric and sulphuric acid, is rearranged to form trinitro-N-methylaniline:

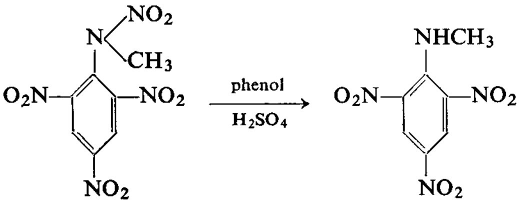


Hughes and Ingold [18] suggest the following explanation of the rearrangement:



This rearrangement, which is of great importance for the manufacture of tetryl, will be illustrated when the production of this substance is discussed.

The majority of aromatic–aliphatic nitramines undergo denitration on heating with phenol, especially in the presence of sulphuric acid. Tetryl, for example, undergoes the following reaction:

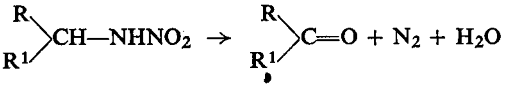


Nitramines dissolved in concentrated sulphuric acid give a blue colour with diphenylamine reagent.

With primary nitramine sulphuric acid may promote the separation of nitric acid, which results in extensive decomposition of the substance. This will be discussed in more detail when dealing with nitroguanidine (p. 26).

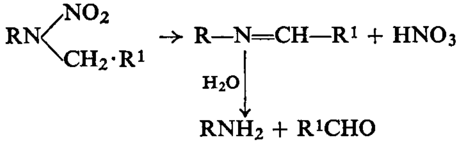
There is as yet no evidence that in the presence of sulphuric acid secondary amines lose nitric acid which would be capable of nitrating phenol. Attack by concentrated sulphuric acid, presumbaly loosens the linkage between the nitrogen atoms, leading to the expulsion of the nitronium ion $NO_2^{\oplus}$, which is a nitrating agent.

Most nitramines are fairly resistant to alkalis. Some of the primary amines, e.g. the simple aliphatic ones, are not susceptible to decomposition even under the influence of a hot, 20% solution of potassium hydroxide (van Erp [14]). On the other hand, Hantzsch and Metcalf [19] found that N-nitraminoacetic acid is decomposed by sodium hydroxide. According to Barrott, Gillibrand and Lamberton [20] most primary amines undergo decomposition on treatment with a solution containing 0.8–8% of NaOH at a temperature of 95°C. The reaction proceeds according to the formula:



$$(R)(R^1)CH{-}NHNO_2 \rightarrow (R)(R^1)C{=}O + N_2 + H_2O$$

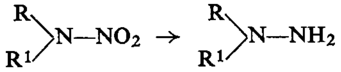
The concentration of alkali required depends on the properties of the radicals R and R^1. The more electrophilic the radicals and the more ácidic the nitramine, the easier the course of reaction. Secondary nitramines are decomposed by an aqueous solution of sodium hydroxide. The reaction conditions, including the concentrations of NaOH solutions differ according to the substance. Van Erp and Franchimont [21] found that the reaction proceeded by the following mechanism:



$$RN(NO_2)(CH_2{\cdot}R^1) \rightarrow R{-}N{=}CH{-}R^1 + HNO_3 \xrightarrow{H_2O} RNH_2 + R^1CHO$$

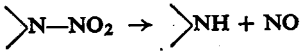
Various products are formed by the reduction of nitramines, depending on the reaction conditions.

Vigorous reduction may involve the rupture of the N—N linkage with the formation of amine and ammonia. Milder reducing agents yield different products, including hydrazine derivatives, e.g.:



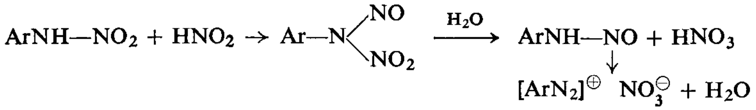
$$(R)(R^1)N{-}NO_2 \rightarrow (R)(R^1)N{-}NH_2$$

Such a reduction may occur quantitatively and hence may be utilized for analytical purposes. According to Cope and Barab [22], the Schulze–Tiemann ($FeCl_2$ $+HCl$) or Lunge ($Hg+H_2SO_4$) methods are suitable for this purpose. In both cases the reaction proceeds as follows:



$$>N{-}NO_2 \rightarrow >NH + NO$$

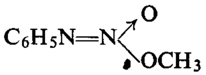
The reaction of primary aromatic nitramines with nitrous acid is specific and leads to the formation of diazonium nitrate (Bamberger [23]). According to Stevens [24] this reaction is also a kind of reduction, and presumably may be represented as follows:



$$\mathrm{ArNH{-}NO_2 + HNO_2 \rightarrow Ar{-}N\begin{matrix}\nearrow NO\\ \searrow NO_2\end{matrix} \xrightarrow{H_2O} \overset{}{ArNH{-}NO} + HNO_3}$$
$$\mathrm{\downarrow}$$
$$\mathrm{[ArN_2]^{\oplus}\ NO_3^{\ominus} + H_2O}$$

Primary nitramines react with diazomethane to yield N-methyl or O-methyl derivatives.

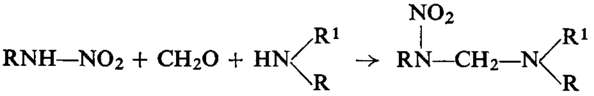
Thus, methylnitramine is converted into dimethylnitramine and phenylnitramine into phenyl-O-methylnitramine:



$$\mathrm{C_6H_5N{=}N\begin{matrix}\nearrow O\\ \searrow OCH_3\end{matrix}}$$

IIIa

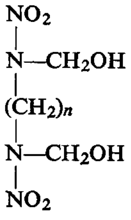
As early as 1910, Franchimont [16] observed that primary nitramines (and nitroparaffins) react with formaldehyde and secondary amines (e.g. piperidine). The formation of aminomethylnitramines (IV) then occurs:



$$\mathrm{RNH{-}NO_2 + CH_2O + HN\begin{matrix}\nearrow R^1\\ \searrow R\end{matrix} \rightarrow R\overset{\overset{NO_2}{|}}{N}{-}CH_2{-}N\begin{matrix}\nearrow R^1\\ \searrow R\end{matrix}}$$

IV

It was shown (Woodcock [25]) that intermediate hydroxymethyl compounds may be formed as for example those of type (V)

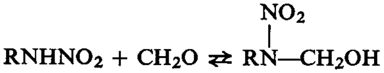


$$\begin{matrix}\mathrm{NO_2}\\ |\\ \mathrm{N{-}CH_2OH}\\ |\\ \mathrm{(CH_2)}_n\\ |\\ \mathrm{N{-}CH_2OH}\\ |\\ \mathrm{NO_2}\end{matrix}$$

V

($n=1$, 3 or 4)

According to Lamberton and his co-workers [26], equilibrium is established in an aqueous solution:



$$\mathrm{RNHNO_2 + CH_2O \rightleftarrows R\overset{\overset{NO_2}{|}}{N}{-}CH_2OH}$$

VI

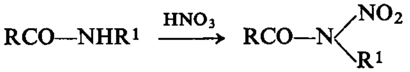
The hydroxymethyl derivative (VI) is, however, more stable in an acid medium. In a neutral medium the equilibrium shifts markedly to the left.

PREPARATION OF NITRAMINES

Nitramines and nitramides arise in various ways depending on the amines and amides subjected to nitration. There are direct and indirect nitration methods.

DIRECT NITRATION

Direct nitration with anhydrous nitric acid (98%) can be accomplished most conveniently in the presence of monosubstituted N-alkylamides. A secondary nitramide is then formed:

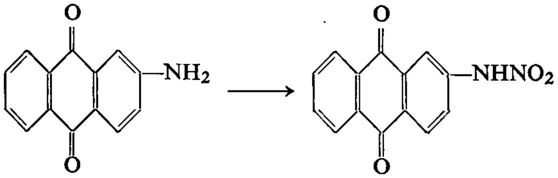


$$RCO{-}NHR^1 \xrightarrow{HNO_3} RCO{-}N\begin{matrix} \diagup NO_2 \\ \diagdown R^1 \end{matrix} \qquad (1)$$

One of the direct methods of nitrating primary amines is based on this reaction. An amine is acylated to form a primary amide which is in turn nitrated according to reaction (1) and then hydrolysed to release the acyl group. This procedure will be discussed more fully in later chapters.

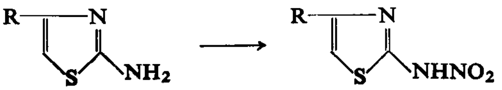
Generally, reaction (1) is not successful with non N-substituted, i.e. primary amides, most of which undergo decomposition when nitrated. Primary aliphatic amines also decompose under the action of concentrated nitric acid.

Similarly, primary aromatic amines undergo complex reactions when heated with nitric acid. The amine derivatives of anthraquinone, pyridine and thiazole are exceptions: the amino group in these compounds is decomposed by the nitrating mixture. This was noticed by Scholl [27], who proposed the following method for nitrating β-aminoanthraquinone:

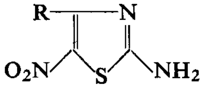


Chichibabin [28] and Razorenov observed that the amino derivatives of pyridine are nitrated in a similar way. For example, a mixture of nitric and sulphuric acids converts α-amino-pyridine into α-nitramino-pyridine.

Ganapathi and Venkataraman [29] found that aminothiazole and its homologues can be nitrated in the same way, using a double excess of nitrating mixture.

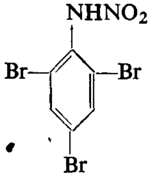


In addition to the compound (I), a certain amount of a compound (II) nitrated in the ring is formed when a stoichiometric quantity of HNO_3 is used. As the investigations of Wright *et al.* [30] subsequently showed, the compound (II) is also obtainable when aminothiazole is treated with a nitrating mixture containing 10–30% of water.

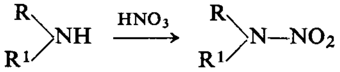


II

At an earlier stage Orton [31] found that some aniline derivatives which are difficult to nitrate in the ring, are liable to form N-nitramines when treated with nitric acid and acetic anhydride. For example, he prepared the corresponding nitramine from 2,4,6-tribromaniline:



The nitration of secondary amines by the above method is generally successful:



$$\begin{matrix}R\\R^1\end{matrix}\rangle NH \xrightarrow{HNO_3} \begin{matrix}R\\R^1\end{matrix}\rangle N{-}NO_2 \qquad (2)$$

It is noteworthy that the conversion of the group $\rangle$NH into $\rangle$N—NO_2 is not always practicable. As early as 1916 Franchimont and Dubsky [32] called attention to the fact that if the group $\rangle$NH has the properties of an imido group (for example —CO—NH—CO—), it is not susceptible to nitration, while the same group with amido characteristics (for example —CO—NH—CH_2—) is readily nitrated. Developing this observation, Wright *et al.* [33, 34] were led to the discovery that very weakly basic amines with the $\rangle$NH group (e.g. in the form of —CH_2—NH—CH_2) are nitrated more readily than strong bases with the same group. Strong bases require the addition of a catalyst for nitration (for example, $ZnCl_2$, HCl; this will be discussed in later chapters) whereas weak bases can be nitrated without a catalyst. Amines of the type R—CH_2—NH—CH_2—R, for example, where R = CN, COOH or $CONH_2$, i.e. amines of a considerably diminished basicity, are nitrated relatively easily.

In some more complex cases, secondary amines can be nitrated with nitrating mixtures. Diethanolnitramine dinitrate (DINA), for example, can be prepared by the action on diethanolamine of a mixture of nitric acid, nitric anhydride and zinc chloride (this is dealt with in more detail on p. 10).

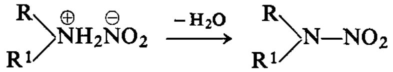
Some amines undergo direct nitration during nitrolysis; nitration is then followed by partial degradation involving the cleavage of the bond between the carbon and nitrogen atoms (p. 12).

INDIRECT NITRATION

Nitration by the "dehydration" of the amine nitrate

This method is commonly applied to the nitration of primary amines (3) and in particular the preparation of nitroguanidine, nitrourea etc., as well as in the nitration of secondary amines (4):

$$\overset{\oplus}{RNH_3}\overset{\ominus}{NO_3} \xrightarrow{-H_2O} RNH{-}NO_2 \qquad (3)$$



$$\begin{matrix}R\\R^1\end{matrix}\!\!>\overset{\oplus}{NH_2}\overset{\ominus}{NO_2} \xrightarrow{-H_2O} \begin{matrix}R\\R^1\end{matrix}\!\!>N{-}NO_2 \qquad (4)$$

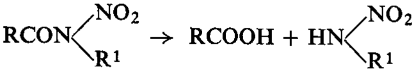
It was applied by Bamberger and Kirpal [35] in the preparation of dimethylnitramine and nitropiperidine with a rather poor yield. They used acetic anhydride as a dehydrating medium.

Wright *et al.* [33, 36] found that the yield of nitramines was considerably improved by adding zinc chloride or hydrogen chloride to the acetic anhydride. Under such conditions dimethylamine yields 65% of dimethylnitramine. It is not impossible that the essence of the action of these additions is to reduce the basicity of the amine and thus facilitate the introduction of a nitro group in accordance with the rule outlined above.

Another method of "dehydration" of the amine nitrate is based on treatment with concentrated sulphuric acid. This is used commercially in manufacturing such primary amines as nitroguanidine (p. 31).

Nitration of primary amines by acylation

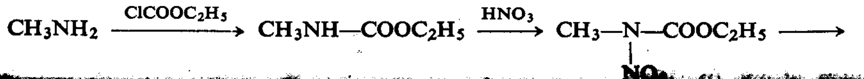
This method involves acylation of the primary amine by introducing an acetyl or oxalyl group followed by nitration of the secondary amine so formed in accordance with the reaction (1). The product thus nitrated undergoes alkaline hydrolysis to yield a primary nitramine:



$$RCON\!\!<\!\begin{matrix}NO_2\\R^1\end{matrix} \rightarrow RCOOH + HN\!\!<\!\begin{matrix}NO_2\\R^1\end{matrix} \qquad (5)$$

Very frequently the transition through urethanes is employed by treating the primary amine with chloroformate. The N-substituted urethane so obtained is nitrated by substituting the free N-hydrogen and then subjecting the product to alkaline hydrolysis which results in the formation of the salt of a primary nitramine and a base. The free nitramine is obtained by acidification.

This type of reaction can be illustrated by the nitration of methylamine according to Franchimont [37] (6):



$$CH_3NH_2 \xrightarrow{ClCOOC_2H_5} CH_3NH{-}COOC_2H_5 \xrightarrow{HNO_3} CH_3{-}\underset{NO}{\underset{|}{N}}{-}COOC_2H_5 \longrightarrow$$

$$\begin{tikzcd} {} \arrow[r, "2NH_3"] & CH_3{-}N{=}NO_2^{\ominus}NH_4^{\oplus} + NH_2{-}COOC_2H_5 \arrow[d, "HCl"'] \\ & CH_3NH{-}NO_2 + NH_4Cl \end{tikzcd} \qquad (6)$$

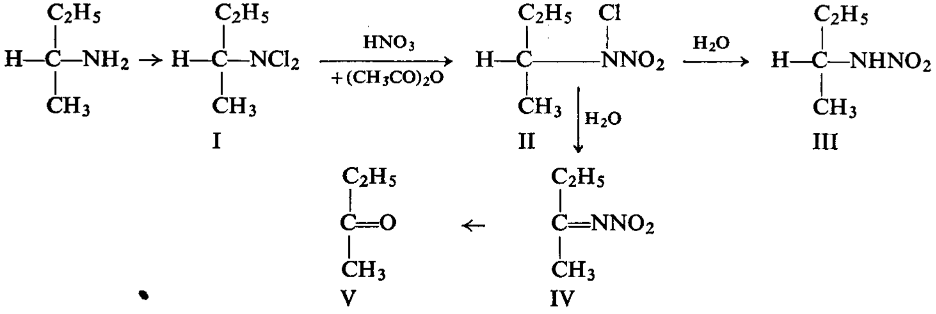
The method was later worked out by Brian and Lamberton [38] to produce previously unobtainable nitramines.

The formation of nitramines through chloramines

This method was originally suggested by Berg [39]. It consists in acting with silver nitrate on chloramines:

$$RNHCl + AgNO_3 \rightarrow RNHNO_2 + AgCl$$

Wright *et al.* [40] elaborated a new method of preparing nitramines by acting on chloramines with nitric acid in the presence of acetic anhydride. A typical example is the preparation of sec-butylnitramine (III) (Smart and Wright; Suggitt, Myers and Wright [40]) from dichloramine (I):



The intermediate (II) is unstable and is hydrolysed in water to form (III) and (IV). The latter (2-butanenitramine) is also unstable and decomposes to butanone-2 (V).

The intermediate formation of chloramine explains the catalytic action of hydrochloric acid in the nitration of amines, as mentioned above. The following reaction mechanism was drawn up by Wright [41]

$$2HCl + 2HNO_3 + 3(CH_3CO)_2O \rightarrow 2CH_3COOCl + N_2O_3 + 4CH_3COOH \qquad (a)$$

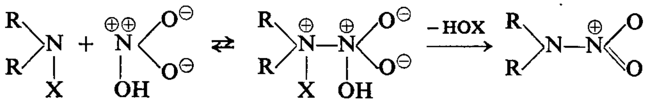
$$R_2NH + CH_3COOCl \rightarrow R_2NCl + CH_3COOH \qquad (b)$$

$$R_2NCl + HNO_3 \rightarrow R_2NNO_2 + HOCl \qquad (c)$$

$$HOCl + (CH_3CO)_2O \rightarrow CH_3COOCl + CH_3COOH \qquad (d)$$

Thus hydrochloric acid reacts in the presence of nitric acid to yield chlorine acetate (a)—a compound with cationic chlorine. The latter in turn forms a chloramine (b) which is nitrated to a nitramine (c).

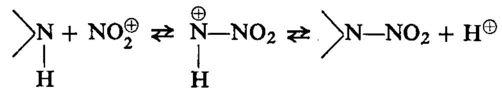
The mechanism of the nitration of amines has not yet been explained fully. Wright *et al.* [34, 42] suppose that the nitration of secondary amines and probably of secondary amides takes place by the formation of intermediate complexes between the amine and nitric acid. It is probable that the bond N—N is formed, followed by the loss of HOX (7):



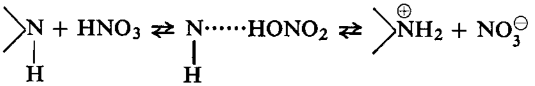
(7)

In catalysed reactions X represents Cl, in uncatalysed reactions it represents H.

This scheme, however, has the disadvantage of ignoring the influence of the nitronium ion ($NO_2^{\oplus}$) on the reaction, whereas, as expounded in the chapter on nitration theories (Vol. I), the nitronium ion is of enormous importance for such a reaction. In this connection Lamberton [43] suggests alternative schemes which appear more probable. Scheme (8) leads to the formation of a nitramine and scheme (9) to a salt of nitric acid:



$$\underset{\displaystyle |\atop H}{>N} + NO_2^{\oplus} \rightleftarrows \underset{\displaystyle |\atop H}{\overset{\oplus}{N}}—NO_2 \rightleftarrows >N—NO_2 + H^{\oplus} \qquad (8)$$

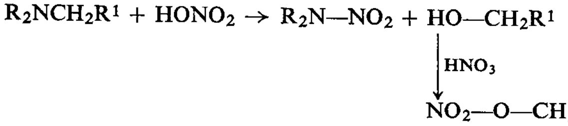


$$\underset{\displaystyle |\atop H}{>N} + HNO_3 \rightleftarrows \underset{\displaystyle |\atop H}{N}\cdots\cdots HONO_2 \rightleftarrows >\overset{\oplus}{N}H_2 + NO_3^{\ominus} \qquad (9)$$

Where there are strong bases which are nitrated with difficulty, reaction (9) predominates over reaction (8). At the same time Lamberton called attention to the reversibility of reaction (9). Indeed, it is known that nitramines such as nitroguanidine or nitrourethanes exhibit nitrating properties in the presence of sulphuric acid, thus behaving as if they can split off the nitronium ion or the nitric acid molecule.

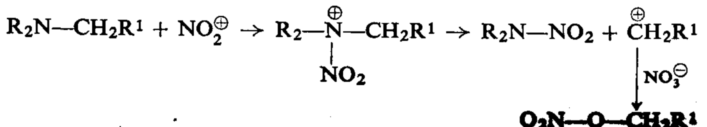
Nitration by nitrolysis

The term "nitrolysis" suggested by Linstead [44] is usually applied to a nitrating mechanism in which both the rupture of C—N bond and the formation of a nitramine occur simultaneously with the formation of alcohol which subsequently undergoes esterification (10):



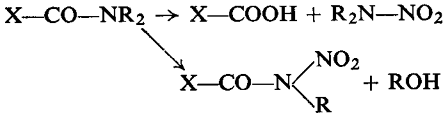
$$\begin{array}{l} R_2NCH_2R^1 + HONO_2 \rightarrow R_2N—NO_2 + HO—CH_2R^1 \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad \big\downarrow HNO_3 \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad NO_2—O—CH_2R^1 \end{array} \qquad (10)$$

Nitrolysis may also proceed without giving rise to alcohol in accordance with eqn. (11). Nevertheless, a nitric ester is formed by the possible action of the $NO_3^{\ominus}$ ion on a free alkyl cation:



$$\begin{array}{l} R_2N—CH_2R^1 + NO_2^{\oplus} \rightarrow R_2—\underset{\displaystyle |\atop NO_2}{\overset{\oplus}{N}}—CH_2R^1 \rightarrow R_2N—NO_2 + \overset{\oplus}{C}H_2R^1 \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad \big\downarrow NO_3^{\ominus} \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad O_2N—O—CH_2R^1 \end{array} \qquad (11)$$

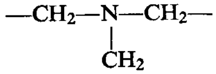
As these equations suggest, the nitration of an amide may lead to a nitramine or a nitramide, according to reaction (12a) or (12b):



$$X{-}CO{-}NR_2 \rightarrow X{-}COOH + R_2N{-}NO_2 \qquad (12a)$$

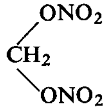
$$X{-}CO{-}NR_2 \rightarrow X{-}CO{-}N\begin{matrix}NO_2\\ R\end{matrix} + ROH \qquad (12b)$$

The nitration of hexamethylenetetramine, which contains the grouping



$$\begin{matrix}{-}CH_2{-}N{-}CH_2{-}\\ |\\ CH_2\end{matrix}$$

to produce cyclonite, is also a nitrolysis reaction. In addition to cyclonite, a nitrate of methylene glycol is also formed as a result of the cleavage of one of the three linkages between each nitrogen and carbon atom:



$$CH_2\begin{matrix}ONO_2\\ ONO_2\end{matrix}$$

Other methods for the preparation of nitramines

Some nitramines may be prepared without treating amines with nitric acid. The classical example is the so-called "E-method" of cyclonite preparation in which a nitramine is formed by dehydration of a mixture of paraformaldehyde and ammonium nitrate, i.e. without using either amine or nitric acid (this will be discussed more fully on p. 109). When a nitramine is required with a non-nitrated aromatic ring which readily undergoes nitration with nitric acid, Bamberger's method [45], involving the oxidation of diazo compounds (13), may be applied.

$$C_6H_5N{=}NOK \xrightarrow{K_3Fe(CN)_6} C_6H_5NK{-}NO_2 \xrightarrow{HCl} C_6H_5NH{-}NO_2 \qquad (13)$$

NITRAMINES AS EXPLOSIVES

Nitramines differ from nitro compounds in possessing a somewhat better oxygen balance, due to the fact that the group $N{-}NO_2$ gives twice the volume of nitrogen as the group $C{-}NO_2$. On the other hand nitramines have a worse oxygen balance than nitric esters.

As regards explosive strength, nitramines occupy a position midway between nitro compounds and nitric esters. They also hold a central position regarding other properties, such as chemical stability and sensitiveness to impact and friction.

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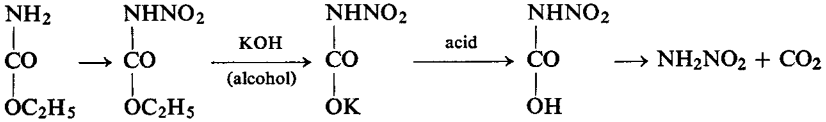
CHAPTER II

ALIPHATIC NITRAMINES AND NITRAMIDES

NITRAMINE (NITRAMIDE)

$NH_2 \cdot NO_2$
m.p. 72–73°C (decomp.)

THIS is one of the simplest nitramines obtained by Thiele and Lachman [1] by the decomposition of nitrourethane:



$$\underset{OC_2H_5}{\overset{NH_2}{CO}} \longrightarrow \underset{OC_2H_5}{\overset{NHNO_2}{CO}} \xrightarrow[\text{(alcohol)}]{\text{KOH}} \underset{OK}{\overset{NHNO_2}{CO}} \xrightarrow{\text{acid}} \underset{OH}{\overset{NHNO_2}{CO}} \longrightarrow NH_2NO_2 + CO_2 \qquad (14)$$

The structure of the compound was the subject of controversy for some time [2]. However, the latest experiments of Clusius [3] with ^{15}N-labelled nitramine have confirmed Thiele's formula [4]:

$$NH_2NO_2 \rightleftarrows NH{=}NO(OH)$$

A carefully-devised method for preparing it was announced by Marlies, La Mer and Greenspan [5]. According to Bell and Wilson [6] the product contains some acidic impurities (about 1%), possibly unchanged nitrourethane.

This substance is an intermediate product of the decomposition of the important explosive nitroguanidine. It is also present in an aqueous solution of nitrourea or a sulphuric acid solution of nitrourea (Davis and Blanchard [7]).

Nitramine is believed to occur in an ammonium nitrate solution in an excess of concentrated sulphuric acid as a result of the dehydration of this salt:

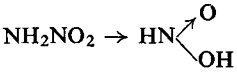
$$NH_4NO_3 \rightarrow NH_2NO_2 + H_2O \qquad (15)$$

Davis and Abrams [8] report the following experimental observations in support of this supposition. On heating a solution of ammonium nitrate in sulphuric acid to 150°C, nitric acid cannot be distilled, but nitrous oxide is evolved, probably from the decomposition of nitramine. If, however, the solution is kept for a long time between 90 and 120°C, nitric acid can be obtained by distillation. The authors' conjecture is that the addition of water to the nitramine takes place according to the reaction (16):

$$NH_2NO_2 + H_2O \rightarrow NH_3 + HNO_3 \qquad (16)$$

Nitramine has explosive properties but it is not of any practical value for many reasons, primarily because of its high reactivity which impairs its chemical stability. It decomposes at a temperature as low as its melting point. At room temperature it decomposes slowly, to form nitrous oxide and water. On heating to 60–65°C decomposition occurs in an aqueous solution. It decomposes explosively on contact with concentrated sulphuric acid.

Bell and Caldin [9] and Caldin and Peacock [10] investigated the decomposition kinetics of nitramine under the influence of alkali in various solvents. Dimethylaniline was used as a base. According to Bell [11] the decomposition of nitramine proceeds through the formation of the aci-form:



$$NH_2NO_2 \rightarrow HN\begin{matrix}\nearrow O\\ \searrow OH\end{matrix}$$

The reaction with a base B would then take the following course:

$$B + HN{=}NO\cdot OH \rightarrow BH^{\oplus} + N_2O + OH^{\ominus} \rightarrow B + H_2O + N_2O$$

The rate and activation energy of decomposition depend to a great extent on the type of solvent used.

METHYLNITRAMINE

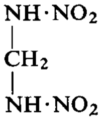
$CH_3NH\cdot NO_2$
m.p. 38°C

This is a powerful explosive, stronger than tetryl but weaker than cyclonite. It is, however, of no practical value chiefly because its preparation is too expensive, requiring first the conversion of methylamine into urethane and then into its nitro derivative. On hydrolysis the latter yields methylnitramine. Similarly, the hydrolysis of dinitrodimethyloxamide (p. 35) leads to the formation of methylnitramine.

Methylnitramine is very readily soluble in water, alcohol, chloroform and benzene but is less soluble in ether. It is a strong acid which easily forms salts, including explosive ones. It is not decomposed by boiling water, even in the presence of alkalis, but it is liable to destructive distillation yielding dimethylnitramine $(CH_3)_2N\cdot NO_2$, m.p. 57°C, methyl alcohol, nitrous oxide and many other products.

Methylnitramine decomposes explosively in contact with concentrated sulphuric acid. It is evolved when aniline reacts with tetryl, a diphenylamine derivative (p. 51) is produced simultaneously. Methylnitramine reacts with picryl chloride to form tetryl. The structure of tetryl (p. 40) was first proved by this synthesis.

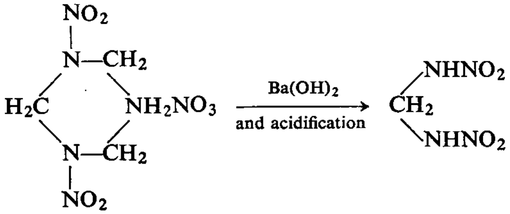
METHYLENEDINITRAMINE



$$NH{\cdot}NO_2{-}CH_2{-}NH{\cdot}NO_2$$

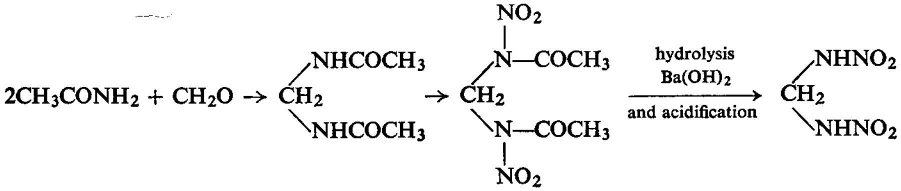
m.p. 101°C

This substance was isolated in the form of its barium salt by Hirst *et al.* [12] when investigating the nitration of hexamethylenetetramine to cyclonite. They found that hexamethylenetetramine, when dissolved in nitric acid at 40°C, yields the product (II) which is hydrolysed by barium hydroxide to form the barium salt of methylenedinitramine. From this the free nitramine may be obtained:



II I

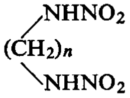
Brian and Lamberton [13] accomplished the synthesis of methylenedinitramine with methylene-bis-N-acetamide (III):



This synthesis served as a basis for the confirmation of the structure of methylenedinitramine.

Methylenedinitramine undergoes decomposition under the influence of strong acids and strong bases. At a pH of about 1.0 and 10.0, however, it is fairly stable although it decomposes readily when the pH ranges between 3 and 8, the maximum of the decomposition rate occurring at pH 5.4 (Lamberton *et al.* [14]). Decomposition is accompanied by the evolution of nitrous oxide and formaldehyde.

The methylenedinitramine homologues with the general formula:

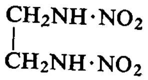


$$(CH_2)_n(NHNO_2)_2$$

are far more stable.

Traube [15] prepared methylenedi-isonitramine, the isomer of methylenedinitramine, in the form of a sodium salt, by the action of nitric oxide on acetone, in the presence of sodium alcoholate. As T. Urbański *et al.* [16] showed, this substance can also be obtained by using paraldehyde instead of acetone. The structure of the isonitramino group has now been established as nitrosohydroxylamine. This substance and its salts, which according to T. Urbański *et al.* possess initiating properties, will be more fully described later (p. 221).

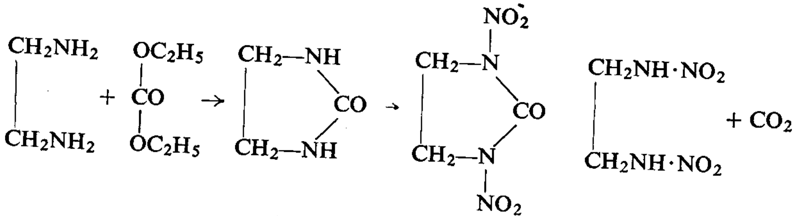
ETHYLENEDINITRAMINE



$$\begin{array}{l} CH_2NH\cdot NO_2 \\ | \\ CH_2NH\cdot NO_2 \end{array}$$

m.p. 175–176°C

Franchimont and Klobbie [17] prepared ethylenedinitramine (EDNA, Haleite) by the nitration of ethylene urea (2-imidazolidone) with a mixture of nitric and sulphuric acids. (According to Schweitzer [18], ethylene urea is obtainable either by the action of urea on ethylenediamine at 110°C (initially) to 240–250°C (finally) in quantitative yield or by the action of urea on ethylene glycol at 160–240°C in 55% yield. W. E. Bachmann *et al.* [19] prepared ethylene urea by the action of ethyl carbonate on ethylenediamine in approximately 60% yield.) Hydrolysis of the dinitroethylene urea so formed gives ethylenedinitramine. Bachmann recommends nitration with mixed nitric acid and acetic anhydride:

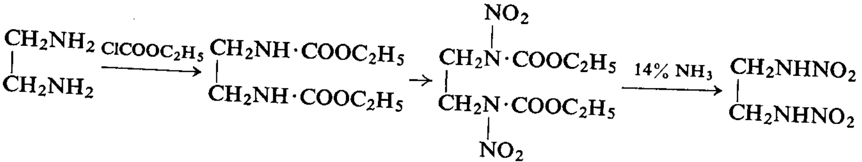


(17)

m.p. 132–132.5°C m.p. 211–212°C

Dinitroethylene urea is highly unstable and readily hydrolysable by heating in water.

Another method of preparing ethylenedinitramine (also by Franchimont and Klobbie [17]), involves the action of chloroformate on ethylenediamine and nitration with nitric acid alone (98%). Bis-urethan after nitration is hydrolysed with ammonia solution (approximately 14%) at about 90°C:

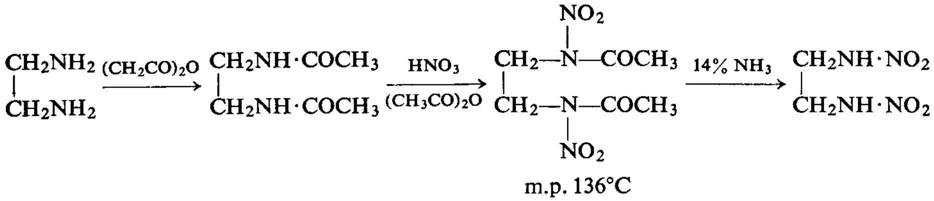


$$\begin{array}{l} CH_2NH_2 \\ | \\ CH_2NH_2 \end{array} \xrightarrow{ClCOOC_2H_5} \begin{array}{l} CH_2NH\cdot COOC_2H_5 \\ | \\ CH_2NH\cdot COOC_2H_5 \end{array} \rightarrow \begin{array}{l} \quad NO_2 \\ \quad | \\ CH_2N\cdot COOC_2H_5 \\ | \\ CH_2N\cdot COOC_2H_5 \\ \quad | \\ \quad NO_2 \end{array} \xrightarrow{14\%\ NH_3} \begin{array}{l} CH_2NHNO_2 \\ | \\ CH_2NHNO_2 \end{array} \quad (18)$$

m.p. 110°C m.p. 82–83°C

According to W. E. Bachmann *et al.* [19] the second of these methods gives a better yield (87% calculated in relation to the ethylenediamine used).

They found that a good yield of ethylenedinitramine may also be obtained from ethylenediamine through diacetylethylenediamine (ethylene-bis-acetamide). The nitration of the latter involves the use of nitric acid (98%) mixed with acetic anhydride:

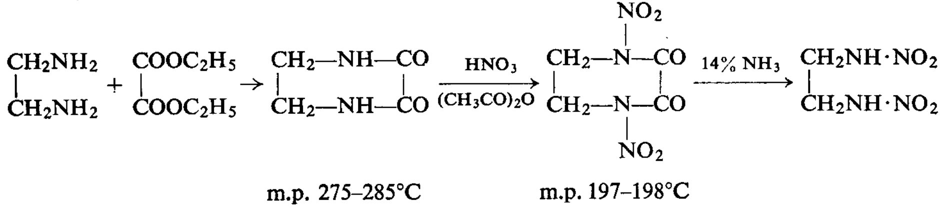


$$\begin{array}{l}CH_2NH_2\\ |\\ CH_2NH_2\end{array} \xrightarrow{(CH_2CO)_2O} \begin{array}{l}CH_2NH\cdot COCH_3\\ |\\ CH_2NH\cdot COCH_3\end{array} \xrightarrow[(CH_3CO)_2O]{HNO_3} \begin{array}{l}\quad\;\; NO_2\\ \quad\;\;\, |\\ CH_2{-}N{-}COCH_3\\ |\\ CH_2{-}N{-}COCH_3\\ \quad\;\;\, |\\ \quad\;\; NO_2\end{array} \xrightarrow{14\%\ NH_3} \begin{array}{l}CH_2NH\cdot NO_2\\ |\\ CH_2NH\cdot NO_2\end{array}$$

m.p. 136°C

It is important to bear in mind that ethylene-bis-acetamide (earlier prepared by A. W. Hofmann [20]) cannot be nitrated with nitric acid alone or nitric and sulphuric acids. The product of nitration is readily hydrolysed by the action of 30% NaOH solution or *ca.* 15% NH_3 solution at room temperature.

The same authors found that ethylenedinitramine may be obtained in a similar way by promoting the transient formation of ethylene oxamide from ethylenediamine and ethyl oxalate:



$$\begin{array}{l}CH_2NH_2\\ |\\ CH_2NH_2\end{array} + \begin{array}{l}COOC_2H_5\\ |\\ COOC_2H_5\end{array} \rightarrow \begin{array}{l}CH_2{-}NH{-}CO\\ | \qquad\qquad\;\; |\\ CH_2{-}NH{-}CO\end{array} \xrightarrow[(CH_3CO)_2O]{HNO_3} \begin{array}{l}\quad\;\; NO_2\\ \quad\;\;\, |\\ CH_2{-}N{-}CO\\ | \qquad\quad\; |\\ CH_2{-}N{-}CO\\ \quad\;\;\, |\\ \quad\;\; NO_2\end{array} \xrightarrow{14\%\ NH_3} \begin{array}{l}CH_2NH\cdot NO_2\\ |\\ CH_2NH\cdot NO_2\end{array}$$

m.p. 275–285°C m.p. 197–198°C

Ethylene oxamide was prepared earlier by van Alphen [21]. It cannot be nitrated either with nitric acid alone (98%) or with mixed nitric and sulphuric acids.

Ethylenedinitramine is produced on a technical scale in the following way:

One part of ethylene urea is introduced at a temperature not higher than 10°C into ten parts of a mixture consisting of:

HNO_3	15.4%
H_2SO_4	74.0%
H_2O	10.6%

After the last portion of ethylene urea has been added, the solution is poured into ice water. The nitroethylene urea thus precipitated is filtered, carefully washed and thrown into boiling water. On hydrolysis carbon dioxide is evolved. Boiling is continued until all the gases have been removed, and then the solution is cooled down. Ethylenedinitramine crystallizes in the rhombic system as white, lustrous crystals, s.g. 1.75 which after filtration are washed with cold water and dried at 50°C.

Hale [22] recommended ethylenedinitramine for use as a high explosive. It is insoluble in ether, but soluble in nitrobenzene and dioxane. The solubility of ethylenedinitramine is given in Table 1.

Ethylenedinitramine is non-hygroscopic and picks up only 0.01% of moisture in damp conditions at room temperature. It is a strong acid and easily forms salts. The potassium salt can be recrystallized from alcohol. The silver and lead salts are highly sensitive to impact (they have a sensitiveness similar to that of mercury fulminate), but have no initiating properties. Ethylenedinitramine is not explicitly toxic.

TABLE 1

SOLUBILITY OF ETHYLENEDINITRAMINE

Temperature °C	Solubility in 100 g of	
	water	95% alcohol
25	0.3	1.25
50	1.25	3.45
75	4.95	10.1
95	16.4	—

Its chemical stability is fairly high and only an insignificant amount decomposes on prolonged boiling in water. Boiling in dilute sulphuric acid causes decomposition with the evolution of nitrous oxide, acetaldehyde and ethylene glycol.

Hale [22] reports that the ignition temperature of ethylenedinitramine is 180°C, i.e. similar to that of nitroglycerine. On heating at 120°C its stability is of the order of that of tetryl.

Ethylenedinitramine is a powerful explosive:

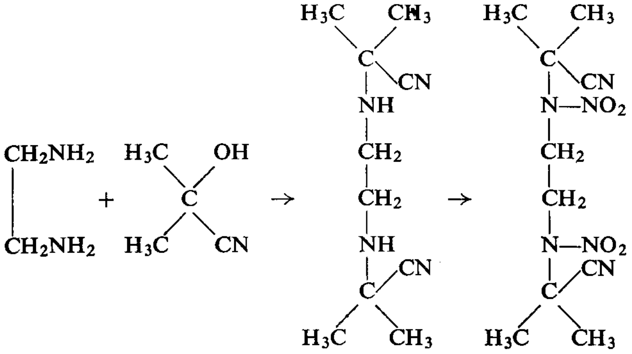
Heat of explosion	1267 kcal/kg
Volume of gases (V_0)	908 l./kg
Rate of detonation at a density of 1.55	7750 m/sec

A. J. B. Robertson [23] found that under a pressure of 100 mm of nitrogen at 174–178°C the thermal decomposition of EDNA is a first order reaction. The activation energy is 30.5 kcal and log $B = 12.8$.

The substance possesses quite uncommon and valuable explosive properties. It is more powerful than tetryl, and considerably less sensitive to impact (as sensitive as picric acid). However, its acidic properties limit its use to a great extent. In this respect it resembles picric acid. Even so ethylenedinitramine, under the name of Haleite, has been accepted in the United States as a military explosive. During World War II, production in that country was carried out by the method outlined above according to eqn. (17)

OTHER NITRAMINES DERIVING FROM ETHYLENEDIAMINE

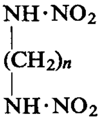
A series of new nitramines, the ethylenediamine derivatives, was prepared by Picard and Meen [24] by the action of acetone cyanohydrin on ethylenediamine and its analogues (i.e. diethylenetriamine etc.), followed by the nitration of the products obtained with mixed nitric acid and acetic anhydride. In the presence of CH_3COCl or HCl or $ZnCl_2$, nitration gives yields as high as 76%. The simplest example of these compounds is the product (II), prepared by the following steps:



m.p. 54.5–56°C m.p. 212°C (decomp.)

I II

Higher homologues of ethylenedinitramine



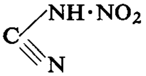
$$NH{\cdot}NO_2-(CH_2)_n-NH{\cdot}NO_2$$

are crystalline substances with the following melting points:

	m.p.
at $n=3$	69°C
$n=4$	163°C
$n=5$	60°C

The explosive properties of these compounds have not been examined.

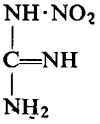
NITROCYANAMIDE



m.p. 137–138°C

Harris [25] isolated this substance by the action of anhydrous hydrogen chloride on the solution of the silver salt of nitrocyanamide in acetonitrile. It has explosive properties but it is of no practical value due to the difficulty of preparing it. On the other hand its salts may be of practical value. These salts and their preparation will be discussed in the chapters dealing with initiating explosives (p. 211).

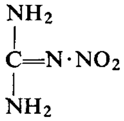
NITROGUANIDINE



$$\begin{array}{l} NH\cdot NO_2 \\ | \\ C{=}NH \\ | \\ NH_2 \end{array}$$

I

or



$$\begin{array}{l} NH_2 \\ | \\ C{=}N\cdot NO_2 \\ | \\ NH_2 \end{array}$$

II

(tautomeric forms)
m.p. 232°C and 257°C

Jousselin [26] prepared nitroguanidine by the action of anhydrous nitric acid or sulphuric acid on guanidine nitrate. The preparation of this substance by the action of sulphuric acid has been developed as an industrial method for the production of nitroguanidine. The method described by Marqueyrol and Loriette [27] follows somewhat different principles. It consists in acting with anhydrous nitric acid on guanidine sulphate which, in turn, is obtained on treating dicyandiamide with sulphuric acid.

Attention has been focussed on the explosive properties of nitroguanidine since the beginning of the present century. Proposals were made for its use as a component of various high explosive mixtures, e.g. fusible ternary mixtures containing ammonium nitrate and guanidine nitrate (Albit) apart from using nitroguanidine itself. Before World War I, detonating fuses filled with nitroguanidine were used in French mines.

As a high explosive nitroguanidine had limited application until World War II, when it acquired a considerable significance owing to the fact that flashless and relatively non-erosive powders containing nitroguanidine, nitrocellulose, nitroglycerine and nitrodiethyleneglycol, were employed very widely. As early as 1901 Vieille [28] pointed out the negligible erosive properties of nitroguanidine as a component of propellant powders. Since that time interest in this substance as a component of propellant explosives has continued to increase. At first, however, nitroguanidine found no practical application since it cannot form a solution with the colloidal propellant and because it remains "foreign" to this colloid it makes the propellant brittle. This is particularly evident in nitrocellulose propellants. Recchi [29], however, called attention to the fact that the incorporation of nitroguanidine into a totally colloidal nitroglycerine propellant is possible without much detriment to its elasticity and mechanical strength. His idea was put into practice when: (1) the production of nitroguanidine from atmospheric nitrogen, starting from cyanamide, was developed and (2) nitrodiethyleneglycol came into use as a component of totally colloidal "double base" propellants, these being notable for their greater elasticity and mechanical strength as compared with propellants containing nitroglycerine.

PHYSICAL PROPERTIES

Nitroguanidine exists in two crystalline forms. The α-form results from the action of sulphuric acid on guanidine nitrate followed by the precipitation of the product with water. This form crystallizes from water in long, fairly flexible needles.

The β-form is produced either alone or together with some of the α-compound, by the nitration of the mixture of guanidine sulphate and ammonium sulphate which results from the action of sulphuric acid on dicyandiamide. The β-form crystallizes from water in thin, elongated plates. It is converted into the α-compound by solution in sulphuric acid and precipitation with water. Both forms of nitroguanidine melt at the same temperature. Several authors quote different melting points: 232, 246, 257°C.

The two forms appear to differ slightly in their solubility in water, neither form being converted into the other. At 25 and 100°C the solubility of the α-form is 4.4 g/l. and 82.5 g/l. respectively. Between these temperatures the β-form appears to be more soluble.

The problem of preparing nitroguanidine in finely powdered form is of great importance, since this is the only form suitable for incorporation into colloidal propellants (nitroglycerine or nitrodiethyleneglycol powders). Rapid cooling of the aqueous solution of nitroguanidine produces very small crystals, but they are still too coarse for use as a component in propellants. The desired fine powder may be obtained by spraying hot nitroguanidine solution onto a cooled, metallic surface, by allowing the spray to drop through a tower in counter current to a stream of cold air and finally, by allowing the product to crystallize from solutions containing substances which regulate the size of the crystals as they are formed.

Pritchard and Wright [30] have described their method for preparing fine-crystalline, free-flowing nitroguanidine. They prepared a hot aqueous saturated nitroguanidine solution which was poured into cold methanol. Ninety per cent of the nitroguanidine precipitated in fine crystals. From the solution containing 10% of nitroguanidine, methanol was distilled off. The remaining aqueous solution was used again for dissolving nitroguanidine. The best ratio (by volume) of water to methanol lies between 1 : 2 and 1 : 1.

The apparent density of the crystals is 0.96, whereas that of ordinary commercial nitroguanidine is about 0.25 and that of the product rapidly crystallized from methanol is about 0.40.

The solubility of nitroguanidine in organic solvents is limited. Desvergnes [31] determined its solubility in various solvents: water, acetone, methyl and ethyl alcohols, ethyl acetate, ether, benzene, toluene, pyridine, chloroform, carbon tetrachloride and carbon sulphide. In all these liquids the solubility of nitroguanidine is negligible, the highest value—for pyridine—being 1.75 g/100 ml at 19°C.

According to Pritchard and Wright 1 part of nitroguanidine is dissolved in 11 parts of water at boiling point and in 375 parts of water at 20°C. The greatest increase of solubility lies between 90 and 100°C.

Nitroguanidine dissolves in concentrated acids yielding labile salts. Its solubility in sulphuric acid has been reported by Davis [32] (see Table 2).

TABLE 2

SOLUBILITY OF NITROGUANIDINE IN SULPHURIC ACID

Concentration of sulphuric acid %	Solubility of nitroguanidine in 100 ml of acid	
	at 0°C	at 25°C
45	5.8	10.9
40	3.4	8.0
35	2.0	5.2
30	1.3	2.9
25	0.75	1.8
20	0.45	1.05
15	0.30	0.55
0	0.12	0.42

T. Urbański and Skrzynecki [33] examined a number of systems containing nitroguanidine and found the following binary and ternary eutectic mixtures—Table 3.

TABLE 3

EUTECTIC MIXTURES WITH NITROGUANIDINE

Components	Content of nitroguanidine in eutectic %	Freezing point of eutectic °C
Nitroguanidine + ammonium nitrate	20	131.5
Nitroguanidine + guanidine nitrate	41	166.5
Nitroguanidine + guanidine nitrate + ammonium nitrate	17.5 and 22.5 of guanidine nitrate	113.2

The ultra-violet absorption spectrum of nitroguanidine was first examined by Baly and Desch [34]. Figure 4 shows a curve plotted according to the investigations of R. N. Jones and Thorn [35]. In a neutral solution with an aqueous solvent the curve shows two maxima at about 210 and 265 μ. The absorption curve is unaffected by the addition of hydrochloric acid but under the influence of 1*N* NaOH solution the two maxima are converted into one, at about 250 μ. These changes may be caused by the tautomeric modifications of nitroguanidine. However, McKay, Picard and Brunet [36] suggest that nitroguanidine may be a resonance hybrid. The structure of nitroguanidine will be discussed later. In the infra-red, nitroguanidine gives an absorption band of asymmetric vibrations of the NO_2 group which deviates considerably from the average values of the NO_2 group in nitramines (approximately 1635 cm^{-1} instead of normal value 1560 cm^{-1}). The existence of tautomeric forms may explain this devation (Bellamy [37]).

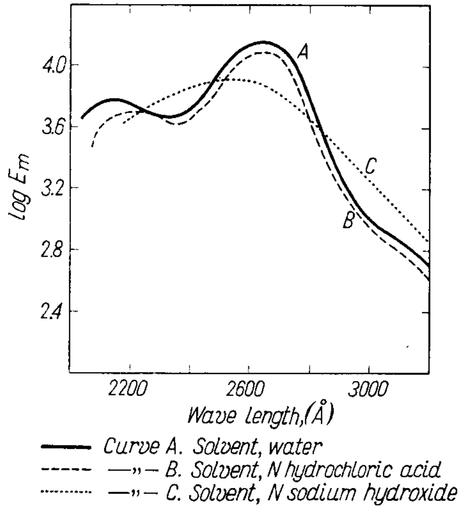
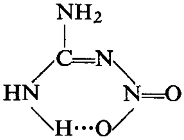


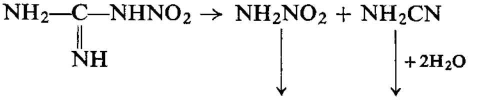
FIG. 4. Spectrum of nitroguanidine, according to R. N. Jones and Thorn [35].

CHEMICAL PROPERTIES

Jousselin [26] wrongly ascribed to nitroguanidine the formula of an N-nitroso compound. Later Pelizzari [38], Franchimont [39] and Thiele [40] considered it to be nitramine. Franchimont proposed a nitroimine structure (II) (p. 22) and later Thiele deduced that it has the structural formula of a primary nitramine (I) (p. 22) by virtue of its ability to form salts. Much later, T. Urbański, Kapuściński and Wojciechowski [41] prepared the complex mercuric salt by the action of mercuric nitrate on an aqueous solution of nitroguanidine and examined its explosive properties. Nitroguanidine does not form salts with other metals. Later on Wright *et al.* [42, 43] once more expressed the opinion that nitroguanidine has the nitroimine structure (II) taking the form of nitramine only when influenced by alkalis. This new structure was based on the fact that unaltered nitroguanidine is precipitated from solution in concentrated alkalis, not a nitroguanidine salt. Similarly according to these authors potentiometric titration of freshly-prepared nitroguanidine solution in alkalis is indicative of a lack of acidic function. This agrees with the well-known observation that metallic vessels containing nitroguanidine do not corrode. Moreover, Wright, Barton and Hall [42] found, that on keeping a nitroguanidine solution for a long time (10–20 hr) in dilute alkalis (0.1 *N* solution of NaOH) under reduced pressure in order to remove volatile by-products, such as ammonia, potentiometric titration demonstrates that the dissolved substance behaves as an acid. According to the authors, this is caused by the conversion of the nitroimine form (II) into the nitramine form (I) under the influence of an alkaline medium. Later Kirkwood and Wright [44] and Kumler and Sah [45] came to the conclusion, on the basis of dipole moment measurements, that nitroguanidine has the structure of a nitroimine or forms a resonance hybrid. This view was also confirmed by de Vries and Gantz [46]. On examining the absorption spectrum in the infra-red, Kumler [47] found that a hydrogen bond occurs in nitroguanidine and in a series of its derivatives:



Nitroguanidine has weakly basic properties and this accounts for its ability to form salts with concentrated acids, e.g. it forms a sulphate with concentrated sulphuric acid. Nitroguanidine is hydrolysed on heating with concentrated sulphuric acid evolving nitrous oxide and carbon dioxide, the former probably derived from hydrolysis of nitramine and the latter from hydrolysis of cyanamide. The latter also yields ammonia on decomposition.



$$\begin{tikzcd} NH_2-\underset{\underset{NH}{\|}}{C}-NHNO_2 \arrow[r] & NH_2NO_2 \arrow[d] & + & NH_2CN \arrow[d, "+2H_2O"] & (19) \\ & N_2O + H_2O & & 2NH_3 + CO_2 & (20) \end{tikzcd}$$

A solution of nitroguanidine in concentrated sulphuric acid also undergoes hydrolysis after standing for some time at room temperature. Then when diluted with water it no longer gives a precipitate of nitroguanidine.

A freshly prepared solution of nitroguanidine in sulphuric acid contains no free nitric acid. but in the presence of substances which are readily nitrated it behaves as if this were so, e.g. the solution nitrates phenol, acetanilide and cinnamic acid and in the presence of mercury reacts in a nitrometer with the evolution of nitric oxide in the same way as nitric acid. Hence in certain cases a solution of nitroguanidine in sulphuric acid may be utilized as a nitrating mixture.

One explanation is that in the presence of these substances nitramine is hydrolysed to form nitric acid [48].

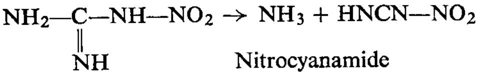
$$NH_2NO_2 + H_2O \rightarrow NH_3 + HNO_3 \qquad (21)$$

Another, more recent explanation, ascribes to nitroguanidine the ability to liberate the $NO_2^{\oplus}$ ion under the influence of sulphuric acid [48].

The decomposition of nitroguanidine by the action of ammonia in aqueous solution also proceeds according to equations (19) and (20).

Barton, Hall and Wright [42] found that the action of alkalis on nitroguanidine involves hydrolysis with the formation of ammonia, nitrourea and the products of the decomposition of nitrourea.

Nitroguanidine demonstrates high stability in aqueous solution on boiling, but on long-continued boiling evolves small amounts of ammonia, possibly due to decomposition according to equation (22):

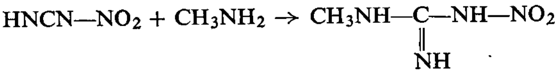


$$\mathrm{NH_2{-}\underset{\underset{NH}{\|}}{C}{-}NH{-}NO_2 \rightarrow NH_3 + \underset{\text{Nitrocyanamide}}{HNCN{-}NO_2}} \tag{22}$$

The ammonia so formed causes the decomposition of the nitramine that results from reaction (19).

According to equation (19) decomposition also occurs on boiling nitroguanidine in an aqueous solution of ammonium carbonate, with liberation of nitrous oxide and ammonia. The latter combines with the cyanamide also resulting from reaction (19) and guanidine carbonate is formed in almost quantitative yield.

In the presence of primary aliphatic amines in aqueous solution nitroguanidine undergoes decomposition according to equation (22). Ammonia is then evolved, and nitrocyanamide combines with the amine to form alkylnitroguanidine, e.g. N-methyl-N′-nitroguanidine:

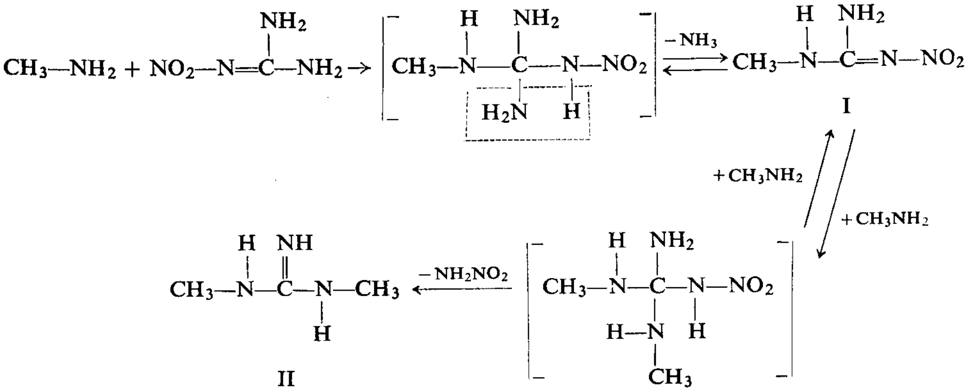


$$\mathrm{HNCN{-}NO_2 + CH_3NH_2 \rightarrow CH_3NH{-}\underset{\underset{NH}{\|}}{C}{-}NH{-}NO_2} \tag{23}$$

Wright and McKay [49] suggest a different reaction mechanism for the N-methyl-N′-nitroguanidine: in the first stage it involves the addition of methylamine to the nitroimine form of nitroguanidine, and this is followed by the liberation of ammonia and the formation of methylnitroguanidine (I).

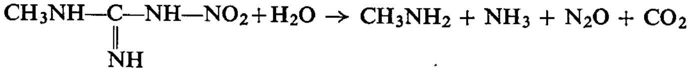
Methylnitroguanidine so produced (I) is capable of further reaction with methylamine to yield dimethylguanidine (II).

These reactions may be characterized by the following mechanism (Wright [50]):



Dimethylguanidine is formed by the liberation of nitramine. The process is irreversible.

The structure of this substance was proved by the facility with which it can be hydrolysed to amine and nitrous oxide (24):



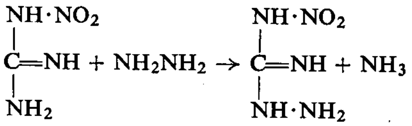
$$CH_3NH-\underset{\underset{NH}{\|}}{C}-NH-NO_2+H_2O \rightarrow CH_3NH_2+NH_3+N_2O+CO_2 \qquad (24)$$

The reaction (24) indicates that the alkyl and nitro groups in N-alkyl-N′-nitroguanidine are linked with different nitrogen atoms.

The same N-alkyl-N′-nitroguanidines are obtainable by the nitration of alkylguanidines (Davis and Elderfield [51]).

With diamines such as ethylenediamine, addition to nitroguanidine leads only to the evolution of ammonia, so that the course of reaction is somewhat different. This will be considered later.

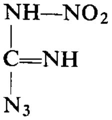
When heated with an aqueous solution of hydrazine (reaction (25)) nitroguanidine yields N-amino-N′-nitroguanidine (II) (Philips and Williams [52]), a white, crystalline substance of marked explosive properties, m.p. 182°C:



$$\underset{\text{I}}{\begin{array}{l} NH\cdot NO_2 \\ | \\ C{=}NH \\ | \\ NH_2 \end{array}} + NH_2NH_2 \rightarrow \underset{\text{II}}{\begin{array}{l} NH\cdot NO_2 \\ | \\ C{=}NH \\ | \\ NH\cdot NH_2 \end{array}} + NH_3 \qquad (25)$$

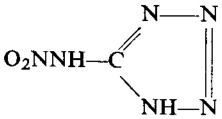
I II

The substance (II) is converted by the action of nitrous acid into nitroguanyl azide (IIa) at 0°C or into nitraminotetrazole (IIb) (Lieber *et al.* [53]) at 70°C. Both substances are explosive:



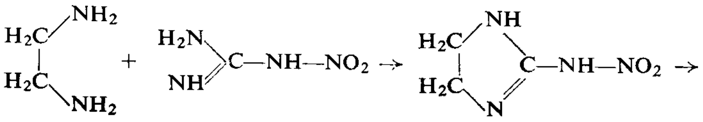
$$\begin{array}{l} NH-NO_2 \\ | \\ C{=}NH \\ | \\ N_3 \end{array}$$

IIa

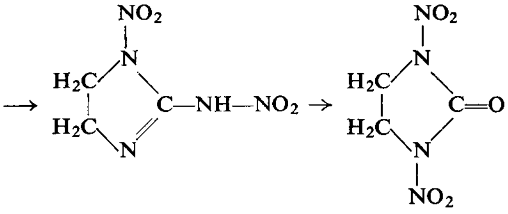


IIb

Under the influence of diamines, such as ethylenediamine, nitroguanidine yields cyclic compounds of type III with evolution of ammonia; they are liable to the further nitration through type (IV) up to cyclic nitramides of type (V) (McKay and Wright [54]).



III



IV V

On reduction, nitroguanidine is converted first into nitrosoguanidine and then into aminoguanidine i.e. guanylhydrazine. The latter is used for the manufacture of tetrazene (p. 206), and in organic chemistry to form crystalline derivatives from aldehydes and ketones, just as semicarbazide forms semicarbazones.

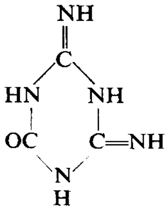
Nitroguanidine and nitrosoguanidine both give a blue colour with diphenylamine in concentrated sulphuric acid and both give the characteristic reactions described below:

(1) To an approximately 25% solution of nitroguanidine in cold water some drops of saturated ferric ammonium sulphate solution are added, then a 24% solution of NaOH. The filtered solution has a red colour resembling that of fuchsine.

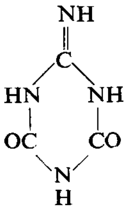
(2) Nitroguanidine is dissolved in acetic acid, diluted to approximately 10%, treated with zinc dust in the cold, set aside for thirteen to nineteen minutes and filtered; 6% cupric sulphate solution is then added to the filtrate. The solution turns intensely blue and on boiling, becomes turbid, gives off gas and deposits a precipitate of metallic copper. If silver acetate is added instead of cupric sulphate a precipitate of metallic silver is deposited on boiling.

EXPLOSIVE PROPERTIES

Nitroguanidine decomposes immediately on melting, evolving ammonia and water vapour and forming solid products. According to Davis and Abrams [8], among the products resulting from the decomposition of nitroguanidine the following substances occur: nitrous oxide, cyanamide, melamine (from the polymerization of cyanamide), cyanic acid (from the decomposition of nitrocyanamide), cyanuric acid (from the polymerization of cyanic acid), and ammeline (VI) and ammelide (VII) (from the co-polymerization of cyanic acid and cyanamide). The decomposition of the above substances involves the formation of carbon dioxide, urea, nitrogen, hydrogen cyanide, cyanogen and compounds not yet fully defined, such as melam, melem, and mellon probably containing condensed triazine rings.



VI



VII

At a temperature below the melting point nitroguanidine is said to be relatively stable—more so than nitric esters and similar in stability to aromatic nitro compounds.

Attention has been paid to nitroguanidine as an explosive since Vieille [28] found that the gases from the decomposition of nitroguanidine are less erosive than those from the decomposition of other explosives of comparable power (Table 4).

TABLE 4

EXPLOSIVE PROPERTIES OF SUBSTANCES CONTAINING NITROGUANIDINE

Substance	Charge g	Pressure, kg/cm^2	Erosion per g	Specific pressure f m
Nitroguanidine	3.90	2020	2.3	9000
Explosive gelatine	3.35	2460	31.4	10,000
Ballistite with addition of 57% nitroglycerine	3.55	2450	24.3	10,000
Nitrocellulose rifle propellant B_7	3.55	2240	6.4	9600

Vieille expressed the opinion that nitroguanidine is less erosive than other explosives of the same power due to its low temperature of explosion. On the basis of experiments with a manometric bomb Patart [55] calculated the following data for nitroguanidine as an explosive:

temperature of explosion	907°C
covolume	1.60
specific pressure f	7140 m

Such a low temperature of explosion was very surprising and the author appears to have been in doubt as to its validity. Indeed, Muraour and Aunis [56] have shown that the temperature of explosion of nitroguanidine may, in fact, be much higher. They pointed out that nitroguanidine ignites with difficulty and undergoes incomplete explosive decomposition. That is why the explosion temperature, as reported by Patart, is so low.

Taking into account the results of experiments conducted with a manometric bomb as well as the chemical composition and specific heat of the products of decomposition Muraour and Aunis calculated the following values for the explosion of nitroguanidine:

temperature of explosion	2098°C
covolume	1.077
specific pressure f	9660 m

Urbański and Kapuściński [57] found the following values for the explosive properties of nitroguanidine (Tables 5 and 6).

TABLE 5

EFFECT OF THE COMPRESSION ON THE DENSITY OF NITROGUANIDINE

Pressure kg/cm^2	Density of loading
220	1.18
345	1.28
695	1.40
1040	1.48
1385	1.52
1730	1.57
2080	1.61
2775	1.65
3465	1.69
4160	1.71
4855	1.75

TABLE 6

RATE OF DETONATION OF NITROGUANIDINE

Density of loading	Rate of detonation in an iron pipe 27/34 mm dia.
0.80	4695
0.95	5520
1.05	6150
1.10	6440
1.20	6775
1.30	6195
1.40	3300
1.45	2640
—	—
—	—
—	—

Cook [58] reports the rate of detonation to be 5460 m/sec at a density of 1.0.

Nitroguanidine may be regarded as an explosive which is powerful, but difficult to detonate. This accounts for the considerable fall in the rate of detonation under increased density of loading. The diameter of loading also exerts a great influence on the rate of detonation, behaviour which is also characteristic of explosives which detonate with difficulty. An explosive of density 0.95 in a pipe of 20 mm inner diameter gave a rate of detonation of 4340 m/sec.

According to T. Urbański, Kapuściński and Wojciechowski [41] the silver and mercuric complex salts of nitroguanidine are more sensitive to impact than nitroguanidine itself, e.g., a weight of more than 10 kg must fall 100 cm to explode nitroguanidine, but the mercuric salt detonates when struck by a 10 kg weight falling only 12.5 cm.

THE PREPARATION OF NITROGUANIDINE

Bourjol [59] reviewed various methods of preparing nitroguanidine from guanidine nitrate and sulphuric acid, and also carried out extensive experiments to find the most convenient laboratory method of carrying out the reaction.

The main features of the reaction, according to Bourjol are:

(1) The rate of reaction depends on the ratio $H_2SO_4 : (H_2SO_4+H_2O)$. The higher the ratio the faster the reaction. The rate is considerably reduced when the concentration of sulphuric acid falls to 82% H_2SO_4, and the reaction practically stops at 79–80% H_2SO_4. The concentration at the beginning and the end should be 94–95% and 85–88% respectively.

(2) The rate of reaction depends on the size of the guanidine nitrate crystals. It is strongly advisable to grind the guanidine nitrate before introducing it into the sulphuric acid.

(3) It is advisable to use enough sulphuric acid to dissolve the guanidine nitrate completely.

(4) The temperature during the reaction should be kept below 30°C. On the other hand, too low a temperature may not be advisable as the solubility of guanidine nitrate may be reduced and the reaction may be too slow. It is advisable to maintain a temperature of 20–25°C at the beginning of the reaction and to raise it at the end to 35–40°C, but not higher.

(5) The reaction solution should be diluted to 15% H_2SO_4 keeping the temperature below 30°C to ensure full precipitation of the nitroguanidine. The product should be washed with an aqueous solution of ammonium carbonate and then with water at 15–25°C.

According to Bourjol the yield is 92.8%.

Cave, Krotinger and McCaleb [60] worked out a general method for preparing explosives in the form of fine crystals. It consists of introducing a hot solution into a cold diluting liquid.

In the case of nitroguanidine, a hot aqueous solution was introduced into cold methanol. Still finer and more uniform crystals were prepared by introducing a cold solution in n-butanol into carbon tetrachloride. The results are given in Table 7.

TABLE 7

Solvent	Diluting liquid	Average crystal size μ	Limits of the crystal size μ	Ratio $\frac{\text{(length)}}{\text{(width)}}$
Water	Methanol	55	3–155	30
n-Butanol	Carbon tetra-chloride	1.5	0.2–4.0	11

The method of manufacturing nitroguanidine adopted in Germany during World War II consists of the addition of guanidine nitrate to a nitrator filled with 98% sulphuric acid, while the temperature is maintained below 45°C by cooling. The nitroguanidine sulphate is formed very rapidly and nitroguanidine is then precipitated by introducing the contents of the nitrator into a diluter containing water, the mother liquor and the wash water at 0°C. The suspension of nitroguanidine in 20% sulphuric acid is separated from the latter by centrifuging, washed with water and is centrifuged again to a 25% content of water.

Crude, acidic nitroguanidine is dissolved in a boiling mixture of water and the mother liquor from previous crystallization. To 1 part of nitroguanidine 14–16 parts of solvent are added. The solution is neutralized with ammonia, filtered and chilled by injecting the hot (approximately 100°C) solution into a vessel under reduced pressure: this results in lowering the temperature of the solution to 45°C. A crystalline suspension of the product is formed and separated in a centrifuge. Thus nitroguanidine containing 6% of water is obtained. The mother liquor is returned for re-use.

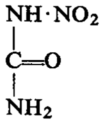
Nitroguanidine occurs in a fine-crystalline form in which it is suitable for the manufacture of flashless propellant. A different form of nitroguanidine is used as a high explosive. When it is to be compressed, its solution is rapidly evaporated under reduced pressure to form a specially fine-crystalline product.

Nitroguanidine intended for use in a fusible mixture with trinitrotoluene takes the form of fairly large, very regular crystals. For this purpose a colloidal substance is added to the nitroguanidine solution, which is allowed to crystallize slowly.

In the method outlined above 136 kg of guanidine nitrate and 300 kg of 98% sulphuric acid are used to produce 100 kg of nitroguanidine.

Another method of nitroguanidine preparation is that of Marqueyrol and Loriette mentioned already [27]. According to Aubertein [61], here nitroguanidine is formed by the following reactions: dicyandiamide is heated with 60% sulphuric acid at 150°C to form guanidine sulphate which however is not isolated. Instead, the reaction mixture is treated directly with a 30% excess of anhydrous nitric acid at 25°C. Nitroguanidine, m.p. 257°C, is prepared in this manner in a 91% yield.

NITROUREA

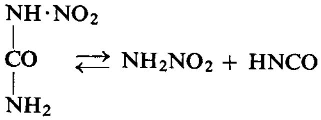


$$\begin{array}{l} NH\cdot NO_2 \\ | \\ C{=}O \\ | \\ NH_2 \end{array}$$

m.p. 159°C (decomp.)

Nitrourea, like nitroguanidine, is prepared by the action of sulphuric acid on urea nitrate. It was recommended as an explosive by Badische Anilin und Soda-Fabrik in 1915 [62] but without success, as it was not sufficiently stable. In the presence of water it decomposes at a little above 60°C with the evolution of nitrous oxide.

Davis and Blanchard [7] found that an aqueous solution of nitrourea or its solution in concentrated sulphuric acid is hydrolysed to nitramine and cyanic acid according to the equation:



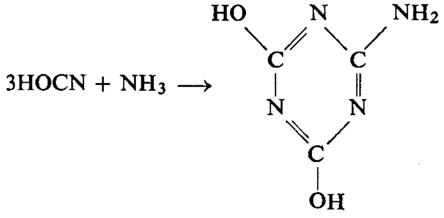
$$\begin{array}{l} NH\cdot NO_2 \\ | \\ CO \\ | \\ NH_2 \end{array} \rightleftarrows NH_2NO_2 + HNCO$$

The reaction is reversible since nitramine in aqueous solution combines with cyanic acid to reform nitrourea. Nitrourea is decomposed by gaseous ammonia, a reaction which, according to Watt and Makosky [63] proceeds as follows:

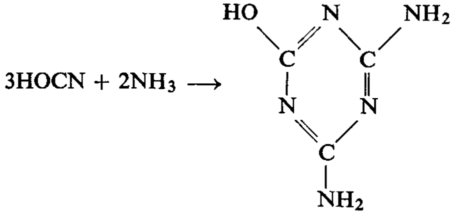
$$H_2NCONHNO_2 \longrightarrow HOCN + N_2O + H_2O + NH_3$$

$$HOCN + NH_3 \longrightarrow NH_4OCN \longrightarrow NH_2CONH_3$$

The cyanic acid can react with ammonia to produce ammelide (I) and ammeline (II):



I



II

In addition, a polymer with the empirical formula $(C_5H_{11}O_5N_7)_n$ is produced.

Reaction with liquid ammonia at —33°C probably proceeds in a manner similar to that described by Davis and Blanchard: it is believed that nitramine (decomposing into N_2O and water) and urea (apparently from cyanic acid and ammonia) are formed.

The action of ammonia on nitrourea does not lead to the formation of nitroguanidine.

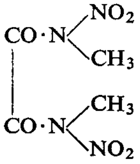
Urbański, Kapuściński and Wojciechowski [41] showed that nitrourea is a more powerful explosive than nitroguanidine. Its lead block expansion is 310 cm³.

As a primary nitramine, nitrourea can form salts. The potassium, silver, mercuric (Thiele and Lachman [64]) and ammonium (Hantzsch and Wiegner [65]) salts are described in the literature.

T. Urbański *et al.* [41] found that the silver and mercuric salts are much more sensitive to impact than nitrourea itself, but have no initiating properties.

OTHER ALIPHATIC NITRAMINES

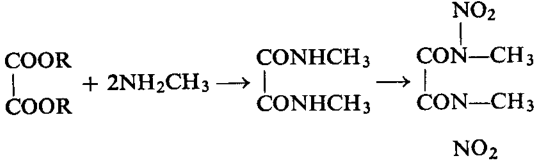
DINITRODIMETHYLOXAMIDE (MNO)



$$\begin{array}{l} CO\cdot N(NO_2)CH_3 \\ | \\ CO\cdot N(CH_3)NO_2 \end{array}$$

m.p. 124°C

This substance was prepared by Franchimont [66] by the action of anhydrous nitric acid on N-dimethyloxamide. The latter is obtained readily by the interaction of methylamine with methyl or ethyl oxalate:



$$\begin{array}{l}\mathrm{COOR}\\ |\\ \mathrm{COOR}\end{array} + 2\mathrm{NH_2CH_3} \longrightarrow \begin{array}{l}\mathrm{CONHCH_3}\\ |\\ \mathrm{CONHCH_3}\end{array} \longrightarrow \begin{array}{l}\mathrm{CO\overset{NO_2}{N}{-}CH_3}\\ |\\ \mathrm{CO\underset{NO_2}{N}{-}CH_3}\end{array}$$

The product of nitration of dimethyloxamide is soluble in nitric acid and is separated by pouring the solution into water. It decomposes on treatment with concentrated sulphuric acid or on boiling with aqueous ammonia or barium hydroxide solution, forming the corresponding methylnitramine salt. Similarly, long-continued boiling in water results in complete decomposition, with the formation of oxalic acid and methylnitramine.

In spite of being hydrolysed so readily its chemical stability is exceptionally high. Haid, Becker and Dittmar [67] report that dinitrodimethyloxamide, like trinitrotoluene, tetryl and penthrite, does not evolve oxides of nitrogen on being heated at 100°C for 30 days.

T. Urbański [68] found the substance to be only slightly sensitive to impact: it does not explode under the impact of a 5 kg weight falling 90 cm. The rate of detonation of dinitrodimethyloxamide was determined by T. Urbański in a tin plate tube 21 mm dia.:

density 0.87	6500 m/sec
density 1.22	6440 m/sec
density 1.33	7130 m/sec

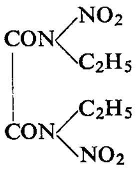
The lead block expansion was 370 cm^3.

T. Urbański examined the possibility of mixing this substance with penthrite (PETN) and picric acid to lower the melting points of these explosives.

Dinitrodimethyloxamide forms eutectic mixtures with penthrite and picric acid, as follows:

with 37% penthrite	m.p. 100.5°C
with 45% picric acid	m.p. 78.6°C

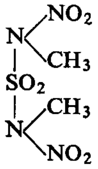
DINITRODIETHYLOXAMIDE



m.p. 34–35°C

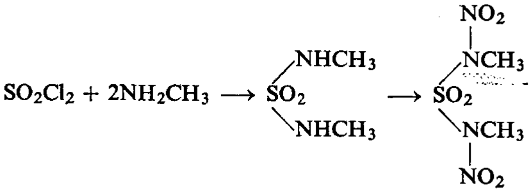
In general this substance has the same chemical properties as its dimethyl homologue, described above. It is a weaker explosive than the dimethyl derivative and shows only slight sensitiveness to impact (less than trinitrotoluene). It gives a lead block expansion of 220 cm^3.

DINITRODIMETHYLSULPHAMIDE



m.p. 90°C

This substance was prepared by Franchimont [69] from dimethylsulphamide obtained by the interaction of methylamine and sulphuryl chloride:

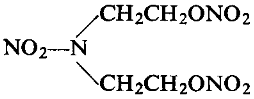


The nitration is carried out with a large excess of anhydrous nitric acid (10 parts of acid to 1 part of sulphamide). The product is precipitated by pouring the nitric acid solution into water.

It dissolves with difficulty in water, moderately well in chloroform and benzene, and readily in hot alcohol. Its ignition temperature is 160°C.

It is a very powerful explosive, as reported by Naoúm and Meyer [70]. It gives a lead block expansion of 395 cm^3, i.e. similar to that of tetryl, but has the disadvantage of being highly sensitive to impact.

NITRODIETHANOLAMINE DINITRATE (DINA)



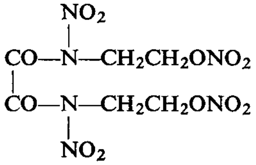
m.p. 49.5–51.5°C

In the inter-war period a certain interest was taken in the nitric esters of amino and amido alcohols. The simplest of these was the product of nitration of diethanolamine, i.e. nitrodiethanolamine dinitrate.

The method of preparation was described by Wright, Chute, Herring and Toombs [71]. They treated diethanolamine with a mixture of nitric acid and acetic anhydride in the presence of hydrogen chloride as a catalyst. Instead of hydrogen chloride, its salts such as zinc chloride may be used. The yield amounts to 90%, but is much lower without a catalyst.

The substance is a very powerful explosive, similar to nitroglycerine in this respect. It is capable of gelatinizing nitrocellulose and hence can be used instead of nitroglycerine in propellants.

DINITRODI-(β-HYDROXYETHYL)-OXAMIDE DINITRATE (NENO)

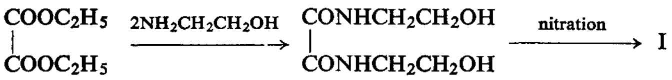


$$\begin{array}{l} \qquad\;\; NO_2 \\ \qquad\quad | \\ CO-N-CH_2CH_2ONO_2 \\ | \\ CO-N-CH_2CH_2ONO_2 \\ \qquad\quad | \\ \qquad\;\; NO_2 \end{array}$$

m.p. 88°C

I

This substance was prepared by Herz [72] who recommended it as an explosive. It is obtainable from oxalic ester by the following reactions:



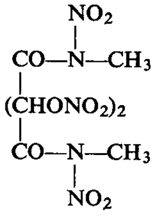
$$\begin{array}{l} COOC_2H_5 \\ | \\ COOC_2H_5 \end{array} \xrightarrow{2NH_2CH_2CH_2OH} \begin{array}{l} CONHCH_2CH_2OH \\ | \\ CONHCH_2CH_2OH \end{array} \xrightarrow{\text{nitration}} I$$

In explosive power, it occupies an intermediate position between penthrite and tetryl. Its lead block expansion is 450 cm³.

According to Domański and Mieszkis [73] the rate of detonation, at a density of loading of 0.93 in a paper tube 10 mm dia., is 5200 m/sec (under the same conditions the rate of detonation of penthrite was approximately 6000 m/sec). Cook [58] found the rate of detonation to be 5530 m/sec at a density of loading of 1.0. The substance is similar to tetryl in sensitiveness to impact. Its chemical stability is slightly less than that of tetryl. Its ignition temperature ranges from 165 to 170°C.

In spite of many advantages, this substance has not achieved practical application due to its high cost.

DINITRODIMETHYLDIAMIDE OF TARTARIC DINITRATE



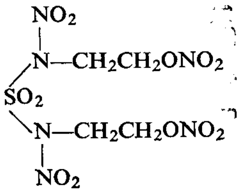
$$\begin{array}{l} \qquad\;\; NO_2 \\ \qquad\quad | \\ CO-N-CH_3 \\ | \\ (CHONO_2)_2 \\ | \\ CO-N-CH_3 \\ \qquad\quad | \\ \qquad\;\; NO_2 \end{array}$$

m.p. 114°C (decomp.)

T. Urbański [74] prepared this substance by the nitration of the dinitrodimethyldiamide of tartaric acid with a mixture of nitric acid and acetic anhydride at a temperature below —2°C. It is capable of gelatinizing nitrocellulose.

It is a very powerful explosive (the rate of detonation at a density of 0.80 in a cartridge 10 mm dia. is 4060 m/sec, and the lead block expansion is 390 cm³) but it is not sufficiently stable since its ignition temperature is only slightly above its melting point. It is also very sensitive to impact—like nitroglycerine.

DINITRODI-(β-HYDROXYETHYL)-SULPHAMIDE DINITRATE



Herz [72] described the preparation of this substance by the action of ethanolamine on sulphuryl chloride, followed by the nitration of the dihydroxyethylsulphamide so obtained.

In explosive properties and explosive power it is similar to dinitrodi-(β-hydroxyethyl)-oxamide, described above.

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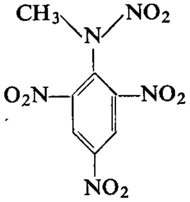
CHAPTER III

AROMATIC NITRAMINES

TETRYL

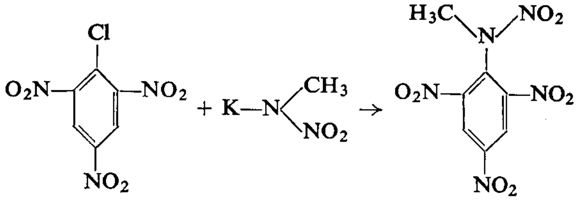
THE key representative of aromatic nitramines is the trinitro derivative of phenylmethylnitramine—tetryl. This is 2,4,6-trinitrophenylmethylnitramine or picrylmethylnitramine or N-2,4,6-tetranitro-N-methylaniline.



Tetryl is a widely-used explosive. It is also known under the names of Pyronite, Tetrylit, Tetralite, Tetralita. In England it has been known for some time as Composition Exploding—CE. The incorrect name—tetranitromethylaniline—may sometimes be encountered in the literature.

Tetryl, known since 1877, has been used as an explosive since 1906. During World War I because of its explosive power and sensitiveness to initiation it was employed in the filling of blasting caps and as a "priming" to fill detonating gains (boosters). It is still used for the same purpose, although to a much lesser extent since the introduction of PETN and cyclonite. During World War II tetryl was also utilized as a component of high explosive mixtures.

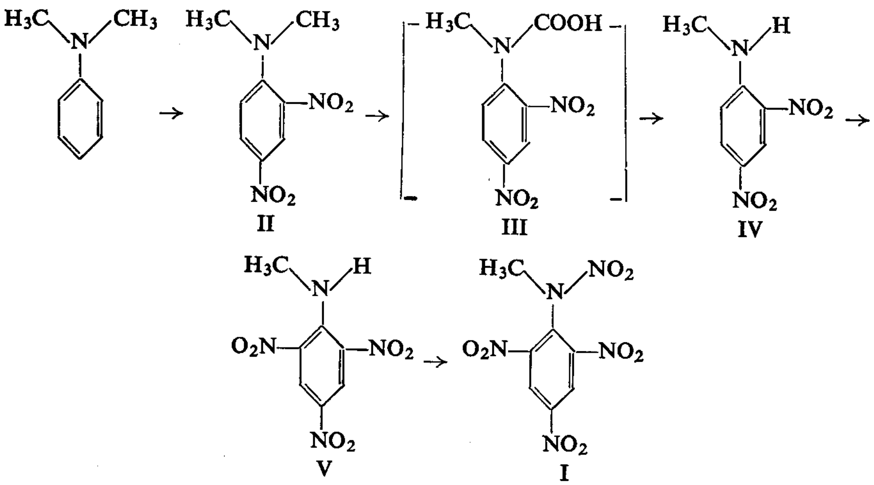
Mertens [1] was the first to obtain tetryl in 1877 by the action of fuming nitric acid on a dimethylaniline solution in sulphuric acid or by boiling a dinitrodimethylaniline solution in fuming nitric acid. Soon afterwards Michler *et al.* [2] prepared it by the action of fuming nitric acid on quaternary dimethylaniline salts. Neither of these authors gave the correct structure of the product. Romburgh [3] later explained more precisely the conditions of tetryl formation from methyl- and dimethylaniline. He also postulated and then proved its structure by synthesizing it from potassium methylnitramine and picryl chloride:



NITRATION OF DIMETHYLANILINE

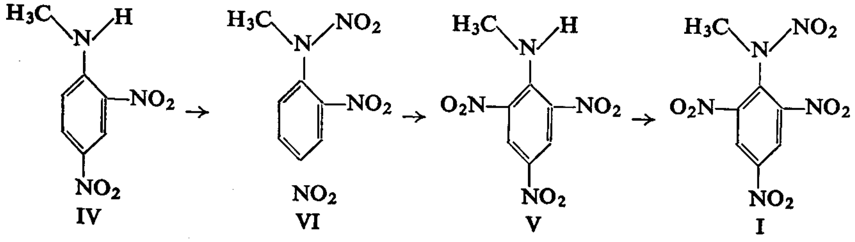
Nitration of dimethylaniline results in the oxidation of one of the methyl groups to the carboxyl group which is not strongly linked to nitrogen and is readily split off as carbon dioxide. Thus, as the nitration of dimethylaniline proceeds, gases consisting of NO and NO_2 (from the reduction of nitric acid) and of CO_2 (from the oxidized N-methyl group) are evolved abundantly.

The reaction mechanism was originally represented as follows:



Indeed, all the above indicated intermediates with the exception of the hypothetical product (III) have been isolated from the reaction mass.

The more recent work of Clarkson, Holden and Malkin [4] shows, however, that the reaction proceeds somewhat differently. In fact, the dinitroderivative (II) which undergoes demethylation to the substance (IV) is formed first, and then the nitramine (VI) is isomerized (p. 5) to the trinitro derivative (V), before the latter is nitrated to tetryl:



The last step (V) to (I) is reversible: if tetryl is dissolved in concentrated sulphuric acid and allowed to stand the N-nitro group is expelled and trinitromethylaniline (V) is formed (cf. p. 5).

The empirical equation for the preparation of tetryl from dimethylaniline is as follows:

$$C_6H_5(CH_3)_2 + 10HNO_3 \rightarrow C_6H_2(NO_2)_3N(NO_2)CH_3 + 6NO_2 + CO_2 + 8H_2O$$

Hodgson and Turner [5] examined the action of various concentrations of nitric acid alone on dimethylaniline, by nitrating 5 g test specimens of the latter on a laboratory-scale.

They prepared tetryl by treating dimethylaniline with a 20-fold volume of nitric acid, s.g. 1.52 at —5 to 0°C.

They also obtained a lower-nitrated product by employing nitric acid, s.g. 1.42 at 0°C. Later authors (Clarkson, Holden and Malkin [4]) found that this product was N-2,4-trinitroethylaniline. At room temperature the reaction proceeds violently and decomposition with a tendency to explosion readily occurs in the nitrator. Nitric acid of lower concentrations, s.g. 1.34 and 1.254, gives 2,4-dimethylaniline at 0°C in quantitative yield. At a higher temperature they obtained a mixture of this compound with 2,4-dinitromethylaniline.

The oxidizing action of nitric acid predominates when a still lower concentration is used—specific gravity 1.12. In this case, originally described by Mertens [6] (who suggested a wrong structure) and fully described by Romburgh [7] 3,3′,5,5′-tetranitrotetramethylbenzidine is formed as well as 2,4-dinitrodimethylaniline. Nitric acid, s.g. 1.024 does not react with dimethylaniline, but in the presence of nitric oxides, or $NaNO_2$, leads to the formation of *p*-nitrosodimethylaniline.

Recently, T. Urbański and Semeńczuk [8] made it clear that tetryl may be safely prepared by nitrating dimethylaniline with nitric acid, s.g. 1.40. Essential safety precautions for the procedure are:

(1) The use of a large excess of nitric acid

$$\left(\frac{\text{nitric acid}}{\text{dimethylaniline}} = ca.\ 40 \text{ by weight}\right)$$

(2) The conduct of the reaction in two stages.

In the first stage dimethylaniline is dissolved in nitric acid, the temperature not being allowed to exceed 7°C. It is then gradually raised to 80°C. When the vigorous reaction has subsided, the mixture is heated at 90°C.

On cooling, the solution deposits crystals of tetryl. To obtain complete precipitation of the product, water may be added to the solution. The yield of tetryl is 78%.

The reaction can also be carried out by dissolving dimethylaniline first in an excess of nitric acid, s.g. 1.40 (e.g. in the weight ratio of nitric acid to dimethylaniline of approximately 15 : 1) then adding excess nitric acid, s.g. 1.50 to this solution, until the final weight ratio is approximately 25 : 1, finally proceeding as above. In this way tetryl, m.p. 129.5°C is obtained in approximately 83% yield.

This method is suitable for continuous operation in a series of small nitrators. A higher temperature is maintained in each successive nitrator, e.g. from 5 to 90°C. By thus dividing production among a large number of reactors, an acceptable degree of safety is achieved.

T. Urbański and Semeńczuk found that tetryl prepared with nitric acid alone is of high purity, possibly because it is not contaminated with 2,4,6-trinitro-N-methylaniline formed from tetryl as a result of the loss of the N-nitro group on heating with sulphuric acid, present in an ordinary nitrating mixture.

Developing their method further, Semeńczuk and T. Urbański [9] devised a way of nitrating dimethylaniline with nitric acid alone in the presence of an organic solvent inert to nitric acid. This has two advantages: by diluting nitric acid with a solvent, the course of the reaction is moderated; and by using a relatively low-boiling solvent, e.g. chloroform, a "thermostatic" medium is created, the upper temperature of which is limited by the boiling point of the solvent.

As early as 1938, Shorygin and Topchiyev [10] nitrated dimethylaniline with a solution of nitrogen dioxide in chloroform, but they were only able to obtain 4-nitrodimethylaniline with a small amount of 3-nitrodimethylaniline. No demethylation of the N-dimethylamino group occurred.

Semeńczuk and T. Urbański found that the following solvents may be used: dichloromethane, chloroform, carbon tetrachloride and tetrachloroethane. Their nitration method consisted of introducing a solution of dimethylaniline into fuming nitric acid diluted with the same solvent, maintaining a temperature of approximately 5°C. The mixture was then warmed cautiously to 40°C. On approaching this temperature, strong evolution of nitrogen dioxide occurred and the temperature rose. When chloroform or dichloromethane was used, the solvent distilled off at 61°C. The remaining solution, free from solvent, was warmed to 80°C until a light orange colour was established. When the reaction was complete, water was added to precipitate tetryl. The yield was high, 98% of theoretical and the purity of the product was very satisfactory, m.p. 129°C. When carbon tetrachloride was used, it was removed either by decantation or by distillation at about 77°C. Higher boiling solvents such as tetrachlorethane should be removed only by decantation, after which the acid layer should be diluted with water as described above.

Semeńczuk and T. Urbański also showed that dimethylaniline may be nitrated to tetryl by a mixture of nitric acid with acetic acid or acetic anhydride. As yet the only other results mentioned in the literature with reference to this method are those of Orton [11]. He asserted that dimethylaniline gives no N-nitro derivative when reacted with a mixture of nitric acid with acetic anhydride or acetic acid; he obtained only 2,4-dinitromethylaniline.

Semeńczuk and T. Urbański employed various proportions of nitric acid, s.g. 1.50, to acetic anhydride or acetic acid. The best results were obtained when the volume ratio was used

$$\frac{\text{nitric acid}}{\text{acetic anhydride or acetic acid}} = \frac{50}{50}$$

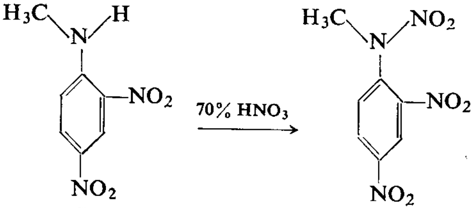
The spontaneous reaction which occurred after introducing dimethylaniline into the nitrating mixture caused the temperature to rise to about 40°C. After the reaction subsided, it was necessary to warm the reaction mixture and to keep it at 80°C until the reaction was complete.

Water was added to the cooled reaction solution and pure N-2,4,6-tetranitromethylaniline precipitated. The yield was 90% of theoretical.

Thus, Orton's statement should be limited to the specific experimental conditions which he himself used.

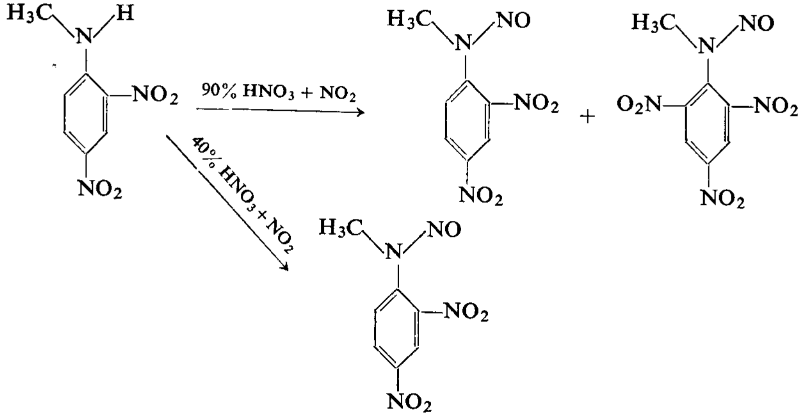
NITRATION OF DINITROMETHYLANILINE

The conditions of nitration of dinitromethylaniline with nitric acid were recently studied by Lang [12]. He explained that in order to introduce the N-nitro group it is necessary to use nitric acid with a concentration of more than 70%. The nitration then proceeds as follows:



IV VI

In the presence of nitrogen dioxide, the reaction proceeds differently, and the N-nitroso derivative is formed. When 99% nitric acid is used together with NO_2, a mixture of di- and trinitro nitroso derivative is produced, while 40% nitric acid gives only a dinitro derivative



The nitration of 2,4-dinitromethylaniline to tetryl with nitric acid alone was also studied by Issoire and Burlet [13]. These authors found that nitration may be carried out by means of nitric acid, s.g. 1.44 (75% concentration) and over. When using nitric acid, s.g. 1.44–1.46 (75–80% concentrations) the temperature of nitration should be maintained above 70°C. The final temperature may be lower if the final concentration of acid in the nitrator is higher than 85%. For instance when using 95% nitric acid (s.g. 1.50) in such quantity that by the end of nitration the concentration is less then 85%, it is sufficent to maintain a temperature of 50°C during that latter period.

The authors obtained a quantitative precipitation of tetryl by diluting the contents of the nitrator to a 50–55% concentration of HNO_3. Tetryl is practically insoluble in such dilute acid hence the precipitation is quantitative.

Tetryl prepared in this way was contaminated by the following substances:

(1) chlorodinitrobenzene occurring in dinitromethylaniline obtained by the action of methylamine on chlorodinitrobenzene;

(2) 2,6-dinitromethylaniline which also contaminates technical dinitromethylaniline.

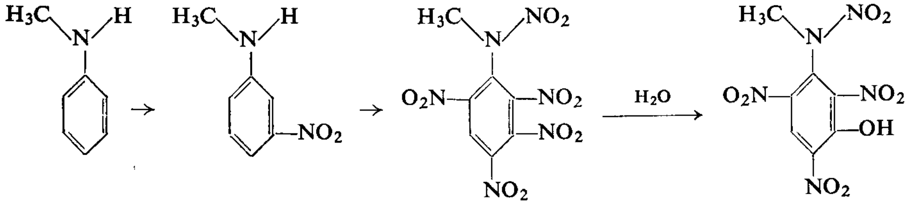
Issoire and Burlet found that 2,6-dinitromethylaniline is nitrated with much greater difficulty than the 2,4-isomer. To obtain tetryl from the 2,6-isomer, nitration should be carried out with nitric acid, s.g. 1.50, i.e. a concentration higher than 95%.

The evolution of heat resulting from the introduction of the nitro group into methylaniline was calculated by Garner and Abernethy [14] as follows. On transition of:

methylaniline to *p*-nitromethylaniline 36.4 kcal/mole,
p-nitromethylaniline to 2,4-dinitromethylaniline 25.2 kcal/mole,
2,4-dinitromethylaniline to 2,4,6-trinitromethylaniline 11.9 kcal/mole,
2,4,6-trinitromethylaniline to tetryl 1.0 kcal/mole.

By-products formed during the preparation of tetryl

Apart from tetryl a number of other substances may be found in the products of the reaction. One of them is 2,3,4,6-tetranitrophenylmethylnitramine, *m*-nitrotetryl (VII). This compound was originally reported by Romburgh [15] as accompanying tetryl. Romburgh originally thought that *m*-nitrotoluene is particularly readily formed when tetryl is prepared from methylaniline, due to the fact that the nitro group is directed to the *meta* position by the methylamino group:



VII

VIII

A nitro group at the *meta* position is readily hydrolysed in water to the phenolic group with the formation of the nitro derivative of N-methyl-*m*-aminophenol (VIII). Since technical dimethylaniline usually contains a certain amount of methylaniline, its nitration product always contains a small quantity of the product (VII). This substance may be removed by boiling in water in order to hydrolyse it to the compound (VIII).

Later Romburgh and Schepers [16] explained that the substance (VII) is also formed from dimethylaniline if nitration is carried out in the presence of a large excess of sulphuric acid (20-fold with respect to dimethylaniline). It is evident that the presence of this substance is undesirable owing to the poor stability of the nitro group in the *meta* position and to the formation of metal salts of the substance (VIII) which are sensitive to impact.

According to Desvergnes [17] methylaniline does not form *m*-nitrotetryl when nitrated first with dilute acids and then with more concentrated ones.

Recently, Bogdał and D. Smoleński [18] made an extensive investigation of the conditions of formation of *m*-nitrotetryl. Contrary to the previous work of Romburgh [15] they found that *m*-nitrotetryl was formed in larger quantity when dimethylaniline was nitrated. Methylaniline yielded a smaller amount of *m*-nitrotetryl under identical nitration conditions.

According to these authors the following conditions lead to the formation of *m*-nitrotetryl:

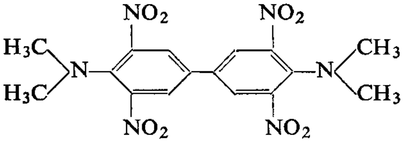
(1) If nitrating mixtures (nitric and sulphuric acids) are used for nitrating dimethyl- and methylaniline dissolved in sulphuric acid, the percentage of *m*-nitrotetryl is higher than when nitrating with nitric acid alone: the figures observed were 39 and 16% respectively.

(2) As the concentration of nitrating mixture falls, the percentage of *m*-nitrotetryl is considerably reduced, e.g. when the water content is 20–25%, the percentage of *m*-nitrotetryl falls to below 1%. This agrees with Desvergnes [17].

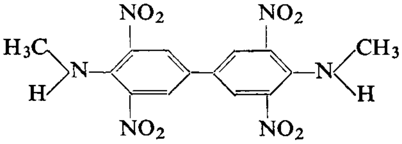
(3) A lower temperature of nitration favours the formation of *m*-nitrotetryl, e.g. when dimethylaniline is nitrated at 65 and 0°C the corresponding percentages of *m*-nitrotetryl are 11 and 30%, respectively.

Bogdał and Smoleński [18] also found that the nitration of methylaniline with less concentrated nitration mixtures readily led to formation of oxidation products.

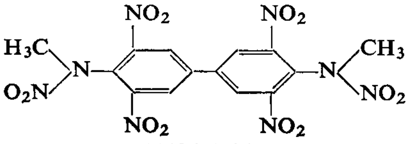
The other substances which are formed apart from tetryl are the benzidine derivatives (IX), (X), and (XI).



IX, decomposition at 272°C



X, decomposition above 200°C



XI, m.p. 222°C (with decomp.)

These substances are insoluble in benzene and hence easily removable from tetryl by crystallization in this solvent. They are fine-crystalline products of a yellowish colour. They increase with the amount of water contained in the nitrating acid. Michler and Pattison [19] proved that N-tetramethylbenzidine is formed by heating dimethylaniline with sulphuric acid.

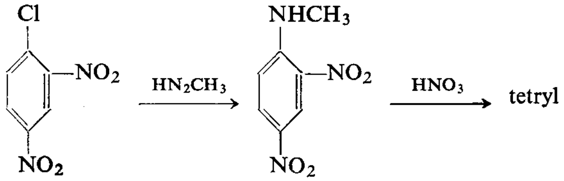
The same reaction undoubtedly occurs when dimethylaniline is nitrated. Mertens [6] isolated all three substances from the reaction of nitric acid with dimethylaniline and the substances (X) and (XI) by the treatment of methylaniline with nitric acid. Van Romburgh [7, 20] elucidated the structure of these compounds, in particular the position of nitro groups.

The presence of undesirable impurities such as *m*-nitrotetryl and substances which are insoluble in benzene necessitates fairly laborious purification of tetryl. The by-products are formed at the very beginning of the nitration process, before the formation of dinitrodimethylaniline (II). Nitration of highly pure dinitrodimethylaniline yields tetryl containing no such impurities.

GENERAL RULES FOR THE PREPARATION OF TETRYL

In technical operations dimethylaniline is employed as a starting material chiefly because it is obtainable more easily and is much cheaper than methylaniline. Moreover, tetryl prepared from dimethylaniline is purer than that from methylaniline. Hence the preparation of tetryl from dimethylaniline is more economic, in spite of the greater consumption of nitric acid by dimethylaniline which uses up nitric acid to oxidize one of the N-methyl groups. The yield is not higher than 80%, due to the side-reactions.

Since methylamine prepared from methyl alohol and ammonia has become available commercially, the preparation of tetryl from dinitromethylaniline obtained from chlorodinitrobenzene and methylamine has been widely used.



IV

The yield of nitration of dinitromethylaniline amounts to 95%, hence this method is the more economic.

Nitration is usually carried out in such a way that the solution of dimethylaniline in sulphuric acid is introduced into a nitrating mixture rich in nitric acid. The nitration reaction proceeds vigorously, and it is therefore most important to control the reaction temperature. Formerly it was believed that for safety's sake the lowest possible temperature of nitration should be maintained. Later it became clear that at such a temperature nitration is not brought to completion and a large quantity of incompletely nitrated products accumulates, which may lead to an accident since at a certain moment these products begin to react, emitting a great amount of heat and so creating the possibility that the contents of the nitrator may explode. Thus, too low a temperature of nitration of dimethylaniline is considered to be unsafe.

The nitration of dimethylaniline is now conducted at 68–72°C, with very vigorous stirring. It is usually carried out by pouring gradually a sulphuric acid solution of dimethylaniline sulphate into the nitrating mixture. Due to the high temperature and vigorous stirring the nitration reaction proceeds at once so that there is no danger of the accumulation of under-nitrated products.

Some of the older factory regulations drew attention to the possibility of resinification of the product when a high nitration temperature was used and therefore recommended maintaining a low temperature, i.e. 30–45°C. It was found, however, that resinification of the product can be avoided by very vigorous stirring at high temperatures and by employing a nitrating mixture fairly rich in nitric acid, e.g. 66.5% HNO_3, 16% H_2SO_4, 17.5% H_2O.

The nitration method described above is particularly suitable for use in a continuous system.

The purification of tetryl aims at removing by-products such as tetranitro derivative (VII), substances insoluble in benzene and the spent acid occluded by the crystals. The product is washed with cold water and then treated with hot water. This brings about the conversion of compound (VII) to (VIII)—the latter is soluble in hot water. The tetryl is then dissolved in benzene and insoluble constituents removed by filtration. The resulting solution is washed with water until it is completely free from acid. Alternatively, tetryl may be dissolved in acetone, precipitated with water, and finally deacidified.

PHYSICAL PROPERTIES

Tetryl crystallizes in the form of crystals which are colourless immediately after preparation and crystallization but which rapidly turn yellow under the influence of diffused light. The technical product is usually pale yellow.

Chemically pure tetryl melts at 129.45°C although for technical purposes a melting point of 128.8 or 128.5°C is acceptable.

Its crystals belong to the monoclinic system. The product used in industrial practice should be crystalline in form and be easily pourable into a mould for compression. According to Davis [21] a product with mixed, i.e. relatively large and small crystals (Fig. 5), is best suited for this purpose.

Such a product may be prepared by various methods, e.g. by mixing a coarse crystalline substance derived from crystallization in benzene with a fine crystalline one obtained by the precipitation of tetryl with water from an acetone solution. Another method (according to Crater [22]) consists of pouring the benzene solution into water heated to above the boiling point of benzene. Alternatively, crystallization from dichlorethane (according to Rinkenbach and Regad [23]) may produce an acceptable form of tetryl.

The specific gravity of the crystals is 1.73, whereas the product, when fused and poured into a mould, solidifies to a mass with a density of 1.62. Under a pressure of 2000 kg/cm^2 a density of 1.71 can be attained.

FIG. 5. Tetryl in a free flowing form, according to Davis [21].

The specific heat of tetryl is as follows (C. A. Taylor and Rinkenbach [24]):

at 0°C	0.213 cal/g°C
at 20°C	0.217 cal/g°C
at 50°C	0.223 cal/g°C
at 80°C	0.228 cal/g°C
at 100°C	0.231 cal/g°C
at 120°C	0.234 cal/g°C

Belayev and Matyushko [25] give 0.225 as the specific heat of tetryl.

Tetryl has a heat of fusion of 20.6 kcal/kg, a heat of combustion of 854.3 kcal/ /mole, hence the calculated heat of formation ΔH_f is +7.5 kcal/mole (Garner and Abernethy [26]) or +23.7 kcal/mole (Kast [27]).

According to Prentiss [28] the thermal conductivity of tetryl at 25°C is 0.00088. Belayev and Matyushko [25] give 0.00023.

Tetryl is virtually insoluble in water. It dissolves moderately well in concentrated mineral acids, but in spent acid its solubility is barely 0.3%. Conversely, concentrated nitric acid is a good solvent for tetryl. When a solution in concentrated nitric acid is diluted slowly with water, for instance by placing it in a moist atmosphere, gradual precipitation of tetryl occurs. Tetryl dissolves very readily in acetone.

Its solubility in benzene varies [29] depending on whether the substance is heated with benzene to a given temperature (A) or the solution, saturated at a high temperature, is cooled to a given temperature (B). The corresponding values are given in Table 7.

TABLE 8

SOLUBILITY OF TETRYL IN BENZENE

Solubility	Temperature °C				
	15	25	35	45	55
(A) Heating in 100 g of benzene	3.9	5.5	7.4	9.7	13.25
(B) Cooling a saturated solution	10.2	12.2	14.9	18.25	22.5

The big difference between the two states of equilibrium is presumably accounted for by the formation of tetryl solvates with benzene at higher temperatures and their greater solubility in benzene.

The solubility of tetryl in other solvents based on the data of various authors, mainly those of C. A. Taylor and Rinkenbach [24] is tabulated below [21]:

TABLE 9

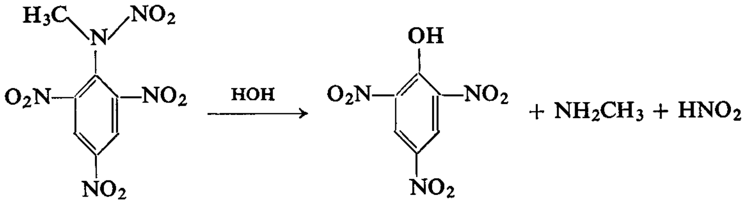
SOLUBILITY OF TETRYL (g IN 100 g OF SOLVENT)

Temperature °C	Water	Alcohol 95%	Carbon tetrachloride	Chloroform	Dichloroethane	Carbon disulphide	Ether
1	2	3	4	5	6	7	8
0	0.0050	0.320	0.007	0.28	1.5	0.0090	0.188
5	0.0058	0.366	0.011	0.33	—	0.0120	0.273
10	0.0065	0.425	0.015	0.39	—	0.0146	0.330
15	0.0072	0.496	0.020	0.47	—	0.0177	0.377
20	0.0075	0.563	0.025	0.57	3.8	0.0208	0.418
25	0.0080	0.65	0.031	0.68	—	0.0244	0.457
30	0.0085	0.76	0.039	0.79	—	0.0296	0.493
35	0.0094	0.91	0.048	0.97	—	0.0392	—
40	0.0110	1.12	0.058	1.20	7.7	0.0557	—
45	0.0140	1.38	0.073	1.47	—	0.0940	—
50	0.0195	1.72	0.095	1.78	—	—	—
55	0.0270	2.13	0.124	2.23	—	—	—
60	0.0350	2.64	0.154	2.65	18.8	—	—
65	0.0440	3.33	0.193	—	—	—	—
70	0.0535	4.23	0.241	—	—	—	—
75	0.0663	5.33	0.237	—	—	—	—
80	0.0810	—	—	—	—	—	—
85	0.0980	—	—	—	—	—	—
90	0.1220	—	—	—	—	—	—
95	0.1518	—	—	—	—	—	—
100	0.1842	—	—	—	—	—	—

CHEMICAL PROPERTIES

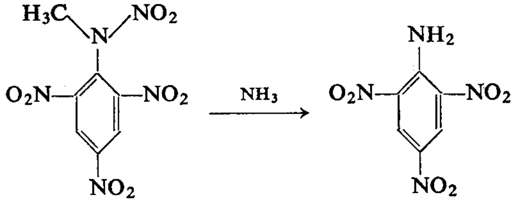
Tetryl is highly resistant to the action of dilute mineral acids. For instance long-continued boiling with dilute sulphuric acid fails to decompose it, whereas in concentrated sulphuric acid the N-nitro group is split off with the formation of trinitromethylaniline (N-methylpicramide) (V) and nitric acid, as shown by Davis and Allen [30] and later confirmed by Lang [12]. This reaction proceeds fairly quickly at elevated temperatures (e.g. 60°C and above) but slowly at room temperature. A solution in sulphuric acid, when brought into contact with mercury, reacts as nitric acid: in the presence of mercury the N-nitro group is reduced to nitric oxide. This enables tetryl to be determined quantitatively in the nitrometer.

When tetryl is boiled with a solution of sodium carbonate or a dilute (e.g. 2%) aqueous solution of potassium or sodium hydroxide, the nitramino group is hydrolysed as follows [3, 6, 31]:

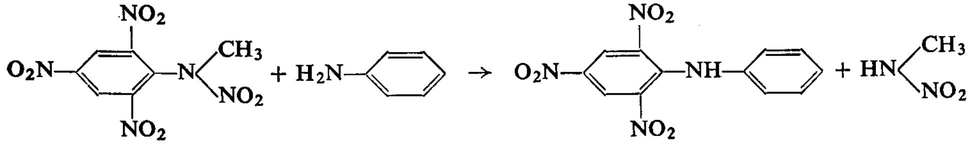


The products obtained are picric acid (in the form of the corresponding picrate), methylamine, and nitrous acid (as nitrite).

On heating with alcoholic ammonia a picramide is formed [3]:



Tetryl combines with aniline in benzene solution even at room temperature to form 2,4,6-trinitrodiphenylamine (XII) and methylnitramine:



XII

m.p. 179.5–180°C

The substance (XII) is precipitated as red crystals, and methylnitramine can be extracted from the solution with water.

The conversion of tetryl into picric acid or methylpicramide (V) may also proceed under milder conditions. Thus Farmer [32] and Desvergnes [33] found that picric acid can be formed simply by heating tetryl for a prolonged period of time, e.g. at 120°C. According to some authors heating in high-boiling solvents (e.g. in xylene) leads to the conversion of tetryl into N-methylpicramide (V) and picric acid, together with resinous products and unidentified crystalline products.

When heated with phenol, tetryl is converted into trinitrophenylmethylamine (V) (Romburgh [7]; cf. p. 5).

With tin and hydrochloric acid, tetryl is reduced and hydrolysed to form 2,4,6-triaminophenol.

Tetryl combines with an excess of sodium sulphide to form a 13% solution. Even at room temperature the nitro groups are reduced with the formation of a non-explosive substance. This reaction is exploited for the destruction of waste tetryl.

Tetryl is reduced at 80–90°C by the action of a 10% sodium sulphite solution to form a non-explosive product. In a similar manner tetryl reacts with sodium thiosulphate to yield yellow-coloured, unidentified products.

Yefremov *et al.* [34] studied systems containing tetryl by thermal analysis and found that it forms additive compounds with phenanthrene, fluorene or retene in the mole ratio 1 : 1 which do not melt uniformly. It also forms an additive compound in the same ratio with naphthalene, m.p. 86.8°C.

According to Yefremov and Khaibashev [35], Giua [36], C. A. Taylor and Rinkenbach [37], tetryl and trinitrotoluene form an additive compound in the ratio of one mole of tetryl to two moles of trinitrotoluene which readily dissociates and melts at 61.1°C (Taylor and Rinkenbach report m.p. of the addition compound as 68°C).

Tetryl also forms an ordinary eutectic mixture with 76.5% trinitro-*m*-xylene, m.p. 118.8°C and with 29.5% trinitroanisole, m.p. 22.8°C [35].

At room temperature tetryl appears to be perfectly stable. At 100–120°C the methylnitramino group of tetryl decomposes slightly giving off a certain amount of formaldehyde and nitrogen oxides. On studying the decomposition of tetryl at 120°C under reduced pressure, Farmer [32] found that in 40 hr 1.5–3.0 cm^3 of gases are evolved. He also examined its decomposition at lower temperatures and found that the temperature coefficient of decomposition is 1.9 $cm^3/5°C$. By extrapolating the curve in the system: decomposition rate–temperature, Farmer calculated that a decomposition lasting 40 hr at 120°C would take 1700 years at 20°C.

Tests lasting for many years have shown that 20 years of storage, at room temperature involve no discernable changes in tetryl, nor was any distinct decomposition of tetryl observed at 65°C after 12 months; at 75°C after 6 months and at 100°C after 100 hr.

The decomposition rate of tetryl increases sharply (approximately 50-fold) at its melting point. If tetryl contains admixtures which lower its melting point, it begins to decompose at a lower temperature corresponding to the melting point of the mixture. For example, addition of TNT to tetryl markedly increases its rate of decomposition at the melting point of the mixture. This is probably due to the more energy rich and less stable liquid state (see Vol. II, p. 182). When studying the decomposition kinetics of pure tetryl or of tetryl containing an admixture of picric acid at 140–150°C, Hinshelwood [38] came to the conclusion that the speeding up of the reaction rate results in the formation of picric acid due to the hydrolysis of tetryl at that temperature. The larger the amount of picric acid so formed, the higher is the decomposition rate of the molten tetryl.

Desvergnes [33] found that when tetryl having a m.p. 128.5°C was heated for 24 hr at 100°C its m.p. was lowered by 0.4°C after 600 hr of heating the m.p. had fallen to 71°C.

On heating tetryl at 120°C at reduced pressure (a few mm Hg) the gas evolved in the early stages of the experiment consisted almost entirely of nitrogen and carbon monoxide.

Towards the end of the test appreciable quantities of carbon dioxide were produced. No nitric oxide was detected at any stage of the experiment.

According to van Duin [39] the ignition temperature of tetryl is 196°C; when it is heated from 100°C at the rate of 20°/min, ignition occurs at 187°C.

T. Urbański and Schuck [40] found that tetryl explodes when dropped onto a heated copper surface:

at 236°C	after 6.2 sec
at 260°C	after 2.0 sec
at 280°C	after 1.1 sec
at 302°C	after 0.4 sec
at 310°C	instantly

According to Farmer [32] the activation energy of the thermal decomposition of tetryl $E=60.0$ kcal and log $B=27.5$. Hinshelwood [38] reports similar values. A. J. B. Robertson [41] found, however, that at higher temperatures (211–260°C) $E=38.0$ kcal and log $B=15.4$. According to Szyc-Lewańska [42] at still higher temperatures (260–300°C) the activation energy is even lower, viz. $E=$ approximately 20.0 kcal (based on the data given above [40]).

Roginskii and Lukin [43] found that tetryl is not liable to explode when heated at 150°C in a sealed ampoule, though at temperatures above 150°C, e.g. between 150 and 170°C, explosion may ensue as result of chain reactions occurring during decomposition on long-continued heating.

EXPLOSIVE PROPERTIES

Lenze [44] was the first to examine the explosive properties of tetryl. It is a more powerful explosive than TNT (its strength, depending on the method of investigation applied, ranges between 110 and 130% of that of TNT). Its sensititiveness to impact and friction, particularly to rifle fire, is higher than that of TNT.

The explosive decomposition of tetryl, like that of other explosives, depends on the method of initiation, density etc. Haid and Schmidt [45] give the following equation for the decomposition of tetryl, at a density of 1.56:

$$C_{24.4}H_{17.4}O_{27.9}N_{17.4} = 5.59CO_2 + 10.85CO + 5.91H_2O + 1.89H_2$$
$$+ 0.03C_mH_n + 0.27CH_4 + 0.6HCN + 0.58C_2N_2 + 7.82N_2 + 5.8C$$

The heat of explosion is 1095 kcal/kg, the volume of gases 750 l./kg, the temperature of explosion 3530°C.

Kast [27] gives similar values: 1090 kcal/kg, 710 l./kg, 3370°C respectively.

According to Carlton Sutton [46], depending on its density tetryl may explode or detonate with widely varying intensity and therefore with different heats of explosion or detonation:

at a density of 0.9 and less	with 935 kcal/kg (explosion)
at a density of 1.1–1.3	with 1070 kcal/kg
at a density of 1.45–1.71	with 1160 kcal/kg (detonation)

The sensitiveness of tetryl to impact, as reported by several authors, may be expressed as 70–80% of the impact energy necessary to cause the explosion of picric acid.

According to a number of authors, the explosive power of tetryl, determined in the lead block, varies between 340 and 390 cm^3, i.e. between 114 and 120% of the value for picric acid.

The rate of detonation of tetryl is reported by various authors as follows:

at a density of 1.0 and 1.53	5450 m/sec and 7215 m/sec respectively (J. Marshall [47])
at a density of 1.0	5600 m/sec (Cook [48])
at a density of 1.43	6425 m/sec (Selle [49])
at a density of 1.63–1.65	7200 m/sec (Kast [27])
at a density of 1.63–1.65	7520 m/sec (R. Robertson [50])
pressed pellets (no density given)	7230 m/sec (Koehler [51])

E. Jones and Mitchell [52] found that under the influence of a standard No. 6 detonator, a charge of tetryl at a loading density of 0.94 and 25 mm dia. initially detonates at a low rate which increases after a certain distance (the authors give no figures).

The explosive power of tetryl at a loading density of 0.3, was compared with that of other explosives in a manometric bomb by Koehler [51] who determined the following pressure values from which the temperatures of explosion have been computed:

TABLE 10

Explosive	Pressure kg/cm^2	Temperature of explosion °C
Tetryl	4684	2911
Picric acid	3638	2419
Trinitrotoluene	3749	2060
Trinitrobenzene	3925	2356

When confined in a 24 mm diameter tube, tetryl is capable of burning. According to Andreyev [53], at a density of 0.9, the rate of burning of tetryl can be expressed as a function of temperature by the equation:

$$\frac{1}{u_m}=31.50-0.055\ T_0$$

The diagram (Fig. 6) shows the dependence of u_m and $\frac{1}{u_m}$ on temperature.

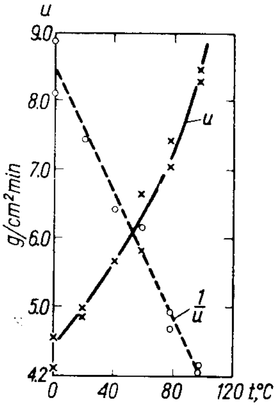


FIG. 6. Rate of burning of tetryl against initial temperature, according to Andreyev [53].

A very important property of tetryl is its sensitiveness to initiation by a primer—hence its rapid rise in importance as an explosive for use in detonating caps, gains (boosters) etc. Martin [54] gives the following figures comparing the sensitiveness to initiation of tetryl and trinitrotoluene, under the influence of various primary explosives (Table 11).

TABLE 11

Primary explosive	Minimum charge (grammes) for detonation of	
	Trinitrotoluene	Tetryl
Mercury fulminate	0.36	0.29
Silver fulminate	0.095	0.02
Lead azide	0.09	0.025
Silver azide	0.07	0.02

W. Taylor and Cope [55] determined the minimum charge of a mixture of mercury fulminate (90%) and potassium chlorate (10%) necessary to detonate mixtures of trinitrotoluene and tetryl (Table 12).

TABLE 12

Composition of mixture per cent		Weight of initiator g
Trinitrotoluene	Tetryl	
100	0	0.25
90	10	0.22
80	20	0.21
50	50	0.20
0	100	0.19

TOXICITY

Tetryl is a toxic substance. Breathing its dust induces symptoms of poisoning. A concentration of 1.5 mg/m^3 of tetryl dust in the air is reported noxious (Troup [56]) but a lower concentration may be toxic. Tetryl has a particularly potent effect on the skin, producing symptoms of an allergic character: the skin turns yellow and dermatitis develops. Thus workers employed in production, especially those engaged in handling tetryl, should be provided with protective clothing. Parts of the body exposed to tetryl dust should be protected by barrier cream containing 10% of sodium perborate. Daily baths are essential. The presence of tetryl dust in the air often causes irritation of the upper respiratory tract. Tetryl poisoning is also accompanied by general symptoms such as lack of appetite, insomnia, giddiness etc.

The symptoms usually occur 2–3 weeks after beginning work with tetryl. In many cases (60–68%) some adaptation occurs and the effects of the poison appear less pronounced.

Witkowski *et al.* [57] report that in one factory in the U.S.A. during World War II out of 1258 workers engaged in handling tetryl 944 fell ill, while in another, 404 out of 800–900 were affected.

TETRYL MANUFACTURE

Nitration of dimethylaniline

According to Sokolov [58] dimethylaniline used for the manufacture of tetryl should be a pale-yellow liquid, s.g. 0.955–0.960 at 15°C, b.p. 192–194°C, not less than 95% of the substance distilling between 192.7 and 193.7°C. It must not contain water or aniline. Only traces of methylaniline are permissible.

The nitric and sulphuric acids should be purified to the extent usually required for nitrating acids. Nitric acid of 92–98% concentration, containing not more than 3% of nitric oxides is commonly utilized. The concentration of sulphuric acid may vary between 96 and 99%. The nitrating mixture should be rich in nitric acid, i.e. containing not less than 65% of HNO_3.

The production of dimethylaniline sulphate

In the manufacture of tetryl, it is usual not to nitrate dimethylaniline directly, but to dissolve it first in concentrated sulphuric acid and then to nitrate the dimethylaniline sulphate so obtained. Straightforward nitration of dimethylaniline proceeds so violently, that it can be carried out only under the special conditions described on pp. 42–43. Many years' experience of tetryl manufacture has shown that the ratio of sulphuric acid to dimethylaniline should not be lower than 3 : 1, a smaller amount of sulphuric acid may be detrimental to the nitration process. (Nitration by a periodic (discontinuous) method may cause ignition in the nitrator due to the fact that a portion of dimethylaniline was not previously converted into sulphate.) The proportion of sulphuric acid to dimethylaniline should not however be too high, e.g. a ratio of 100 : 1 has a detrimental effect on the yield of tetryl. While the dimethylaniline is dissolving the temperature should be maintained between 20 and 45°C, but not higher, to avoid sulphonation of the benzene ring.

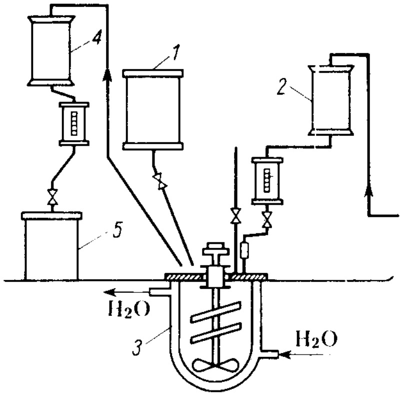


FIG. 7. Flow diagram of plant for dissolving dimethylaniline in sulphuric acid, according to Sokolov [58].

The lay-out of a plant for dissolving dimethylaniline in sulphuric acid (according to Sokolov [58]) is shown, with some modifications, in Fig. 7. It comprises a dosing tank (*1*) for sulphuric acid and dosing tank (*2*) for dimethylaniline. First, 14,400 kg of 96% sulphuric acid are poured into reactor (*3*) followed by 1000 kg of dimethylaniline maintaining the temperature between 25 and 30°C. The dimethylaniline is poured in over a period of about 3 hr, and the contents of the reactor are then maintained for 30 min at 40°C and finally cooled to 20°C. The solution of dimethylaniline sulphate so obtained is pumped over to container (*4*), whence it flows down to nitrator (*5*).

Before nitration the solution of dimethylaniline sulphate is tested for the presence of free dimethylaniline by treating a test sample with a large amount of water. If free dimethylaniline is present the solution is cloudy. This test is of great importance (see above).

Nitration (see Bain [59] and Rinkenbach [29]). A continuous method of nitration at 70°C is the safest and most advantageous. The lay-out shown diagrammatically in Fig. 8 is typical.

The nitrating acid is metered in the dosing tank (*1*) and the dimethylaniline solution in the dosing tank (*2*). Both liquids are introduced into the nitrator *I*, their rate of inflow being so regulated that 15.4 parts of the dimethylaniline solution in sulphuric acid mix with 9.2 parts of nitrating mixture composed of:

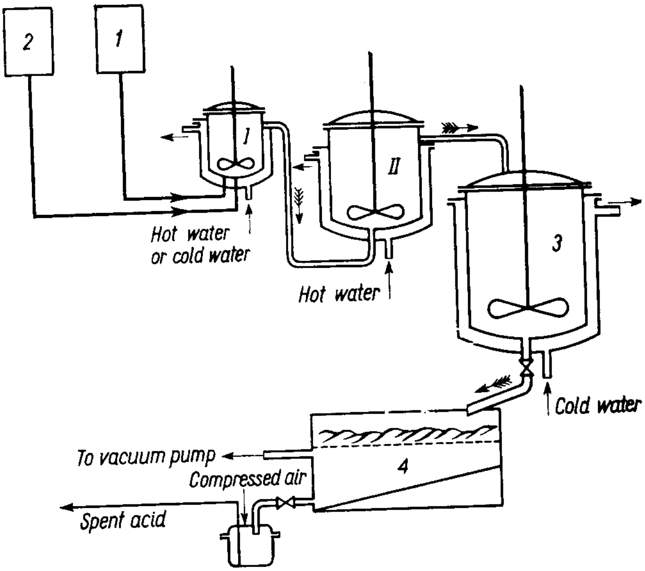


FIG. 8. Flow diagram of plant for continuous nitration of dimethylaniline.

HNO_3	67%
H_2SO_4	16%
H_2O	17%

The contents of the nitrator are heated to a temperature of 68°C and heating is then discontinued and the temperature in the nitrator maintained at 60 to 72°C. The nitrator is cooled externally, if necessary. For safe and efficient nitration very vigorous stirring is essential to ensure that the reacting liquids are mixed almost instantaneously. Since the mixture is kept in nitrator *I* for a very short period, reaction may be incomplete. Its contents are discharged via an overfall to a larger reactor *II*, also provided with a stirrer. In reactor *II* the same temperature (70°C) is maintained by heating. Here the reaction is completed and the liquid, together with the partly crystallized product, is allowed to run into crystallizer (*3*) in which the whole is cooled to 20°C and afterwards discharged to the vacuum filter (*4*). Tetryl is collected on the filter and the spent acid is passed on to be denitrated.

Here, as in other continuous processes involving rather risky exothermic reactions, the following precautions for ensuring the safety of personnel are of utmost importance:

(1) A stainless steel cooling coil should be fitted inside the nitrator to make possible a rapid heat removal to enable the contents to be cooled very rapidly (the coil is not shown in Fig. 8).

(2) Vigorous and reliable stirring is essential. The stirrer should be provided with a spare d.c. motor driven by a battery, to replace the main motor in case of damage. A compressed air pipe should also be fitted to supply air to the nitrator as a last resort.

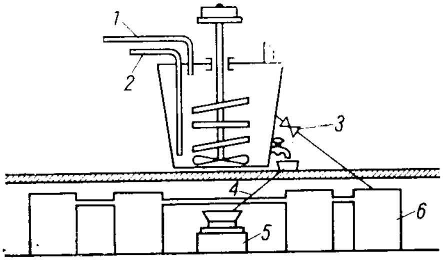


FIG. 9. Flow diagram of plant for washing tetryl, according to Sokolov [58].

On nitration, carbon dioxide and nitrogen dioxide are evolved. These gases are passed to water absorption towers where considerable amounts of nitric acid are recovered.

Washing the tetryl. The filtered product is despatched in aluminium barrels from the nitration department to a special room where it is poured into a washing tank (Fig. 9). The tank of 1350 l. capacity, fitted with a stirrer, may be of wood lined with stainless steel. It is fed with water through pipe (*1*), and is heated by direct steam injection through pipe (*2*).

The contents of the tank are stirred with water for 30 min and allowed to stand for 30–40 min. The aqueous layer is decanted through the top valve (*3*) into a number of settling tanks (*6*). The tetryl is washed first with cold water, and then by a succession of washings at increasing temperatures: 40, 60, 80, and 90 or 100°C.

After washing the product is discharged through a wide valve and channel (*4*) to a vacuum filter (5). After filtration and the removal of water, wet tetryl containing 16–18% of water is passed on for crystallization. Tetryl is also collected from the settling tanks every 10 days. This tetryl may contain sand and other mechanical impurities, and must therefore be crystallized.

Washed tetryl should not contain more than 0.015% of acid (calculated as H_2SO_4). If the acidity is higher, the product is given an additional wash. Washed tetryl crystallizes into yellow or reddish-yellow crystals.

Crystallization from benzene. For crystallization wet, freshly washed, deacidified tetryl is used. It is introduced into container (*1*) (Fig. 10) equipped with a mixer, a heating jacket and a reflux condenser (*2*). Container (*1*) is filled with benzene. The whole is heated, while stirring, until the tetryl is dissolved. The solution is then passed through the warmed filter (*3*). The products insoluble in benzene are retained on the filter. The clarified benzene solution, with an aqueous layer, is conveyed to the warmed separator (*4*) in which the lower aqueous layer is separated. The aqueous layer contains the residual acid washed out of the benzene solution of tetryl. The benzene solution is transferred to the crystallizer (*5*) in which the crystallization of tetryl takes place on cooling. The crystals of tetryl are then separated from the mother liquor on the vacuum filter (*6*). Tetryl should not be separated in centrifuge, as this is considered too dangerous.

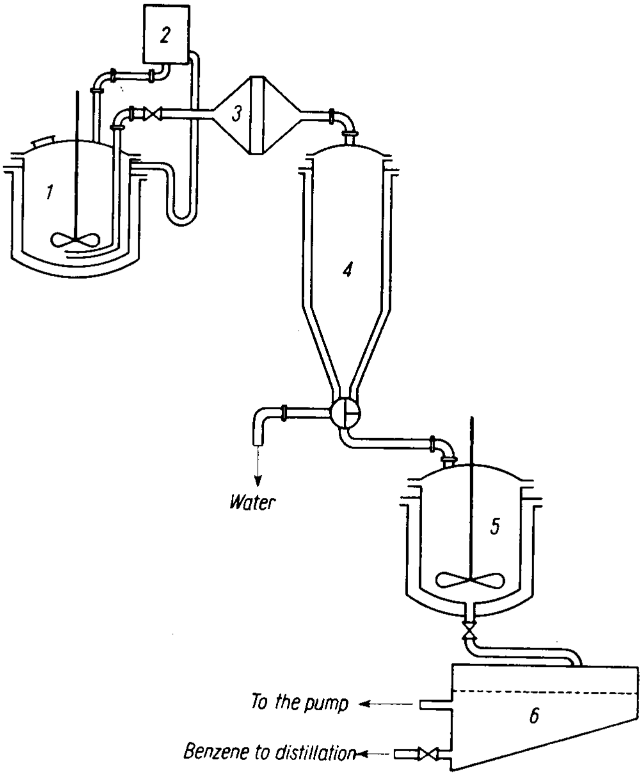


FIG. 10. Flow diagram of plant for the crystallization of tetryl.

The tetryl is then dried for 24 hr in a shelf drier at 55–60°C. This period, however, may be reduced to 12 hr if a vacuum drier is employed.

All possible safety measures usually employed with sensitive and dangerous explosives must be taken in the drier, e.g. the frequent dusting of heaters, sweeping of floors etc.

The dried, crystalline tetryl is sifted on vibrating, well-earthed copper screens.

Crystallization from acetone. Tetryl may be crystallized from acetone by cooling, but crystallization by precipitation with water is preferable, as this permits removal of traces of acid and gives a very fine crystalline product which, when mixed with the product prepared by crystallization from benzene, forms a free-flowing mixture. The plant is, in principle, similar to that represented in Fig. 10, except that separation is unnecessary and a much larger crystallization vessel is needed to hold both the solution and the added water.

According to the Soviet standard specification WST 5, top-grade tetryl should meet the following requirements:

Freezing point, min.	127.7°C
Moisture and volatile matter, max.	0.02%
Substances insoluble in acetone, max.	1 %
Acidity (calculated as H_2SO_4), max.	0.01%

According to U.S. requirements [59], high grade tetryl should possess the following characteristics:

M.p.	128.5–129.1°C
Acidity	not more than 0.08% (H_2SO_4)
120°C vacuum test	not more than 4.0 cm^3 of gas evolved in 40 hr.

Nitration of dinitromethylaniline

According to the German (Griesheim) method [60] tetryl is manufactured in two stages: first dinitromethylaniline is prepared and this is then nitrated.

Dinitromethylaniline is produced by the reaction of chlorodinitrobenzene with methylamine in the presence of sodium hydroxide. A solution is prepared consisting of 300 l. of water, 1140 l. of 35% aqueous sodium hydroxide solution and 1225 kg of 25% aqueous methylamine solution. This solution is added over a period of 12 hr to a vigorously stirred suspension of 2000 kg of chlorodinitrobenzene in 1350 l. of water heated to 95–100°C.

All is stirred for one hour longer and then the product is cooled (still stirring). After being allowed to crystallize, it is centrifuged. The dinitromethylaniline so obtained is nitrated in a similar manner to dimethylaniline. Nitration proceeds without such an abundant evolution of gaseous products, it is less violent and may be conducted at a lower temperature.

According to Desseigne [61] the reaction is carried out with a 20% excess of HNO_3. The concentration of sulphuric acid employed for dissolving the dinitromethylaniline and in the nitrating mixture is so matched that the nitrating mixture always contains 16% of water as the sulphuric solution of dinitromethylaniline is poured into the nitrator during nitration. The composition of the nitrating mixture is:

HNO_3	78%
H_2SO_4	6%
H_2O	16%

To dissolve dinitromethylaniline in sulphuric acid a mixture of 860 parts of spent acid from a previous nitration is used, together with 168.5 parts of 95% sulphuric acid and 117.5 parts of 20% oleum. The spent acid contains:

HNO_3	1.0%
NO_2	0.5%
H_2SO_4	82.5%
H_2O	16.0%

The dinitromethylaniline solution in sulphuric acid is introduced slowly into the nitrator containing the nitrating mixture. The addition takes about 1 hr and the temperature of the mixture is maintained at 30°C.

The precipitation of tetryl begins about 10 min after the reaction has started.

After mixing the two solutions, the temperature is raised to 50–55°C and maintained thus for 40 min. The presence of crystals in the semi-liquid mixture results in a violet colour which gradually changes to grey and then to yellow. Nitration is judged to be complete when the colour turns pale-yellow. The contents of the nitrator are then cooled to 20°C and the product is filtered off on a vacuum filter. Spent acid (1290 parts) is drawn off, $\frac{2}{3}$ of it returning to nitration and $\frac{1}{3}$ going to denitration.

The filtered tetryl is added to water (500 parts) so heated that on the addition of tetryl its temperature is 50°C. The mixture is then stirred for 10–15 min, and the tetryl filtered and washed with cold water until free of acid (helianthine test). After washing, the tetryl is dried at 70°C.

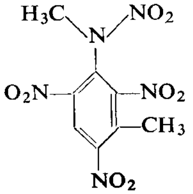
From 100 parts of dinitromethylaniline 138.6 parts of tetryl can be obtained, i.e. 95.3% of the theoretical yield. The m.p. of the tetryl so produced is 128.4°C. If necessary, it can be re-crystallized.

The raw material consumption per 1000 kg of tetryl produced is:

720 kg	of dinitromethylaniline
617 kg	of 95% sulphuric acid
642 kg	of 20% oleum
507 kg	of nitrating mixture containing 87% of HNO_3 and 5% of H_2O
165 kg	of 50% nitric acid.

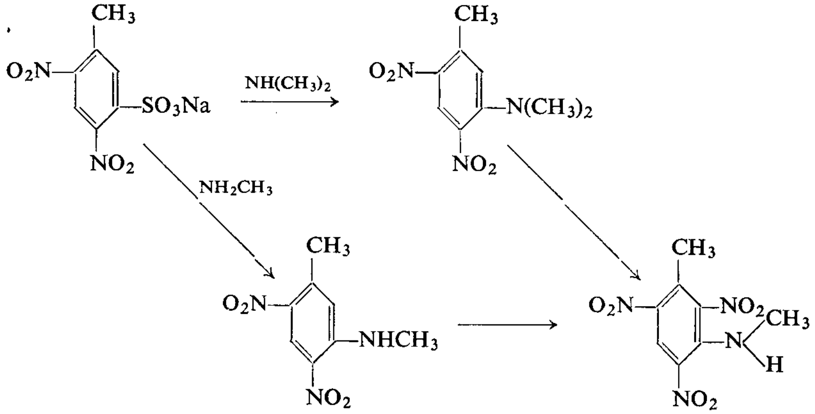
HOMOLOGUES AND ANALOGUES OF TETRYL

2,4,6-Trinitro-3-methylphenylmethylnitramine (methyltetryl, tolyltetryl)



m.p. 101–101.5°C

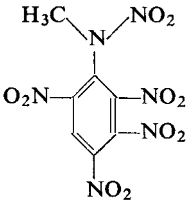
Romburgh [62] prepared this product by the nitration of N-dimethyl-*m*-toluidine, British authors [63] obtained it in the following manner during World War I using the product of sulphitation of γ-trinitroluene, the main isomer of α-trinitrotoluene (Vol. I):



This course of reaction was confirmed by T. Urbański and Schuck [40] who also found that the final product is somewhat more stable to heat than tetryl. Instantaneous explosion, for example, occurred on contact with a metal surface heated to 320°C (tetryl explodes at 310°C).

It is an explosive of approximately the same power as picric acid.

2,3,4,6-Tetranitrophenylmethylnitramine and its derivatives

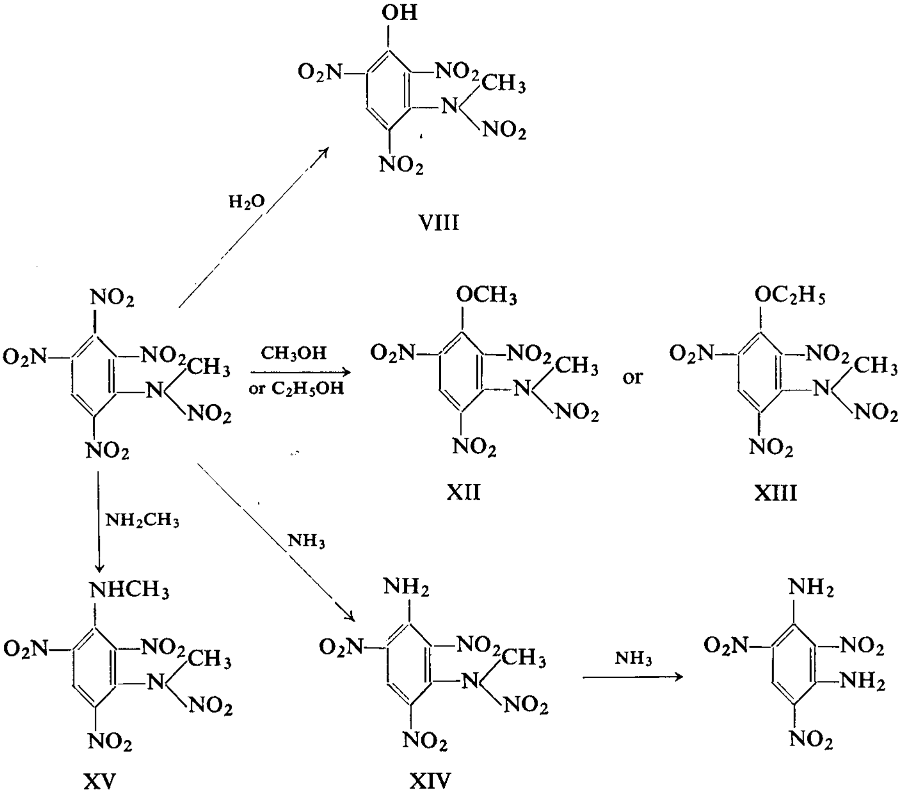


m.p. 146–147°C

VII

According to Romburgh [64, 16] this substance is thought to be an impurity of tetryl arising during the nitration of dimethylaniline and, with peculiar ease, when methylaniline is nitrated. This is due to the fact that from the beginning of nitration the nitro group may take the *meta*-position with respect to the methylamine group.

The formation of this substance by the nitration of *m*-nitromethylaniline was examined by Blanksma [65] and the conditions of its conversion into a number of other substances by the substitution of the nitro group at the *meta*-position with the OH, OCH_3, NH_2, $NHCH_3$ groups were elucidated by van Duin and van Lennep [66]:



These are the following compounds:

(VIII) 2,4,6-trinitro-3-methylnitraminophenol (m.p. 183°C)
(XII) 2,4,6-trinitro-3-methylnitraminoanisole (m.p. 96–97°C)
(XIII) 2,4,6-trinitro-3-methylnitraminophenetole (m.p. 98–99°C)
(XIV) 2,4,6-trinitro-3-methylnitraminoaniline (m.p. 188°C; under the prolonged influence of more concentrated ammonia 2,4,6-trinitro-*m*-phenylenediamine is formed; Vol. I)
(XV) 2,4,6-trinitro-3-methylnitramino-N-methylaniline (m.p. 190–192°C).

All these substances have been examined [66] with reference to their sensitiveness and stability (Table 13).

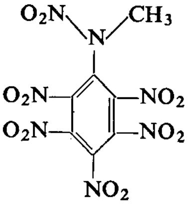
Owing to the presence of the phenolic group, the substance (VIII) forms explosive salts. Its lead salt, however, is of no practical value owing to its hygroscopicity.

The substance (XV) is susceptible to further nitration resulting in the formation of a dinitramine described below (so-called ditetryl).

TABLE 13

Substance	Sensitiveness to impact Maximum height of drop (cm) not causing explosion		Ignition temperature °C	Stability
	2 kg	10 kg		
VIII	30–33	–	197	Stable at 95°C for 3 days
XII	–	15–16	198	Decomposition at 90°C after 2 hr
XIII	–	16–19	202	Decomposition at 90°C after 2 hr
XIV	43–45	–	201	Stable at 95°C for 30 days
Tetryl (standard)	50–51	14	196	Stable at 95°C for 185 days

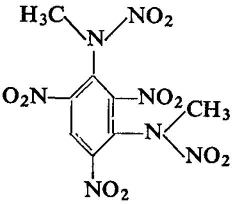
2,3,4,5,6-Pentanitrophenyl-N-methylnitramine (N-2,3,4,5,6-hexanitro-N-methylaniline)


m.p. 132°C (decomp.)

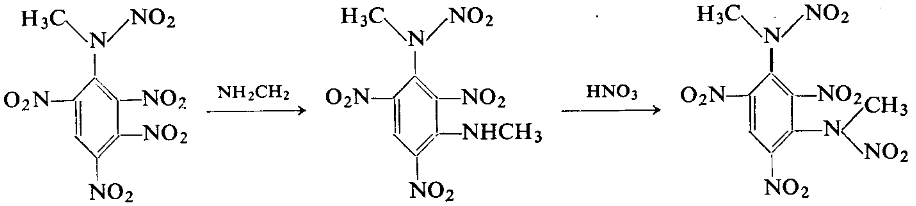
This substance was obtained by Blanksma [67] by the nitration of a mixture of 3,5-dinitro-N-methylaniline and 3,5-dinitro-N,N-dimethylaniline.

It is unstable and decomposes readily above its m.p. or when boiled in water.

2,4,6-Trinitro-1,3-di(methylnitramino)-benzene (ditetryl)


m.p. 206°C

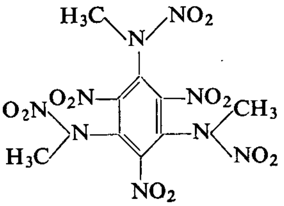
Romburgh [68] was the first to prepare this explosive compound by the nitration of N,N′-dimethyl- or N,N′-tetramethyl-*m*-phenylenediamine. A more practical method was developed by van Duin and van Lennep [66] who started from tetranitrophenyl-methylnitramine (VII) (p. 63):



Its chemical properties are very similar to those of tetryl.

Ditetryl is more sensitive to impact than tetryl (it is exploded by a 2 kg weight falling 21–26 cm as compared with 49–51 cm for tetryl). Its ignition temperature is 214°C (that of tetryl is 196°C). It is much less stable than tetryl: decomposition occurred on heating at 95°C for 4 days (tetryl withstands 185 days heating [66]).

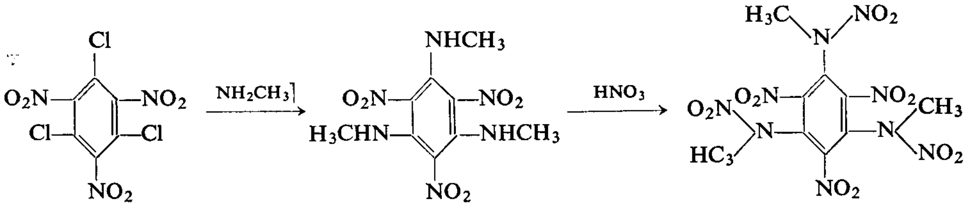
2,4,6-Trinitro-1,3,5-tri(methylnitramino)-benzene (tritetryl)



m.p. 280°C (decomp.)

This product was prepared by Blanksma [69] by the nitration of 2,4,6-trinitro-1,3,5-trimethylaminobenzene. The latter was obtained from 3,5-dichloro-(or dibromo)-2,4,6,-trinitroanisole by the action of an alcoholic solution of methylamine.

T. Urbański [70] reported a more convenient method of tritetryl preparation, starting from symmetrical trichlorotrinitrobenzene:



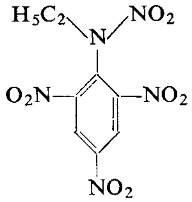
m.p. 268–270°C

T. Urbański investigated its explosive power in a manometric bomb at a density of 0.05 and found it to be more powerful than trinitrotoluene (by about 46%):

Trinitrotoluene	**– pressure 420 kg/cm²**
Tetryl	**– pressure 580 kg/cm²**
Tritetryl	**– pressure 613 kg/cm²**

According to Médard [71] tritetryl gave a lead block expansion of 130 (taking the value for picric acid as 100). Under a pressure of 1500 kg/cm^2, a density of 1.43 was obtained.

2,4,6-Trinitrophenylethylnitramine (ethyltetryl)

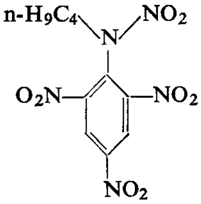


m.p. 96°C

Romburgh [3] was the first to prepare this substance both by nitrating ethylaniline and by nitrating diethylaniline. It is comparable to tetryl in its physical and chemical properties. As an explosive it is weaker than tetryl. Its sensitiveness to impact and its explosive power, measured in the lead block, are somewhat greater than those of picric acid.

According to Médard [71] ethyltetryl gave a lead block expansion of 104 (taking the value for picric acid as 100). Under a pressure of 1500 kg/cm^3, a density of 1.63 was obtained.

2,4,6-Trinitrophenyl-n-butylnitramine (butyltetryl)



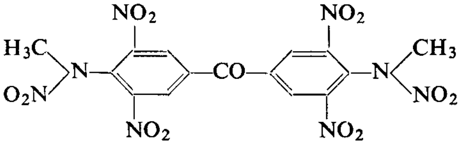
m.p. 97.5–98°C

This product has been prepared both by the nitration of N-n-butylaniline and by the action of n-butylamine on chlorodinitrobenzene followed by nitration of dinitro-N-n-butylaniline.

Tetryl and butyltetryl are alike in their physical and chemical properties. The latter is notable for its low sensitiveness to impact, very similar to that of trinitrotoluene. Since it is slightly more powerful than trinitrotoluene and at the same time highly sensitive to detonation by mercury fulminate, it was suggested (Davis [72]) for use in detonators, gains (boosters) and other initiating or priming charges.

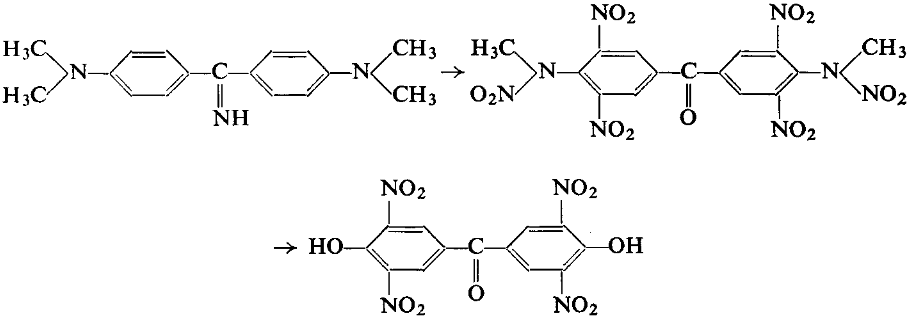
THE POLYCYCLIC ANALOGUES OF TETRYL

3,5,3′,5′-Tetranitro-4,4′-di(methylnitramino)-benzophenone

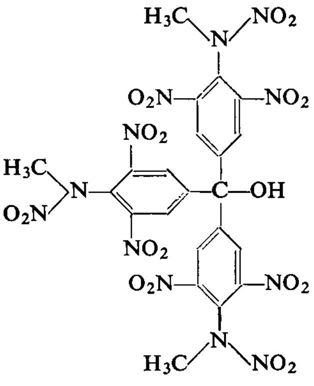


m.p. 200°C

Romburgh [73] prepared this substance by nitrating Michler's ketone. Galinowski and T. Urbański [74] obtained the same substance by nitrating auramine with a mixture of nitric and sulphuric acids. On heating with 2% KOH the substance was converted into the corresponding nitrophenol.



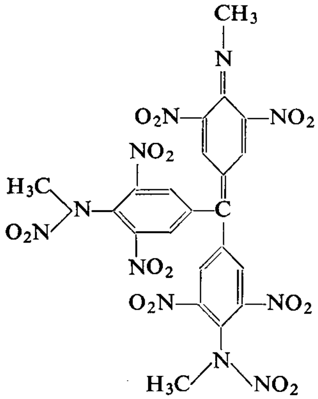
3,5,3′,5′,3″,5″-Hexanitro-4,4′,4″-tri(methylnitramino)-triphenylcarbinol



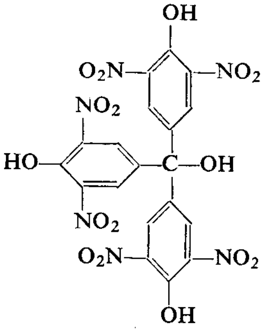
I, decomposition 228°C

Galinowski and T. Urbański [74] prepared this substance by nitration of crystal violet with a mixture of nitric and sulphuric acids. On heating with 2% KOH two products were formed: a semi-quinone (II) and a phenol (III).

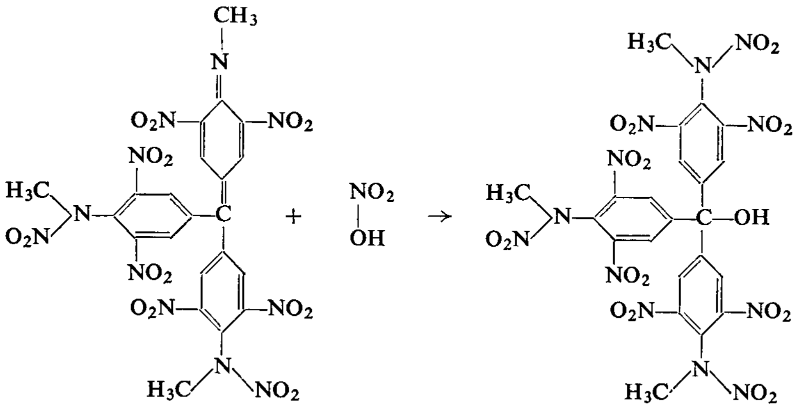
Compound (II), on treatment with concentrated nitric acid, adds a molecule of nitric acid and reverts to compound (I):



II



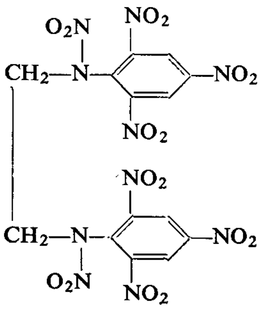
III



II

I

Hexanitrodiphenylethylenedinitramine (also called **ditetryl***, **bitetryl**, **or octyl)**



m.p. 218°C

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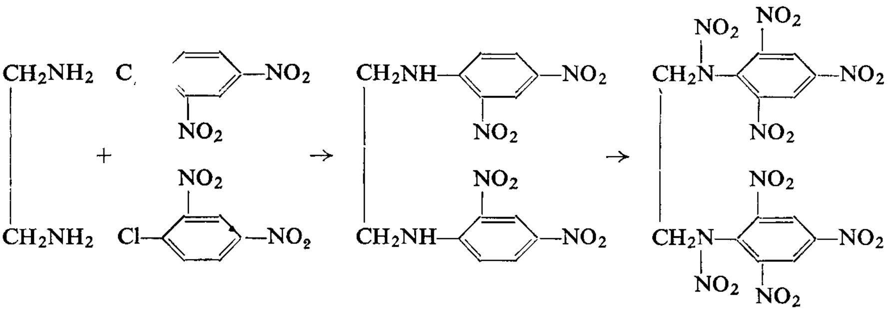
* The same name is applied to the compound described on p. 65.

It seems probable that this compound may find a practical application. It was first prepared by Bennett [75] by the nitration of diphenylethylenediamine with a mixture of concentrated sulphuric acid and anhydrous nitric acid at 30–35°C. Later Cox [76] worked out a practical method for its use in detonators.

It is most conveniently prepared by the interaction of ethylenediamine and chlorodinitrobenzene, followed by the nitration of the amine so obtained:

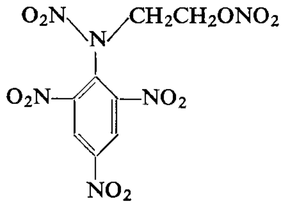


The substance is fairly stable. It resembles tetryl in its explosive power, but is more like penthrite in its sensitiveness to impact.

According to Médard [71] compression under 1500 kg/cm^2 gives a density of 1.50. Its rate of detonation at a density of 1.60 is 7.350 m/sec and its lead block expansion is 115 (taking the value for picric acid as 100).

NITRAMINO-ESTERS OF NITRIC ACID

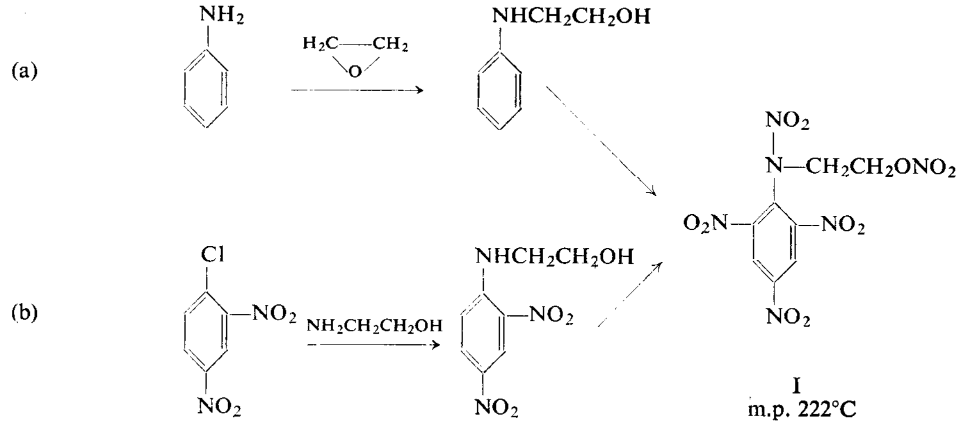
Trinitrophenyl-β-hydroxynitraminoethyl nitrate (pentryl, pentyl)



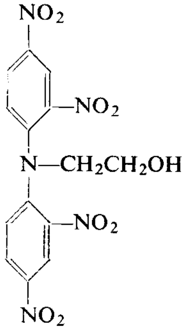
m.p. 126°C

This is a crystalline product readily soluble in most organic solvents, including nitroglycerine. It was prepared and recommended as an explosive by Moran [77], and later examined in detail by Clark [78] and Romburgh [79].

Pentryl has been prepared by two methods: (a) from aniline and ethylene oxide (according to Herz [80]) and (b) from chlorodinitrobenzene and ethanolamine (according to Moran) with the subsequent nitration of N-hydroxyethylaniline or its dinitro derivative:



When using method (b) a certain amount of the diphenylamine derivative (II) is also formed as a by-product:



II

The specific gravity of pentryl is 1.82, and its apparent density 0.45. Under a pressure of about 230 kg/cm^2 a density of 0.74 may be obtained.

In contact with a metal surface heated to 235°C, pentryl explodes in 3 sec. The chemical stability of pentryl is considered satisfactory.

Pentryl is remarkable for its high explosive power which, according to various authors, is equal to or slightly higher than that of tetryl. For instance it gives a lead block expansion 20% larger than that of tetryl. At a density of 0.80 its rate of detonation is 5400 m/sec, that of trinitrotoluene being 4450 m/sec (for an equal sized charge).

Pentryl is less sensitive to impact than tetryl (according to Clark, the maximum height causing no explosion in the drop test is 50 cm for pentryl, whereas for tetryl it is 27.5 cm and for picric acid 42.5 cm).

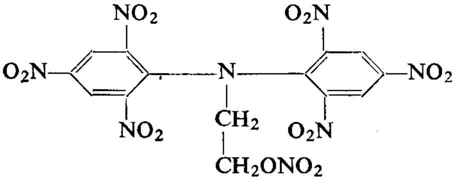
Médard [71] reports that pentryl, at a density of 1.56, detonates at the rate of 7180 m/sec and its lead block expansion is 114 (taking the value for picric acid as 100). Under a pressure of 1500 kg/cm^2, a density of 1.68 is obtained.

The minimum initiating charges for pentryl as compared with other explosives (according to Clark [78]) are listed in Table 14.

TABLE 14

Substance	Mercury fulminate g	Lead azide g
Pentryl	0.150	0.025
Tetryl	0.165	0.03
Picric acid	0.025	0.12
Trinitrotoluene	0.240	0.16

Hexanitrodiphenyl-β-hydroxynitraminoethyl nitrate



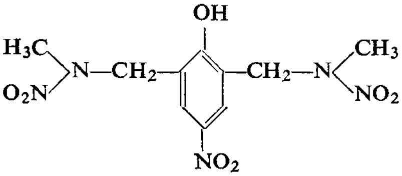
m.p. 184°C

According to Clark [81] this compound is obtained by the nitration of tetranitrodiphenyl-β-hydroxyaminoethane (II) which is formed as a by-product when preparing dinitrotriphenyl-β-hydroxyaminoethane from chlorodinitrobenzene and ethanolamine (see above, p. 71).

The explosive properties of hexanitrodiphenyl-β-hydroxynitraminoethyl nitrate are similar to those of pentryl. It is slightly more stable on heating; its ignition temperature lies between 390 and 400°C. It is somewhat less sensitive to impact than pentryl and rather more powerful (by 3%) in the lead block test. It requires a stronger initiator than pentryl, tetryl or picric acid, but a weaker one than trinitrotoluene.

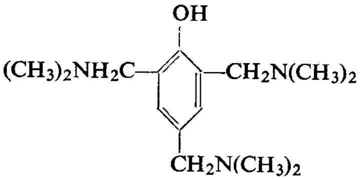
NITRAMINONITROPHENOLS

The only compound of this type described in the literature is 2,6-di-(methylnitraminomethyl)-4-nitrophenol (I). The location of the C-nitro group has not been determined so that a formula with NO_2 at the *ortho* position with respect to the phenol group is also possible.



I, m.p. 156°C

This compound has been described by Semeńczuk [82]. It was prepared by the **nitration of 2,4,6-tri-(dimethylaminomethyl)-phenol (II) with nitric acid, s.g. 1.40,** at 40°C. The starting substance was obtained by the condensation of phenol with formaldehyde and dimethylamine, according to Bruson and MacMullen [83].



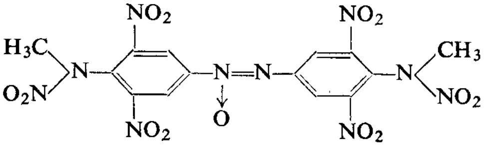
II

Vigorous reaction with nitric acid, s.g. 1.40, e.g. at 80°C, for 2 hr, causes the substance (I) to undergo nitrolysis and nitration to form picric acid.

The substance (I) is a moderately powerful explosive: it gives an expansion of 250 cm³ in the lead block. It is less sensitive to impact than trinitrotoluene. Its ignition temperature (195–200°C) is about the same as that of tetryl. It forms inflammable salts. The lead, thallous and potassium salts burn violently with a sharp report.

NITRAMINO-AZOXY COMPOUNDS

By the nitration of bis(4,4′-dimethylamino)-azoxybenzene T. Urbański and J. Urbański [84] obtained a hexanitroazoxy derivative (azoxytetryl) of the structure (I) i.e. 3,3′,5,5′-tetranitro-bis(4,4′-nitromethylamino)-azoxybenzene

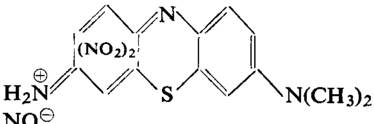


m.p. 208–209°C (decomp.)

NITRO METHYLENE BLUE

A few nitro derivatives of methylene blue have been described. By introducing one nitro group under mild conditions (nitric acid of *ca.* 20% and sodium nitrite) methylene green was obtained [85].

According to Gnehm [86] methylene blue, when subjected to the action of nitric acid (density 1.33, i.e. 52%) in presence of acetic acid diluted to 50%, yields "dinitrodimethylthionine" nitrate of suggested structure (I).

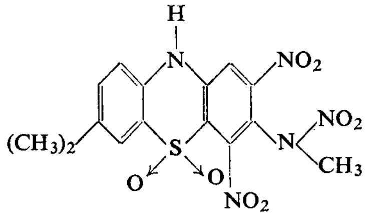


I

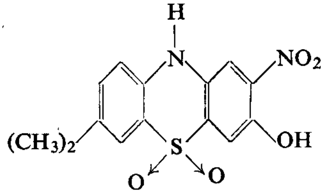
The position of two nitro groups was unknown.

According to the author mentioned, one of the two dimethylamino groups was fully demethylated.

Experiments carried out by T. Urbański, Szyc-Lewańska and Kalinowski [87] suggest the structure of 2,4-dinitro-3-(methyl)nitramino-7-(dimethyl)amino-5,5-dioxyphenothiazine (II) for the Gnehm product. The phenol produced by alkaline hydrolysis has the structure of 2,4-dinitro-3-hydroxy-7-(dimethyl)amino-5,5-dioxyphenothiazine (III)

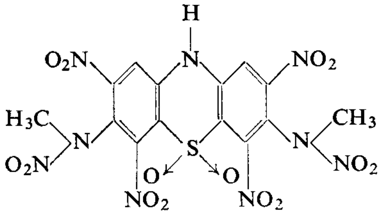


II

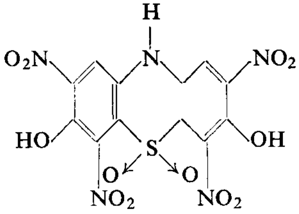


III

According to the same authors [87] energetic nitration of methylene blue may yield 2,4,6,8-tetranitro-3,7-di(methylnitramino)-5,5-dioxyphenothiazine (IV). This substance, when warmed with a 2% solution of NaOH, underwent the usual hydrolysis of the nitroamino group, placed in *ortho* position, to two nitro groups and yielded phenol (V).



IV



V

The product of Gnehm forms an intermediate stage between methylene blue and product (IV).

The nitro compound (IV) possesses interesting properties: it burns readily without melting.

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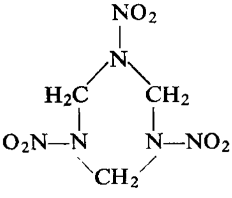
CHAPTER IV

HETEROCYCLIC NITRAMINES

CYCLONITE

CYCLONITE or cyclo-trimethylenetrinitramine (1,3,5-trinitrohexahydro-sym-triazine, 1,3,5-trinitro-1,3,5-triazacyclohexane) is a very



I

important explosive. It is also known as Hexogen, RDX and T4. It achieved great importance during World War II as a constituent of many explosive mixtures from which a high power was required. Cyclonite was used in detonators and primers, and in detonating gains or boosters replacing tetryl. It was used extensively in mixtures with trinitrotoluene, as a so-called hexolite, semi-liquid, fusible explosive. Mixtures of trinitrotoluene and cyclonite with aluminium, and plastic explosives containing cyclonite were also used. Some of these contained ammonium nitrate.

Cyclonite was first prepared by Lenze [1]. The method of manufacture by the nitration of hexamethylenetetramine nitrate with nitric acid is described in Henning's patent [2] of 1899.

The author did not cite the product as an explosive — he recommended its use in medicine — but in later patents [3] he proposed the use of cyclonite in the manufacture of smokeless propellant. In 1921 Herz [4] modified Henning's method by nitrating hexamethylenetetramine itself, not its nitrate. Hale [5] described in detail the preparation of cyclonite by nitrating hexamethylenetetramine, and reported its explosive properties.

Investigations carried out at that time revealed the outstanding value of cyclonite as an explosive: its high chemical stability, which is not much lower than that of aromatic nitro compounds, and its great explosive power, which considerably surpasses that of aromatic nitro compounds, such as trinitrotoluene and picric acid.

PETN, which has about the same power, compares unfavourably with cyclonite, the latter being less sensitive to mechanical stimulus and having a higher chemical stability.

Thus during the inter-war period in countries with well developed chemical industries, and in particular in Germany, Britain and U.S.S.R., new, more economical and safer methods of cyclonite preparation were worked out. During World War II similar work was also carried on in the United States and Canada. German methods became generally known after the war. Since it was found that the methods elaborated in Britain, Canada and the United States were not essentially different from those employed in Germany, the majority of them were also published. These methods consist in principle of synthetizing cyclonite from various forms of formaldehyde (e.g. paraformaldehyde, hexamethylenetetramine or simple Schiff bases) and from ammonium nitrate or hexamethylenetetramine nitrate as a source of nitramino groups. They will be discussed in detail further on.

During World War II Germany produced 7000 tons of cyclonite a month; by the end of the war the United States was manufacturing about 15,000 tons a month.

PHYSICAL PROPERTIES

Cyclonite is a white substance, crystallizing in the orthorhombic system (Terpstra [6]; Hultgren [7]). The refractive indexes n_D for different axes are: $\alpha = 1.5775$; $\beta = 1.5966$; $\gamma = 1.6015$. The melting points reported by various authors are 202°C, 203.5°C, 204.1°C and 206–207°C.

The specific heat of cyclonite is 0.30 cal/g°C, its heat of combustion 2285 kcal/kg, and its heat of formation — 96 kcal/kg, i.e. $-\Delta H_f = -21.3$ kcal/mole. Cyclonite is therefore an endothermic compound and this is one of the factors which render it so highly explosive.

The vapour pressure of cyclonite at various temperatures (according to Edwards [8]) is:

at 110.0°C	4.08×10^{-5} cm Hg
at 121.0°C	1.04×10^{-4} cm Hg
at 131.4°C	2.57×10^{-4} cm Hg
at 138.5°C	4.00×10^{-4} cm Hg

These figures correspond with the empirical equation:

$$\log p = 10.87 - 5850 \frac{1}{T}$$

where p denotes vapour pressure in cm Hg, and T is the absolute temperature.

Cyclonite crystals have a specific gravity of 1.820. When compressed the densities given in Table 15 are obtained. A density of 1.73 may be obtained under a pressure of 2000 kg/cm² provided that a desensitizer (e.g. wax) is added to reduce friction.

Cyclonite is practically insoluble in water. Majrich [9] reports its solubility as 0.01% at 0°C and 0.15% at 100°C. Cyclonite is soluble in concentrated nitric acid. In sulphuric acid at concentrations above 70% solution is accompanied by decomposition.

Table 15

Pressure kg/cm^2	Density
750	1.46
1000	1.50
1250	1.54
1500	1.56
1750	1.58
2000	1.60

In most organic liquids cyclonite dissolves with difficulty. The best solvent, from which it can be crystallized, is acetone. Table 16 contains solubility data for cyclonite (in g per 100 g of solution).

Table 16

Solubility of cyclonite in organic solvents (according to T. Urbański and Kwiatkowski [10]

Temperature °C	Methyl alcohol	Ethyl alcohol	Isoamyl alcohol	Ethyl ether	Acetone	Benzene	Toluene	Carbon tetrachloride
0	0.140	0.040	0.020	—	4.18	—	0.016	—
10	0.180	0.070	0.023	0.050	5.38	0.020	0.018	—
20	0.235	0.105	0.026	0.055	6.81	0.045	0.020	—
30	0.325	0.155	0.040	0.075	8.38	0.055	0.025	—
34	—	—	—	0.090	—	—	—	—
40	0.480	0.235	0.060	—	10.34	0.085	0.050	—
50	0.735	0.370	0.110	—	12.80	0.115	0.085	0.005
58	—	—	—	—	15.27	—	—	—
60	1.060	0.575	0.210	—	—	0.195	0.125	0.007
64.5	1.250	—	—	—	—	—	—	—
70	—	0.880	0.320	—	—	0.300	0.210	0.015
78.1	—	1.180	—	—	—	—	—	—
79.5	—	—	—	—	—	0.400	—	—
80	—	—	0.500	—	—	—	0.295	—
90	—	—	0.850	—	—	—	0.465	—
100	—	—	1.325	—	—	—	0.640	—
110	—	—	1.900	—	—	—	0.980	—
120	—	—	2.990	—	—	—	—	—
131.6	—	—	3.870	—	—	—	—	—

The solubility of cyclonite (in g per 100 g of solution) in other solvents as reported by various other authors is given in Table 17. It is insoluble in carbon disulphide, soluble in hot aniline and phenol.

T. Urbański and Rabek-Gawrońska [11] found that cyclonite dissolves in molten, highly-nitrated aromatic hydrocarbons, substituted urea derivatives, and camphor to form eutectics of the composition given in Table 18. It is almost insoluble in molten diphenylamine.

TABLE 17

SOLUBILITY OF CYCLONITE IN OTHER ORGANIC SOLVENTS

Temperature °C	Chloroform	Methyl acetate	Ethyl acetate	Cyclohexanone	Nitrobenzene	Pyridine	Mesityl oxide
20	0.008	2.95	0.517	—	—	1.60	—
25	—	—	—	12.7	1.5	—	3
50	—	6.0	—	—	—	—	—
97	—	—	—	27	12.4	—	12

TABLE 18

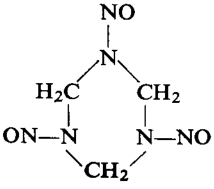
EUTECTIC MIXTURES WITH CYCLONITE

Second component	Content of cyclonite in eutectic mixture %	Freezing point of eutectic °C
p-Nitrotoluene	about 0.5	50.4
p-Nitroanisole	about 0.5	50.9
α-Nitronaphthalene	about 1.5	55.4
m-Dinitrobenzene	8	85.5
α-Trinitrotoluene	2.5	78.6
1,3,5-Trinitrobenzene	about 3	113.8
Picric acid	12	112.9
Tetryl	10	118.1
sym-Dimethyldiphenylurea	17	112.4
sym-Diethyldiphenylurea	3	70.4
Camphor	22	137.5

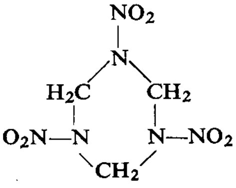
CHEMICAL PROPERTIES

Herz [4] first suggested a hypothetical structural formula for cyclonite. This formula is now considered to be correct since it has been confirmed by a number of methods of synthesis discussed later.

It has been established that cyclotrimethylenetrinitrosoamine (II), a product of the nitrosation of hexamethylenetetramine, is oxidized with nitric acid (about 40%) to cyclonite (I). This confirms the structure of cyclonite.



II



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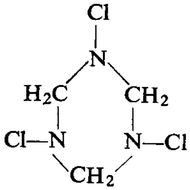
It also provides a method of obtaining a chemically pure preparation, free from octogen. The reaction proceeds stepwise. It will be discussed more fully on p. 123 (Brockmann, Downing and Wright [12]).

However, attempts to prepare cyclonite from substances containing a sym-triazine ring, e.g. from N,N′,N″-trichloro-cyclotrimethylenetriamine (III) (obtained by Delépine [13], by the action of hypochlorous acid on hexamethylenetetramine) were a failure.

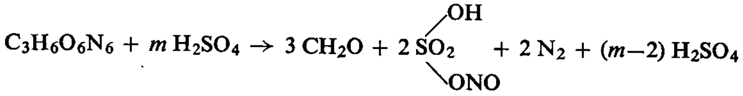
An attempt to prepare cyclonite by reacting the substance (III) with silver nitrite also failed, as it resulted in total decomposition of the molecule.



III

According to Vernazza [14] cyclonite is decomposed at 25°C by concentrated sulphuric acid, to form nitrogen and formaldehyde.

The reaction is said to proceed as follows:



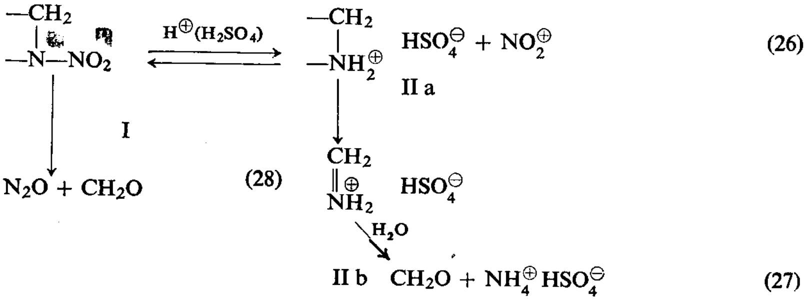
$$C_3H_6O_6N_6 + m\,H_2SO_4 \rightarrow 3\,CH_2O + 2\,SO_2(OH)(ONO) + 2\,N_2 + (m-2)\,H_2SO_4$$

This reaction indicates why the results of analysis of cyclonite in the nitrometer are too low.

Šimeček [15] doubted the correctness of the Vernazza equation and believed that the decomposition of cyclonite by concentrated sulphuric acid at 20–40°C may be expressed by the following empirical equation:

$$C_3H_3O_6N_6 + 2n\,H^{\oplus} \rightarrow 3\,CH_2O + (3-n)\,N_2O + n\,NO_2^{\oplus} + n\,NH_4^{\oplus}$$

Šimeček suggested the following mechanism for the decomposition reaction:



According to reaction (26) concentrated sulphuric acid liberates the nitronium ion from cyclonite (as from nitroguanidine, as reported on p. 26). Cyclotrimethylenetriamine sulphate (II) is formed which is then converted to a Schiff's base sulphate.

The latter is hydrolysed to formaldehyde and ammonium sulphate according to reaction (27). Simultaneously reaction (28) takes place, involving those molecules of cyclonite unaffected by sulphuric acid. Reaction (28) results in the formation of nitrous oxide and formaldehyde.

Šimeček also came to the conclusion that N_2O is not liberated in the nitrometer during the decomposition of cyclonite since formaldoxime $CH_2{=}NOH$ is formed in the presence of formaldehyde hence the analytical results are low.

It should be noted that the presence of water in the sulphuric acid promotes the decomposition of cyclonite. This is particularly easy when the acid contains 1–15% of water. In a strictly anhydrous medium the course of the reaction is much milder. Nitric acid which contains SO_3 does not cause the decomposition of cyclonite.

According to Somlo [16] the action of a 4% solution of NaOH at 60°C produces the total decomposition of cyclonite after 5 hr. Somlo also studied the decomposition of cyclonite by concentrated sodium hydroxide and found it to be complete within 2–4 hr at 60°C. Among the decomposition products he detected nitrates, nitrites, organic acids, ammonia, nitrogen, formaldehyde and hexamethylenetetramine.

Epstein and Winkler [17] reported a preliminary examination of the kinetics of cyclonite decomposition proceeding by a homogeneous phase in acetone solution.

The kinetics of decomposition of cyclonite in an alkaline medium of sodium methoxylate or lithium in a solution of methyl alcohol within the temperature range 19.0–44.93°C was investigated in detail by W. H. Jones [18]. He studied the course of the reaction by determining the concentration of $NO_2^\ominus$ ion with chloramine T, by titrating with acid in the presence of various indicators and by determining the unaltered cyclonite polarographically. On the basis of these analyses Jones drew up four equations, according to which the decomposition reaction proceeds under the influence of a methoxyl anion $(OCH_3)^\ominus$ (A, B and C denote hypothetical intermediate products)

$$\text{Cyclonite} + (OCH_3)^\ominus \xrightarrow{K_1} A + CH_3OH + NO_2^\ominus \tag{29}$$

$$A + (OCH_3)^\ominus \longrightarrow B^\ominus + CH_3OH \tag{30}$$

$$B^\ominus + (OCH_3)^\ominus \longrightarrow C^{2\ominus} + CH_3OH \tag{31}$$

$$C^{2\ominus} \xrightarrow{K_2} D^\ominus + NO_2^\ominus \tag{32}$$

Reactions (30) and (31) proceed very rapidly; K_1 and K_2 are the constants of reactions (29) and (32); $C^{2\ominus}$ is a strong base; $B^\ominus$ and $D^\ominus$ are weaker bases.

The equation for the rate of reaction as deduced by Jones is:

$$\frac{dx}{dt} = K_1(a-3x_1)(b-x_1) + K_2(x_1-x_2) \tag{33}$$

where a denotes the initial concentration of $(OCH_3)^\ominus$ ions, b the initial concentration of cyclonite.

After time t:

x is the total molar concentration of the $NO_2^{\ominus}$ ion; x_1 the molar concentration of $NO_2^{\ominus}$ from reaction (29); x_2 the molar concentration of $NO_2^{\ominus}$ from reaction (32). Jones also deduces the following equations:

$$-\frac{dR}{dt}=K_1R(a-3b+3R) \tag{34}$$

$$-\frac{dZ}{dt}=K_1Z(3b-a+Z) \tag{35}$$

$$-\frac{dY}{dt}=K_1\tfrac{1}{2}(3Y-a)(Y+2b-a)^7 \tag{36}$$

where after time t:

R is the molar concentration of cyclonite; Z the molar concentration of $(OCH_3)^{\ominus}$ (determined by nitration in the presence of phenolphthalein); $Y=Z+C$, i.e. total basicity (determined by titration in the presence of bromothymol blue); C the molar concentration of the $C^{2\ominus}$ ion.

The nature of the intermediate products of reaction was not determined by Jones. Instead, he suggested that the intermediate product A is formed from cyclonite by the elimination of HNO_2 and has the structure given below. He derived the hypothetical structure of the ions $B^{\ominus}$ and $C^{\ominus}$ in a similar manner.

Cyclonite is more stable to heat than penthrite and at a temperature above the melting point of tetryl, e.g. at 140°C, also shows greater stability than the latter.

According to Avogadro [19] the ignition temperature of cyclonite is 215°C (this author reports 185°C for penthrite). T. Urbański and Pillich [20] found the following values for ignition temperatures:

tetryl	203°C
penthrite	209°C
cyclonite	229°C

Heating began at 150°C, the rate of temperature rise was 10°/min. Ignition after a 5 sec delay occurred at 260°C.

Many authors, viz.: Majrich [9], Tonegutti [21] and Haid, Becker and Dittmar [22] point out that cyclonite is more stable than penthrite and tetryl.

A. J. B. Robertson [23] found that the decomposition of cyclonite at a temperature above its melting point (between 213 and 299°C) proceeds as a first order reaction. At 213°C, half the substance decomposes in 410 sec, and at 299°C in 0.25 sec. The gaseous decomposition products contain chiefly N_2, N_2O, NO, CO and CO_2. According to A. J. B. Robertson the activation energy E of the thermal decomposition of cyclonite at these temperatures is 47,500 cal, $\log B=18.5$. The reaction rate in the liquid phase is approximately ten times greater than in the solid phase (below the melting point.)

T. Urbański and Krawczyk [24] studied the stability of cyclonite alone and in mixture with trinitrotoluene and found that:

(1) Samples of cyclonite when heated for 62 hr at 120°C, or for 36.5 hr at 110°C and subsequently for 60 hr at 120°C, contained no acidic decomposition products.

(2) In the Taliani test at 134.5°C cyclonite behaves like tetryl, i.e. it gives a pressure of 11.5 mm Hg after 24 hr heating, as compared with trinitrotoluene which gives 16 mm Hg.

(3) A mixture of 80% cyclonite with 20% trinitrotoluene decomposes somewhat faster, after 24 hr producing a pressure of 39 mm Hg, possibly due to the fact that the cyclonite is partly molten. In spite of this result the mixture should be considered more stable than tetryl.

According to Tabouis, Ortigues and Aubertein [25] cyclonite which has already been subjected to the Abel heat test at 80°C, fails to withstand a repeated test, rapidly darkening a starch–iodide paper. In the authors' opinion this is caused by the presence of traces of nitric acid in the crystals. On heating, this acid is liberated from the crystals, causing the sample to fail when the test is repeated. Cyclonite which contains more than 0.035% of HNO_3 (which is the maximum content permitted by French specifications) may pass in the Abel test the first time. The authors suggest that the traces of nitric acid may be removed by boiling cyclonite in an autoclave at 140°C.

Majrich found that light has a negligible effect on cyclonite. T. Urbański and Malendowicz [26] reported that under the influence of ultra-violet irradiation cyclonite changes colour from white to pale yellow, but undergoes no other alteration. In particular, unlike nitric esters, neither NO, nor NO_2 is evolved from cyclonite.

EXPLOSIVE PROPERTIES

According to Avogadro [19] when exploded cyclonite decomposes with the evolution of CO, CO_2, H_2O, N_2 and an insignificant amount of H_2. This author found the composition of the explosion products (after cooling) to be as follows:

CO	25.22%
CO_2	19.82%
H_2O	16.32%
H_2	0.90%
N_2	37.83%

Avogadro calculated theoretically and found experimentally the following constants:

heat of detonation	1390 kcal/kg
gas volume	910 l./kg
temperature of explosion	3380°C
specific pressure (f)	12,600 m

Other authors gave somewhat lower figures:

1370 kcal/kg	**(Tonegutti [27])**
1359.5 kcal/kg	**(Médard [28])**

The most extensive investigations were those of Apin and Lebedev [29]. They examined the heat of detonation and the gas volume at different densities. The heat of detonation increases from 1290 to 1510 kcal/kg and the gas volume falls from 730 to 630 l./kg when the density is increased from 0.50 to 1.78 g/cm³. The variation of the heat of detonation with density is linear, as shown in Fig. 11. The composition of the gaseous products also changed with density: increase in density was accompanied by an increase in carbon dioxide content.

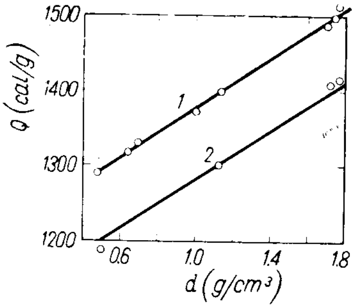


FIG. 11. Heat of detonation of cyclonite against the density of the charge, according to Apin and Lebedev [29]. Curve *1*—liquid water, curve *2*—gaseous water.

Apin and Lebedev gave the following decomposition equation for cyclonite when the density was 1.10:

$$C_3H_6O_6N_6 \rightarrow 0.93CO_2 + 2.01CO + 2.13H_2O + 0.06CH_4 + 3N_2 + 0.75H_2$$

Data concerning the rate of detonation of cyclonite reported by various authors are tabulated below (Table 19).

The values are somewhat higher than those of penthrite.

TABLE 19

RATE OF DETONATION OF CYCLONITE (m/sec)

Density of loading	Kast [31]	T. Urbański and Galas [32]	Laffitte and Parisot [33]	Cook [34]
0.80	—	—	5000	—
0.92	—	—	5500	—
1.0	—	—	—	6080
1.05	—	—	6000	—
1.35	—	7400	—	—
1.40	—	7550	—	—
1.45	—	7705	—	—
1.70	8380	—	—	—

The lead block expansion ranges from 450 to 520 cm³ according to different authors. The relative value taking picric acid as 100, is estimated at about 170.

Cyclonite is less sensitivite to impact than penthrite.

The following figures, based on the investigations of T. Urbański [30], are characteristic of the sensitiveness of cyclonite and tetryl to impact.

The work required to cause:

is:

	10% of explosions	50% of explosions
for penthrite	0.11 kg/cm²	0.20 kg/cm²
for cyclonite	0.14 kg/cm²	0.22 kg/cm²
for tetryl	0.56 kg/cm²	0.92 kg/cm²

According to other authors (e.g. Izzo [35]) the difference in sensitiveness between cyclonite and tetryl is insignificant: as the following drop test figures, using a 2 kg weight, indicate: 30–32 cm for cyclonite, and 40 cm for tetryl.

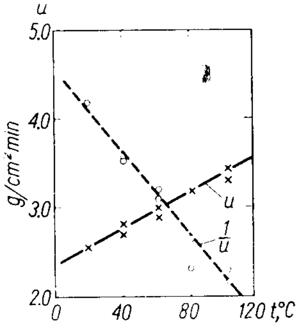


FIG. 12. Rate of burning of cyclonite against the initial temperature, according to Andreyev [36].

Andreyev [36] reports that powdered cyclonite of density about 0.9 burns in tubes of 5–6 mm dia., but when ignited at 20°C cyclonite usually goes out.

Under a pressure of 800 mm Hg the relationship between the mass rate of the burning of cyclonite and the temperature may be expressed by the equation:

$$u_m = -0.0107 + 0.000182\,T_0$$

or

$$\frac{1}{u_m} = 43.92 - 0.0709\,T_0$$

This relationship is illustrated in the diagram (Fig. 12).

The ease with which cyclonite can be detonated is markedly less than that of penthrite, but it is more easily detonated than tetryl.

TOXICITY

No explicitly harmful effect has been noticed among workers employed in the production or handling of cyclonite. Its toxicity appears to be considerably limited by its poor solubility which prevents it entering the blood stream.

Nevertheless the danger of poisoning is always present wherever workers have to deal with cyclonite dust, e.g. in drying and sifting operations and in measuring the dry substance etc. It has been shown that breathing cyclonite dust gives rise to tonic-clonic spasms. These symptoms occur after a few days of breathing the dust. They last for 5–10 min, occurring intermittently and do not pass off at once when the patient is removed from the atmosphere containing cyclonite dust.

The toxicity of cyclonite has led to suggestions for its use as a "selective poison". For instance, it has been patented [37] as a rodenticide. According to the patent specification the lethal dose for rats is 20 mg. It is much less toxic for domestic animals and human being.

CYCLONITE MANUFACTURE

1. THE ACTION OF NITRIC ACID ON HEXAMINE

General information

The oldest and simplest method of preparing cyclonite is based on the introduction of hexamethylenetetramine (hexamine) into an excess of concentrated nitric acid, s. g. 1.50–1.52, free of nitric oxides, at 25–30°C, thereafter pouring the whole into cold water.

According to Hale [5] the reaction may be represented by the following equation:

$$(CH_2)_6N_4 + 4HNO_3 \rightarrow (CH_2\cdot N\cdot NO_2)_3 + 3CH_2O + NH_4NO_3 \qquad (37)$$

whereas Schnurr [38] formulates the reaction as follows:

$$(CH_2)_6N_4 + 6HNO_3 \rightarrow (CH_2\cdot N\cdot NO_2)_3 + 6H_2O + 3CO_2 + N_2 \qquad (38)$$

It appears however that the reaction proceeds according to both equations simultaneously since ammonium nitrate and formaldehyde are formed according to equation (37) and CO_2, N_2 and water according to equation (38). Some of the methylene groups and nitrogen atoms of hexamine are therefore not utilized for the production of cyclonite. The nitration of hexamine with nitric acid requires from four to eight times the theoretical amount of nitric acid.

Apart from the main reactions (37) and (38), side reactions (39) and (40) also take place.

Reaction (39) is a hydrolysis of hexamine resulting in the formation of formaldehyde and ammonia, and reaction (40) consists of the oxidation of formaldehyde with nitric acid.

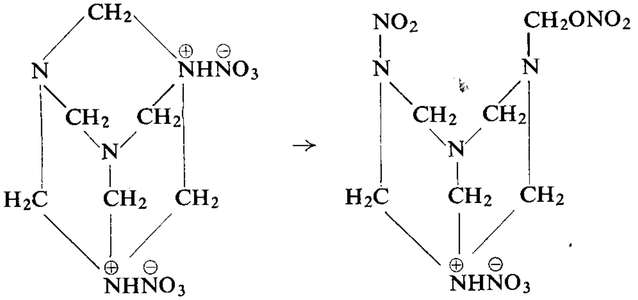
$$(CH_2)_6N_4 + 6H_2O \rightarrow 4NH_3 + 6CH_2O \qquad (39)$$

$$2CH_2O + 2HNO_3 \rightarrow 2HCOOH + H_2O + NO + NO_2 \qquad (40)$$

Apart from the side reactions (39) and (40), others may occur which also result in the formation of explosive substances other than cyclonite.

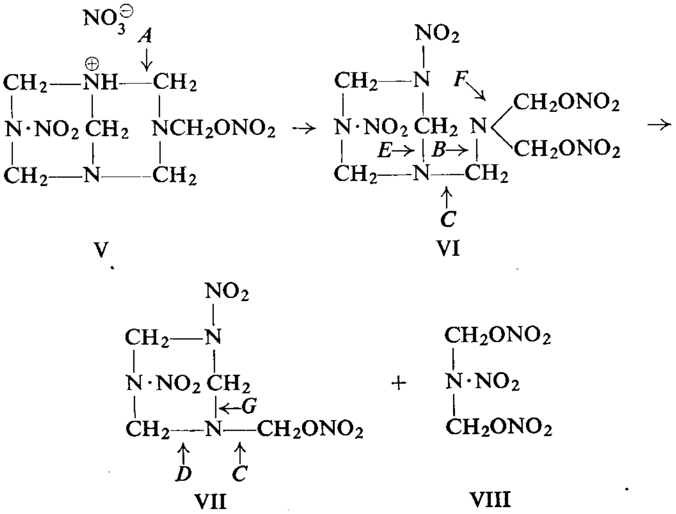
This may be explained by considering the nitration of hexamine with nitric acid as a stepwise degradation by nitrolysis, i.e. the nitration of amine involving the stepwise cleavage of the bond between the nitrogen and carbon atoms. According to Lamberton [39] this idea was first advanced by Linstead. The main work on this subject has been done by British [39] and Canadian [40] authors.

According to the investigations of Hirst, Carruthers *et al.* [41] and Vroom and Winkler [42], the action of nitric acid on hexamine dinitrate (IV) results in the formation of the substance (V) by nitrolysis.



IV V

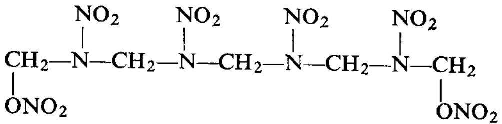
Alcohol groups are esterified with nitric acid. Further nitrolysis may cause the cleavage of N—C bonds. The experimental data (Wright and Myers [43]) indicate that the cleavage of bond *A* most probably occurs with the formation of the hypothetical compound (VI). In turn the latter may undergo nitrolysis at position *B* to form another hypothetical product (VII) [39, 40, 43, 44] and a known compound (VIII) [39, 40, 44], i.e.



V VI VII VIII

On nitrolysis of the bond *C* the compound (VII) finally gives cyclonite. If, however, the bond *D* is nitrolysed, a chain compound may be formed.

Another open-chain methylenenitramine may arise from the compound (VI), if the bounds *E* and *F* are nitrolysed. The compound isolated and identified as 1,9-dinitroxy-2,4,6,8-tetranitro-2,4,6,8-tetrazanonane (IX) is then formed:

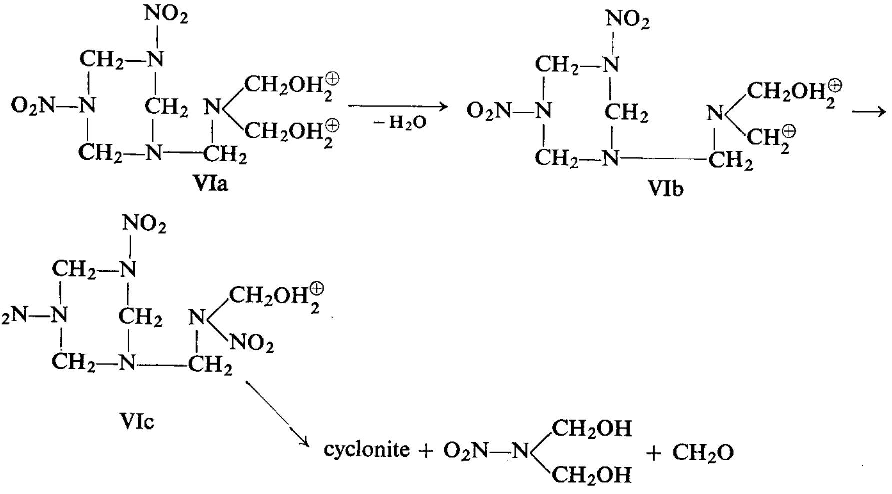


$$\underset{ONO_2}{CH_2}-\overset{NO_2}{N}-CH_2-\overset{NO_2}{N}-CH_2-\overset{NO_2}{N}-CH_2-\overset{NO_2}{N}-\underset{ONO_2}{CH_2}$$

IX

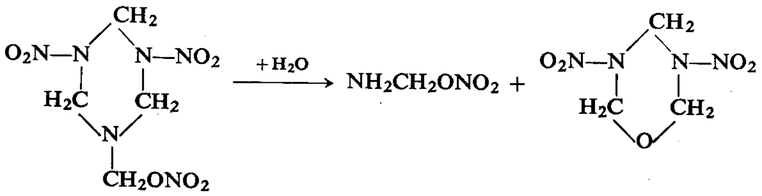
The formation of this substance is favoured by a low nitration temperature. It is unstable and highly sensitive to impact hence its presence in cyclonite is very undesirable.

According to Singh [45] under the influence of the nitracidic ion $(H_2NO_3^{\oplus})$, hexamethylenetetramine first undergoes hydrolysis identical to that leading to the formation of (VI). On hydrolysis the ion (VIa) would be formed or on further heterolysis the ion (VIb), then (VIc). The latter would undergo nitrolysis to form cyclonite, methylnitramine (VIIIa) and formaldehyde:



VIa VIb VIc VIIIa

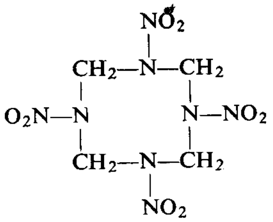
Among the reaction products a cyclic ether is also present to which the structure (X) is ascribed. It is possible that it arises either from the compound (VII) on nitrolysis of the two bonds *D* and *G* and the dehydration of the two alcohol groups so produced, or directly from the compound (VII) on a *sui generis* nitrolysis



VII X

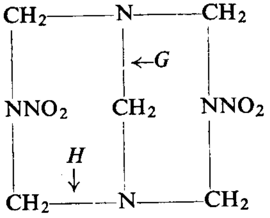
The compound (X) (3,5-dinitro-1-oxa-3,5-diazacyclohexane) dissolves in hot water and crystallizes from solution on cooling. Its melting point is 97°C.

Nitrolysis of the compound (V) may also lead to the formation of the substance (XI) containing an eight-membered ring, called octogen (HMX) (see p. 117) which always accompanies cyclonite, but slightly reduces its power.



XI

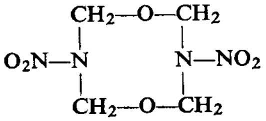
Evidence of the presence of the compound (V) in the intermediate products of nitration has been provided by Wright *et al.* [44] who found that the substance (XII) (1,5-endomethylene-3,7-dinitro-1,3,5,7-tetrazacyclo-octane, or 3,5-dinitro-1,3,5,7-tetrazabicyclo [3,3,1] nonane (DPT)) may be isolated in amount corresponding to 5–12% of the cyclonite by neutralization of the ammonia with spent acid.



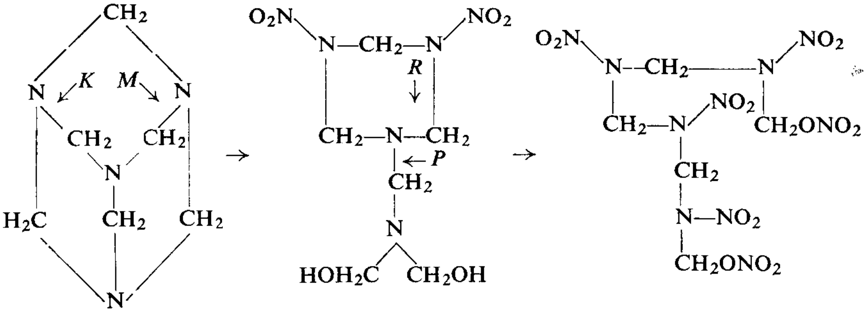
DPT XII
m.p. 213°C

In turn this substance may undergo further nitrolysis which may lead, for example, to the compound (XI) described above while nitrolysis of the bonds *G* and *H* may yield the open-chain compound (IX), which is highly sensitive to impact, and therefore very undesirable.

According to Wright *et al.* [44] DPT can also yield 3,7-dinitro-3,7-diaza-1,5-dioxacyclo-octane (m.p. 263–264°C) under action of nitric acid (99%) and ammonium nitrate:



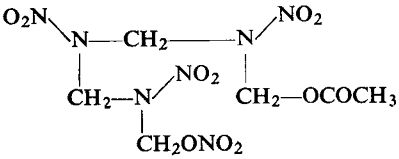
Wright *et al.* [46] pointed out that apart from the compound (VII) nitrolysis of hexamine may also lead to the transient formation of 1-di(hydroxymethyl)-aminomethyl-3,5-dinitro-1,3,5-triazacyclohexane (XIII) [(VI) is the dinitrate of (XIII)] **through the nitrolysis of the bonds *K* and *M*:**



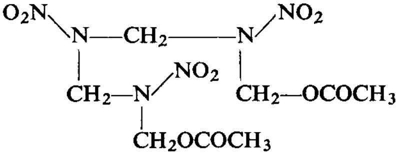
XIII IX

In Wright's opinion the existence of the transient compound (XIII) is proved by the formation of substance (IX) which can be isolated from the products when cyclonite undergoes nitrolysis of the *P* and *R* bonds.

To protect the hydroxyl groups of the compound (VII) or (XIII) by acetylation Wright cooled a solution after nitrolysis to −55°C and then added acetic anhydride at a temperature below −25°C. Apart from cyclonite he isolated 1-acetoxy-7-nitroxy-2,4,6-trinitro-2,4,6-triazaheptane (XIV). The addition of the solution from nitrolysis to acetic anhydride gave a diacetyl derivative: 1,7-diacetoxy-2,4,6-trinitro-2,4,6-triazaheptane (XV):



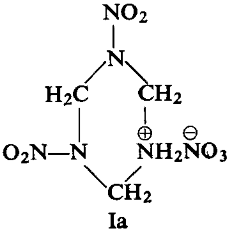
XIV



XV

The nitration of cyclonite at very low temperatures also leads to the formation of a series of other compounds. Some of them are converted into cyclonite by the action of nitric acid at room temperature.

If the nitrolysis of hexamine dinitrate (IV) is conducted at a very low temperature, e.g. −40°C, then, as reported by Hirst *et al.* [41] it is not cyclonite which is formed, but a dinitrate of a dinitro derivative (Ia) (3,5-dinitro-3,5-diazapiperidinium nitrate):



Ia

This was confirmed by Vroom and Winkler [42], who purified the substance (Ia) by dissolving it in anhydrous 75% nitric acid at −20°C, and then adding ice water at temperatures from −20 to −15°C. The purified substance has a melting point of 98–99°C.

The formation of this compound may be explained by the fact that at a low temperature nitrolysis at point *C* (p. 88) is completed to produce amine nitrate and alcohol (or its ester), hence the formation of compound (Ia).

The latter is unstable and undergoes decomposition in hot water with the evolution of formaldehyde, nitrous oxide and ammonium nitrate

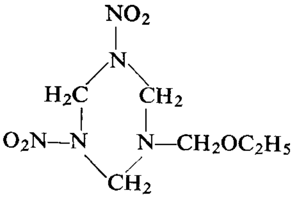
$$\text{Ia} + H_2O \rightarrow 3CH_2O + 2N_2O + NH_4NO_3$$

Cyclonite (I) can be prepared by the action of concentrated nitric acid or acetic anhydride on the compound (Ia) at room temperature. A N-acetyl derivative of dinitro compound (XXIX) (p. 116) is obtained by the action of acetic anhydride on the compound (Ia) in the presence of sodium acetate.

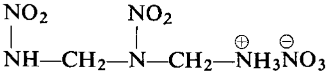
Vroom and Winkler found that under the influence of dilute alkali in an acetone or ethanol medium substance (Ia) gives a compound which, according to the investigations of Chute, McKay, Meen, Myers and Wright [47] is bicyclic (Ic).

Vroom and Winkler believed substance (Ia) to be an intermediate compound in the preparation of cyclonite by the nitrolysis of hexamine. This view was shown to be incorrect by Wright, Berman and Meen [46] who proved that the substance (Ia) cannot exist in the circumstances under which nitrolysis is usually carried out. Therefore Wright *et al.* suggested that the substance (Ia) arises when the reaction solution is diluted, viz. by the nitrolysis of the bonds *C* and *P* in the substances (VII) and (XIII) respectively.

According to Dunning and Dunning [48] the nitration of hexamine dinitrate at a temperatureof about −30°C, followed by treatment of the product with ethyl alcohol permits the isolation of the product of nitrolysis of (VI) at point *B* in the form of an ether (Ib), m.p. 115°C and the compound (IXa) with a chain structure



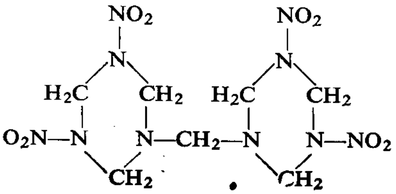
Ib



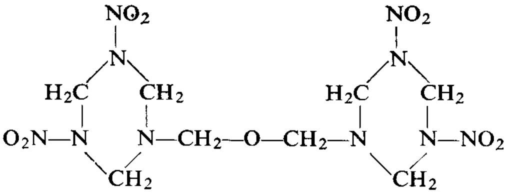
$$\overset{NO_2}{\overset{|}{NH}}-CH_2-\overset{NO_2}{\overset{|}{N}}-CH_2-\overset{\oplus}{N}H_3\overset{\ominus}{N}O_3$$

IXa

In addition, a bicyclic compound (Ic), m.p. 136°C, is present in the products of nitration at a low temperature, whereas nitration of the compound (Ib) with anhydrous nitric acid at a temperature of −30°C leads to the formation of an ether (Id)



Ic



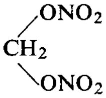
Id

Cyclonite (I) arises from the nitration of compounds (Ib), (Ic) and (Id) at room temperature. The compound (IXa) also yields cyclonite on reaction with acetic anhydride and paraformaldehyde.

According to Karpukhin and Chetyrkin [49] the nitrolysis of hexamine may proceed with the formation of trihydroxymethylamine nitric ester (XVI):

$$\underset{}{(CH_2)_6N_4} + 6HNO_3 \rightarrow \underset{\text{I}}{(CH_2{\cdot}N{\cdot}NO_2)_3} + \underset{\text{XVI}}{N(CH_2O{\cdot}NO_2)_3} + 3H_2O \qquad (41)$$

This may result from the nitrolysis of the compound (VI) at the bond *C*. This ester, like esters (VIII) and (IX), is unstable and readily decomposes. Finally, formaldehyde, split off from hexamine, may yield unstable methylene glycol nitrate (XVII) in the presence of anhydrous nitric acid.



XVII

Owing to the presence of the unstable compounds (VIII), (IX), (XII) and (XIV), various reactions, mainly exothermic, occur in spent acid after the nitration of hexamine and the precipitation of cyclonite with water. Such reactions may lead to explosion hence it is not surprising that the first attempts to manufacture cyclonite, undertaken shortly after World War I, showed that the greatest difficulty in producing cyclonite lies in the danger created by the spent acid. The presence of all these products in spent acid makes its storage extremely dangerous. Some of these by-products may also contaminate cyclonite, lowering its stability.

Searching for ways of getting rid of these products, a method was worked out by which their decomposition was induced under strictly controlled conditions. Decomposition is caused, for instance, by pouring the mixture into hot water after nitration. The amount of water and the temperature are coordinated so that a concentration of 50–55% HNO_3 and a temperature of 70–90°C are maintained. Highly pure cyclonite is precipitated and NO_2 evolved from the decomposition of all unstable products. This is the so-called "degassing process".

Owing to the side-reactions, the yield of nitration of hexamine does not exceed 75–80% (when calculated according to equation (37) or (38)); 110–119 kg of cyclonite can be obtained from 100 kg of hexamine.

Dunning, Millard and Nutt [50] studied the rate of nitration of hexamine with various concentrations of nitrid acid, at 0°C and obtained the results, some of which are given in Table 20 and the graph in Fig. 13.

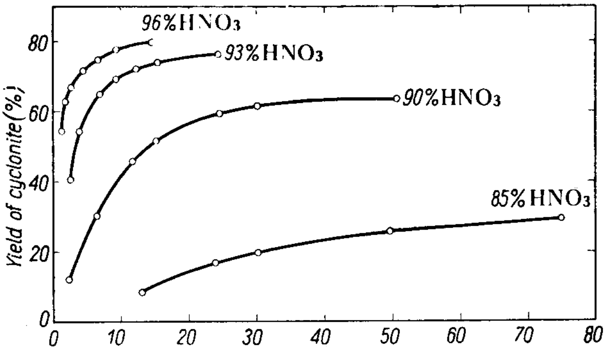


FIG. 13. Rate of nitration of hexamine at 0°C with various concentrations of nitric acid, according to Dunning, Millard and Nutt [50].

Vroom and Winkler [42] also examined the kinetics of the nitration of hexamine to cyclonite with various concentrations of nitric acid at 0°C and drew the following general conclusions:

(1) Maximum yield (about 40% of theoretical calculated on the formaldehyde used i.e. 80% of theoretical calculated on hexamine) can be obtained with all the concentrations of nitric acid used: 88–97% (Fig. 14). The minimum molar ratio of nitric acid to hexamine for maximum yield was found to increase from 26 : 1 with 97% acid to 110 : 1 with 88% acid.

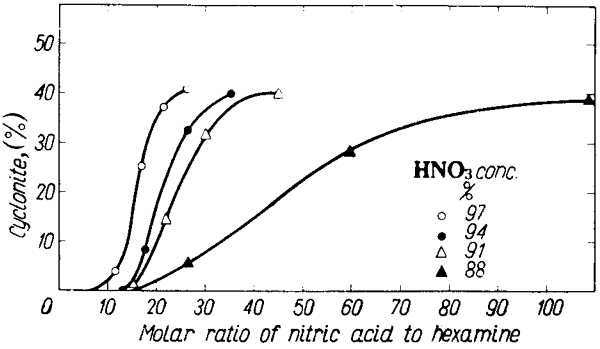


FIG. 14. Effect of nitric acid–hexamine ratio on final yield of cyclonite, according to Vroom and Winkler [42].

(2) The rate of nitrolysis increased rapidly as the molar ratio of nitric acid to hexamine was increased and continued to do so after the molar ratio was raised above that required for maximum yields (Fig. 15).

TABLE 20

Time, min	Concentration of HNO_3				
	99%	96%	93%	90%	85%
	Yield of cyclonite [% of theoretical according to equation (37) or (38)]				
1.5	–	55.7	–	–	–
2.5	66.9	68.7	40.9	13.3	–
6.5	70.2	75.3	65.8	30.5	–
12	74.6	74.7	73.4	45.4	–
24	80.9	79.2	77.2	59.9	14.9
50	80.5	–	–	63.9	26.2
100	–	–	–	–	33.0
120	–	–	–	–	32.6

For 85–96% HNO_3 at 0°C the authors deduce the following empirical equation:

$$x=a\left(1-\mathrm{e}\frac{t}{\tau}\right)$$

According to the British data the heat of nitration of 1 kg of hexamine to cyclonite is 277 kcal/kg. According to the German data (Schnurr [38]) it is about 500 kcal/kg.

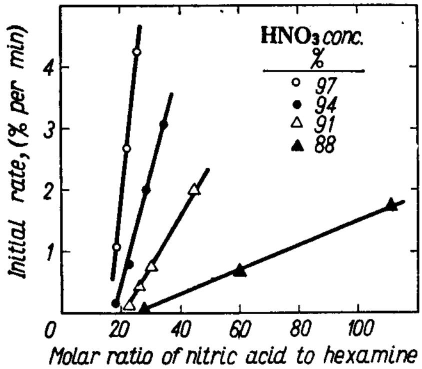


FIG. 15. Effect of nitric acid–hexamine ratio on initial rate of cyclonite formation at 0°C, according to Vroom and Winkler [42].

Gilpin and Winkler [51] report the following heats of nitration when cyclonite is prepared in different ways:

hexamine + nitric acid (97.5%) $-\Delta H=88.0$ kcal/mole
hexamine nitrate + nitric acid (97.5%) $-\Delta H=69.2$ kcal/mole
hexamine dinitrate + nitric acid (97.5%) $-\Delta H=41.7$ kcal/mole

The formation of hexamine dinitrate from hexamine and nitric acid proceeds with a heat effect of $-\Delta H=33.5$ kcal/mole: hexamine nitrate is also converted into dinitrate with a heat evolution of $-\Delta H=15.7$ kcal/mole.

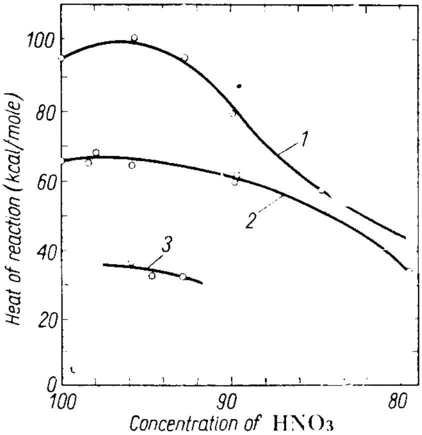


FIG. 16. *1*—Nitration of hexamine at 20°C; *2*—nitration of hexamine at −35.5°C; *3*—nitration of hexamine dinitrate at −35.5°C, according to Dunning, Millard and Nutt [50].

On the basis of these figures the authors infer that hexamine dinitrate is formed at one stage of the nitration of hexamine to cyclonite.

Dunning, Millard and Nutt [50] published a graph (Fig. 16) showing the relation between the heat of nitration of hexamine to cyclonite and the concentration of nitric acid (within the range 80–99%). The graph expresses the integral heat of reaction in kcal per mole of hexamine at 20 and −35.5°C and of hexamine dinitrate at −35.5°C.

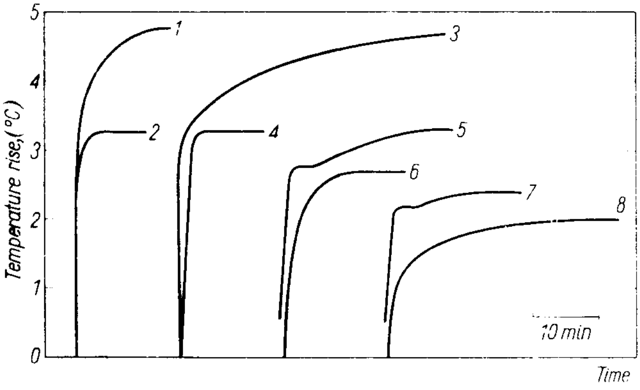


FIG. 17. Temperature changes during the nitration of hexamine with nitric acid, according to Dunning, Millard and Nutt [50]. *1*—Anhydrous acid, nitration temperature 20°C; *2*—anhydrous acid, nitration temperature −35.5°C; *3*—96% acid, nitration temperature 20°C; *4*—96% acid, nitration temperature −35.5°C; *5*—90% acid, nitration temperature 20°C; *6*—90% acid, nitration temperature −35.5°C; *7*—85% acid, nitration temperature 20°C; *8*—85% acid, nitration temperature −35.5°C.

Temperature changes during nitration with various concentrations of acid at 20 and −35.5°C are shown on another graph (Fig. 17). Alterations in the shape of the curves are particularly marked when nitration proceeds at −35.5°C. During nitration with 85% acid at −35.5°C the quantity of heat evolved corresponds to the formation of hexamine dinitrate only.

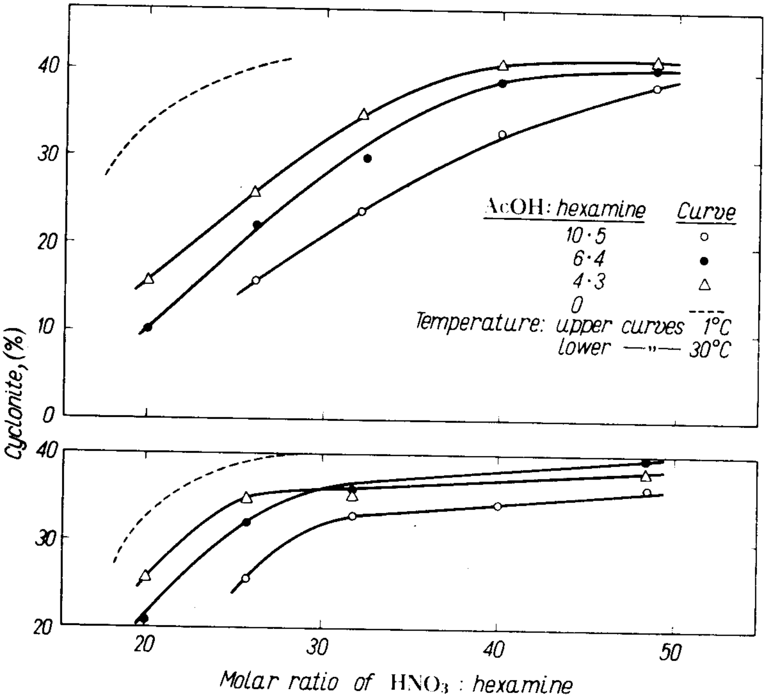


FIG. 18. Effect of nitric acid–hexamine ratio on final yield of cyclonite in acetic acid, according to Kirsch and Winkler [52].

It appears that the reaction stops at this stage under these conditions.

Kirsch and Winkler [52] studied the influence of acetic acid on the nitrolysis of hexamine to cyclonite.

Experiments were made at 1°C and 30°C using various molar ratios of acetic acid/hexamine and varying the nitric acid/hexamine ratio between 26 : 1 and 81 : 1. Acetic acid was found to reduce the reaction rate and the yield of cyclonite (Fig. 18). However even with the most dilute solution of hexamine in acetic acid (molar ratio 10.5 : 1) the final yield of cyclonite approached a maximum of 80% at a molar ratio of nitric acid to hexamine of 48 : 1. In the absence of acetic acid this yield was obtained when the molar ratio was only 26 : 1. It appears that some of the nitric acid was used up in reacting with acetic acid and was therefore unavailable for nitrolysis.

There are various methods of utilizing the spent acid remaining from the nitration of hexamine. It is possible:

(1) To distil off nitric acid and to utilize the ammonium nitrate remaining after distillation for other purposes.

(2) To neutralize the acid with ammonia thus producing ammonium nitrate.

(3) To utilize the acid for preparing hexamine dinitrate and to nitrate the dinitrate, so obtained, to cyclonite. This method was studied by T. Urbański [53] who found, however, that the dinitrate is nitrated to cyclonite with some difficulty, part of the dinitrate remaining unchanged in the product. Since the dinitrate is not sufficiently stable, its presence in cyclonite is undesirable. Nevertheless, it may be used up for a synthesis of cyclonite by adopting a combined method, using hexamine dinitrate, ammonium nitrate and acetic anhydride. This will be discussed in later sections.

A factory at Avigliana (Italy) [54] used an entirely different method for processing and utilizing spent acid containing 45% HNO_3 : after the precipitation of cyclonite in the cold, the acid is subjected to distillation to recover the formaldehyde it contains. It is important to bear in mind that the distillation of acid which has not been passed through the "degassing process" is very dangerous even if carried out at a low temperature under vacuum (40°C is the recommended temperature).

British method

Nitration. In the production method employed in a factory at Bridgwater [55], the nitrator is fed continuously with nitric acid and hexamine and the product of nitration together with the acid flows off, also continuously.

The nitrator of stainless steel, 90 cm long, 32 cm wide, 80 cm high is divided by partition walls into three chambers. Each chamber contains a rotary high-speed stirrer. The first chamber is equipped with three concentric cooling coils of stainless steel 16 mm in diameter with a cooling surface of 1.85 m^2. The next two chambers contain single coils. Gases are expelled to the absorption towers through pipes leading from the lid of the nitrator. The pipe from the first chamber is equipped with a sight glass for observing the colour of the gases. If the colour is brown, the contents of the nitrator should be discharged forthwith into the drowning tank under the nitrator. Hexamine stored on the floor above is introduced by means of a screw conveyer into the first and second chambers of the nitrator through an inlet 5 cm in diameter. The feed mechanism is so arranged that the second chamber receives a quarter of the amount entering the first chamber. The rate at which the total amount of hexamine introduced into the nitrator may be varied is from 56 to 170 kg per hour. The weight of nitric acid introduced into the first chamber through a pipe 2.5 cm dia. is 12 times that of the hexamine.

The temperature in the first and second chambers of the nitrator should not be allowed to rise above 25°C. Control is achieved by intensive cooling. In the third chamber a temperature of 38°C is maintained by passing warm water through the coil.

An overflow for the acid and the reaction product is located in the third chamber about 58 cm from the bottom. The general view of the nitrator is shown in Fig. 19. A drowning tank is situated under the nitrator and connected to it by a pipe 7.5 cm in diameter. The tank is filled with an aqueous solution of urea which, on reaction with nitric oxides, considerably reduces the amount of brown fumes evolved when the nitrator's load is discharged into it.

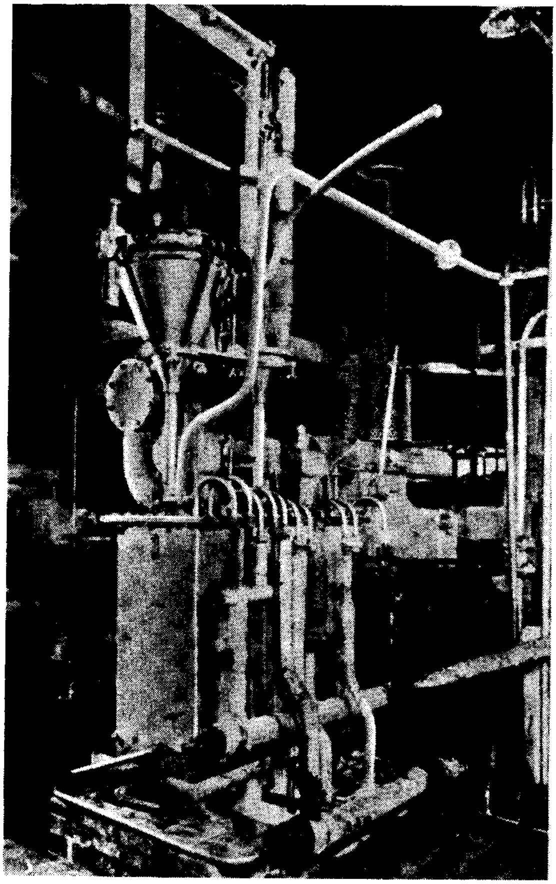


FIG. 19. General view of a continuous nitrator for the preparation of cyclonite [55].

Dilution. The liquid leaving the nitrator through the overflow passes to the diluter below. Here decomposition of unstable nitration products and precipitation of cyclonite takes place. The diluter (Fig. 21), of dimensions 265×60×115 cm, is divided into four chambers, each containing a rotary stirrer (195 r.p.m.) and a heating coil. The diluter is filled continuously up to a level of 65 cm with 55% nitric acid. As the liquid containing more concentrated acid flows in from the nitrator water is added to maintain this concentration. A temperature of 75°C is maintained in the diluter by means of the heating coils.

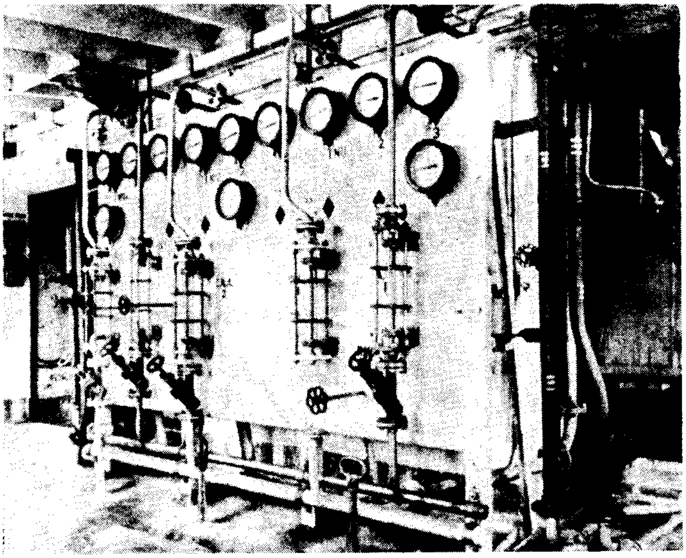


FIG. 20. Nitrator control panel. In the centre the drowning valve handle [55].

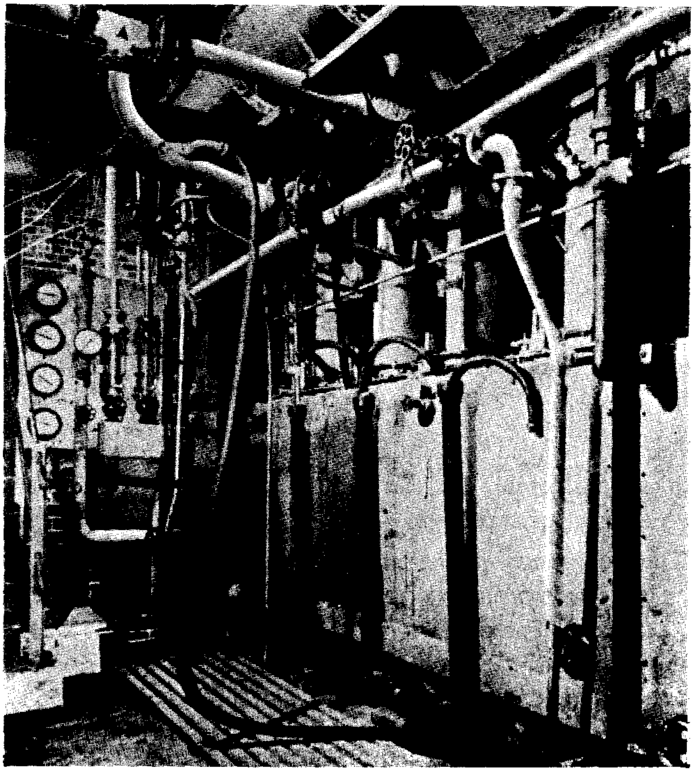


FIG. 21. General view of a diluter [55].

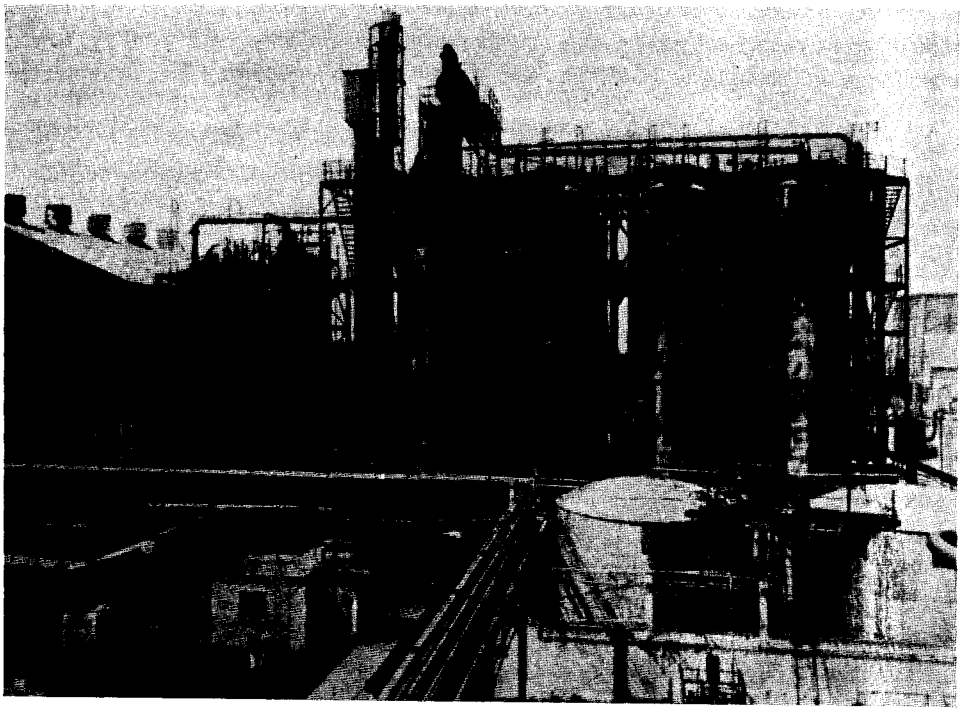


FIG. 22. Stainless steel absorption towers for nitric oxides [55].

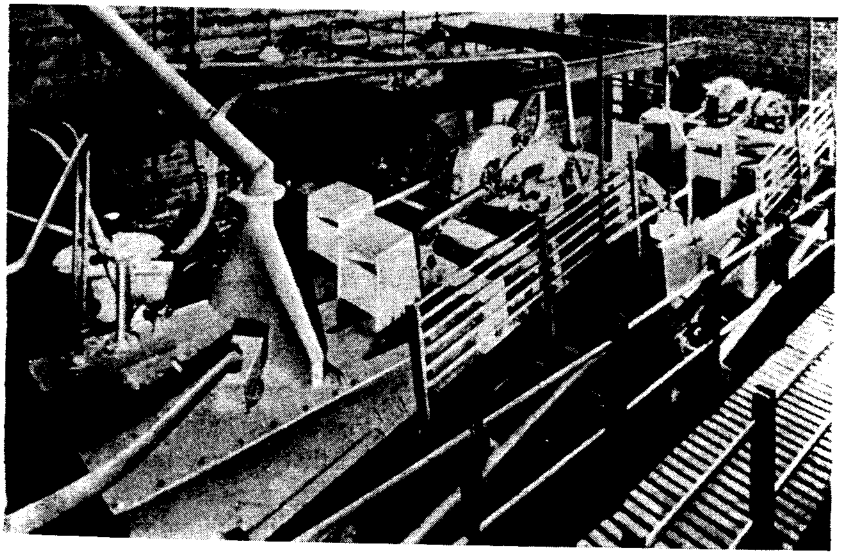


FIG. 23. Continuous vacuum filters (exterior view) [55].

During dilution nitric oxides are evolved abundantly (more than 7 kg/hr). These oxides are extracted by means of a ventilator or steam ejector to a cooling tower where they are brought to 20–30°C. The tower, which measures 1.8 m in diameter and 3.3 m in height, contains steel pipes 38 mm in diameter, cooled externally with water. Here some of the vapour is condensed and nitric oxides pass on to the absorption towers (Fig. 22).

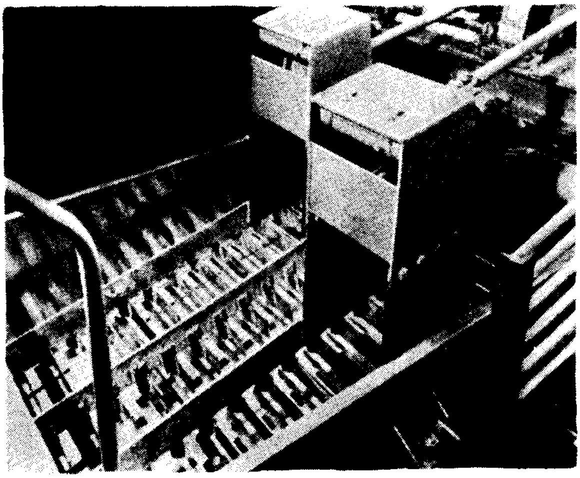


FIG. 24. An interior view of the filter [55].

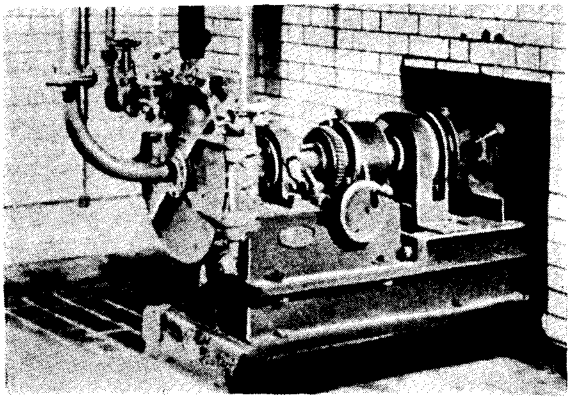


FIG. 25. Disk mill for cyclonite slurry [55].

Filtration. The suspension of cyclonite in nitric acid passes through a pipe 7.5 cm in diameter to a continuous vacuum filter (Fig. 23, 24) encased in stainless steel. The casing is connected with the suction system that conveys nitric oxides to the absorption towers.

The product, after filtration, is conveyed mechanically to another filter on which the cyclonite is washed with cold water until deacidification is as complete as possible. Mechanical scrapers remove wet, washed cyclonite from the filter and it is transferred in trucks to be purified.

Spent acid and that from the absorption towers is distilled over sulphuric acid.

Purification. Crude cyclonite consists of crystals of various sizes. They still contain 0.1–0.2% of nitric acid. For purification a suspension of cyclonite in water is conveyed by suction via a stainless steel container to stainless steel disk mills (Fig. 25) where the cyclonite crystals are finely ground. From the mill the ground product suspended in water is pumped to wooden boiling vats (Fig. 26) 250 cm high and 240 cm dia. The vats have sloping bottoms and are equipped with a stirrer and a pipe supplying live steam. There are two valves in the sides: one, in the lowest part of the vat, can be used for emptying it, the other, 105 cm from the bottom, is used for decantating the liquid. Each load amounts to about 2500 kg of dry cyclonite.

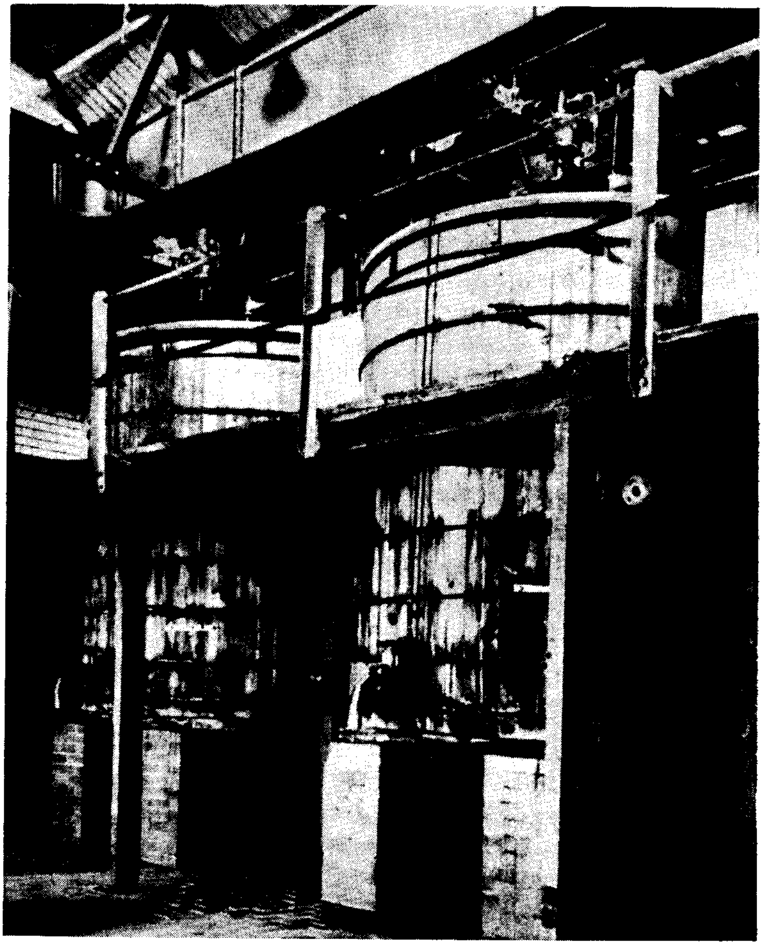


FIG. 26. Cyclonite boiling vats [55].

The suspension of the ground cyclonite in water is allowed to stand in the vat for $\frac{3}{4}$ hr. The liquid is then decanted from above the cyclonite layer and allowed to run through a filter which retains any finely-divided product carried away by the water. After the liquid has been decanted the tub is filled with cold water, its contents are stirred, allowed to stand again, and then decanted. This operation is repeated three times after which the cyclonite is washed with hot water at 90–100 °C for 12 hr. After washing the liquid is decanted and the wet cyclonite is removed from the tub to the filter. The filtered cyclonite containing 10% of water, goes on to the department where explosive mixtures are prepared.

Material balance. To produce 1000 kg of cyclonite, 833 kg of hexamine and 8779 kg of HNO_3 are required; 3482 kg of dilute 55% HNO_3 are recovered plus 3429 kg of HNO_3 from the absorption towers. Thus the net consumption of HNO_3 for nitration is 1868 kg. In addition, 490 kg of H_2SO_4 are used for the concentration of HNO_3.

German method

This has been called the "SH-method" and the cyclonite so obtained "SH-Salz" after Schnurr [38] who developed the process in 1937–38.

Hexamine is added to 99% nitric acid in the proportion of 1 part of hexamine to 8 parts of acid, in a nitrator with a capacity of 1.5 m³ working on the batch system. The temperature is maintained between 5 and 10°C in the nitrator by means of a coil chilled with saline solution. Nitration takes 1 hr.

The contents of a number of nitrators then flow continuously through a series of reactors in which the reaction mixture remains for 2 hr, during which the nitration reaction is completed. In these reactors the temperature is kept at 15–20°C.

When reaction is complete the whole is introduced into a battery of six diluters with water maintained at a temperature of 70–75°C. The first diluter has a capacity of 3 m³, the following four 1.5 m³ each, and the last 3 m³. Sometimes, to initiate decomposition of the unstable nitration products, the presence of a small amount of nitrogen dioxide is required. The amount of water added to the diluter should be such that it maintains a 50% concentration of HNO_3. At this concentration cyclonite is fully precipitated. The suspension of cyclonite in acid then flows to a battery of coolers in which it is cooled gradually to temperatures of 50, 35, and 20°C.

Cyclonite is separated from acid on a vacuum filter and then washed with water.

Originally, the product was purified by boiling with water in an autoclave under a pressure of 3.5 atm, at 140°C for 2 hr. Since this entailed the risk of explosion, it was superseded by crystallization from acetone.

Nitric oxides evolved in the diluter are passed through a cyclone separator which retains liquid droplets, and thence to absorption towers in which the 50% spent acid is concentrated to yield 60% nitric acid.

To produce 1000 kg of cyclonite ("SH-Salz") by this process, 830–840 kg of hexamine and 7100 kg of 99% nitric acid are required, and 5200 kg of HNO_3 are recovered and condensed to its initial concentration. The net consumption of acid is thus 1700 kg.

According to other data the raw material consumption per 1000 kg cyclonite is as follows:

880 kg of hexamine
6800–7760 kg of 99% nitric acid

from which

1720–1850 kg is used in the reaction and
5080–5850 kg, which is recovered as 99% HNO_3.

The German specification for cyclonite ("SH-Salz") is:

melting point	above 200°C
ignition temperature	215–230°C
apparent density	700 g/l.
loss of weight when dried at 100°C for 5 hr should not exceed	0.1%
Abel heat test at 120°C (in a paraffin bath)	10 min without visible change in the test paper (after 20 min a slight coloration is admissible)

An aqueous extract (obtained by boiling cyclonite with water) should have a neutral reaction and contain no $Cl^{\ominus}$, $SO_4^{2\ominus}$ or $NO_3^{\ominus}$ ions. Only traces of ammonia and formaldehyde are admissible (the latter is determined by a fuchsin solution decolorized with SO_2).

The product should not contain more than 0.1% of material insoluble in acetone. The acetone solution should not contain more than 0.2% of acid, calculated as HNO_3. An acetone solution precipitated with water should not contain $SO_4^{2\ominus}$ ions.

Cyclonite intended for high explosive charges should pass through a 0.75 mm mesh sieve. Cyclonite for caps and detonators should pass through a 0.60 mm mesh sieve.

If necessary, cyclonite may be mixed with montan wax.

Cyclonite lots comprised 2500–7500 kg: 12.5 kg in paper bags were packed in cardboard boxes, with lids sealed by means of adhesive tape.

2. PREPARATION OF CYCLONITE FROM HEXAMINE, NITRIC ACID AND AMMONIUM NITRATE

This method was worked out by Knöffler [38], and is known as the "K-method".

It is based on the fact that hexamethylenetetramine contains 6 methylene groups per 4 amino groups, i.e. the number of amino groups is lower then that required for obtaining two molecules of cyclonite. In order to supply the additional two amino groups the appropriate amount of ammonium nitrate is added to the nitrating nitric acid in accordance with the equation:

$$C_6H_{12}N_4 + 2NH_4NO_3 + 4HNO_3 \rightarrow 2(CH_2N\cdot NO_2)_3 + 6H_2O \qquad (42)$$

An increase in yield over that calculated on the basis of the hexamine used is thus obtained. The reaction proceeds only at a high temperature (about 80°C). This has gained favour because the reaction mixture of nitric acid, hexamine and ammonium nitrate may be heated to the desired reaction temperature without fear of an explosion, whereas a reaction mixture without ammonium nitrate may be dangerous even at a temperature just above 25°C.

According to the investigations of T. Urbański and Szyc-Lewańska [56], cyclonite is also formed by the action of nitric acid and ammonium nitrate on hexamethylenetriperoxidediamine which is discussed on p. 225.

It is assumed that cyclonite is formed from this substance since it contains the grouping $-CH_2-N$. Six methylene groups are attached to two nitrogen atoms. The deficiency in nitrogen atoms is made good by ammonium nitrate, as described above.

According to a description from a factory at Elsnig nitration is conducted in reactors with a capacity of 500 l., in which 1 part of hexamine per 8.6 parts of nitric acid plus the calculated amount of ammonium nitrate are added to 99% nitric acid.

A temperature of 15°C is maintained in the nitrator by cooling and the reaction mixture enters the reactor below, which is equipped with a number of vertical pipes warmed externally with hot water. Here the reaction mixture is heated to 80°C and this temperature is maintained for 30 min while the reaction (42) involving ammonium nitrate takes place. The mixture is then introduced into the container below where the whole is cooled to 20°C.

Cyclonite in approximately 90% yield is crystallized in the following way: the product is separated from the spent acid on a rotary filter and after being washed with water and neutralized with a 5% solution of sodium carbonate it is crystallized from acetone.

In the method outlined above it is particularly difficult to utilize the spent acid due to the considerable amount of ammonium nitrate it contains. The usual method in which the nitric acid is recovered by distillation with sulphuric acid and condensation is not practicable since ammonium salts are deposited in the retorts, distillation columns, pipes, valves etc.

The following method has therefore been developed: after the cyclonite has been filtered off, the spent acid is cooled to −12°C. Ammonium trinitrate is then crystallized, separated in a centrifuge and recycled to the nitrator. After centrifuging the acid contains 10% of cyclonite and a considerable amount of ammonium nitrate. It is further processed so as to yield cyclonite, nitric acid being converted into ammonium nitrate.

The acid is allowed to run into a container of 3 m^3 capacity where it is neutralized with gaseous ammonia while the temperature is raised to 70°C. The cyclonite thus formed is separated on a vacuum filter, and the filtrate is cooled when about two-thirds of the ammonium nitrate crystallizes. The latter is separated in a centrifuge, and used in the preparation of explosive mixtures. The small amounts of hexamine dinitrate and ammonium nitrate that remain in the liquor are recovered, as a mixture, by concentrating the solution, after which they are returned to the nitrator.

To produce 1000 kg of cyclonite

480–500 kg of hexamine
4800 kg of ammonium nitrate
8600 kg of nitric acid

are required from which:

3600 kg of ammonium nitrate
7200 kg of nitric acid

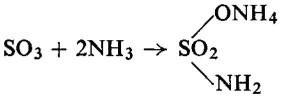
are recovered.

The consumption of ammonium nitrate amounts to 1200 kg and of nitric acid to 1400 kg.

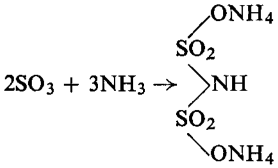
3. PREPARATION OF CYCLONITE FROM SULPHAMIC ACID, FORMALDEHYDE AND NITRIC ACID

A method for the preparation of cyclonite from sulphamic acid, formaldehyde and nitric acid was developed in 1934 by Wolfram [38]. It is known as the "W-method" and the cyclonite so obtained is known as "W-Salz". The W-method is based on the condensation of the potassium salt of sulphamic acid with formaldehyde and the nitration of the condensation product ("white salt", a Schiff's base of the type XVIII) with nitric acid.

Starting from sulphuric anhydride and ammonia the following series of reactions was employed:



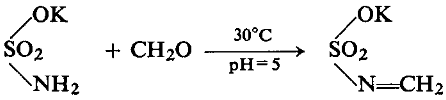
$$SO_3 + 2NH_3 \rightarrow SO_2\begin{array}{l}\nearrow ONH_4\\ \searrow NH_2\end{array} \qquad (a)$$



$$2SO_3 + 3NH_3 \rightarrow \begin{array}{l}\quad\nearrow ONH_4\\ SO_2\\ \quad\searrow\\ \qquad NH\\ \quad\swarrow\\ SO_2\\ \quad\searrow ONH_4\end{array} \qquad (b)$$

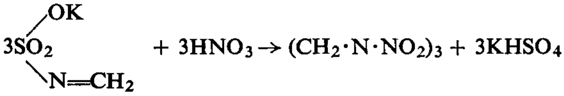
$$NH_4OSO_2NH_2 + (NH_4OSO_2)_2NH + Ca(OH)_2 \rightarrow (NH_2SO_2O)_2Ca + CaSO_4 + 3NH_4OH \qquad (c)$$

$$(NH_2SO_2O)_2Ca + K_2SO_4 \rightarrow 2NH_2SO_2OK + CaSO_4 \qquad (d)$$



$$SO_2\begin{array}{l}\nearrow OK\\ \searrow NH_2\end{array} + CH_2O \xrightarrow[pH=5]{30°C} SO_2\begin{array}{l}\nearrow OK\\ \searrow N{=}CH_2\end{array} \qquad (e)$$

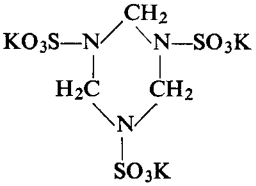
XVIII



$$3SO_2\begin{array}{l}\nearrow OK\\ \searrow N{=}CH_2\end{array} + 3HNO_3 \rightarrow (CH_2\cdot N\cdot NO_2)_3 + 3KHSO_4 \qquad (43)$$

The ammonia evolved in reaction (c) during the preparation of calcium sulphamate is recycled to take part in reactions (a) and (b). Since calcium sulphamate dissolves fairly easily, it is transformed into the sparingly soluble potassium salt by reaction (d).

The mechanism of these reactions has been examined by Binnie, Cohen and Wright [57]. X-Ray investigations of the crystal lattice of this compound and cryometric studies, have shown that the compound XVIII has the structure of a cyclic trimer, i.e. that of 1,3,5-triazacyclohexanetrisulphonic acid (XVIIIa).



XVIIIa

On treatment with nitric acid under completely anhydrous conditions (80% nitric acid and 20% SO_3) the compound (XVIIIa) gives cyclonite by substitution of the sulpho groups with nitro groups (80% of the theoretical yield). The reaction is interesting because the cyclonite is not decomposed in spite of the presence of sulphuric acid in the nitrating mixture. The reason is that the medium is completely anhydrous due to the presence of an excess of SO_3.

For the nitration of compound (XVIII) the following nitrating mixture was used at Krümmel [38]:

HNO_3	80–81%
H_2SO_4	4–5%
SO_3	13–14%
N_2O_4	1–2%

This mixture was prepared from 99% nitric acid and sulphuric anhydride. "White salt" (XVIII) was introduced to the mixture at a temperature of 30°C. The heat evolved during nitration (approximately 500 kcal per kg of cyclonite) was removed by means of a cooling coil. The cyclonite so formed was partly suspended and partly dissolved in the nitrating liquid. Addition of water completely precipitated the product which was separated on a vacuum filter. The composition of the spent acid was:

HNO_3	23%
H_2SO_4	13–14%
$KHSO_4$	10–11%
H_2O	52–54%

The cyclonite was then washed with water and after neutralizing the residual acid with a 5% solution of sodium carbonate it was recrystallized. Initially, cyclonite was crystallized from nitrobenzene. However this proved to be dangerous due to the high boiling point of the solvent; after a plant had been destroyed by an explosion, crystallization from acetone was adopted. The spent acid is denitrated, and $KHSO_4$

recovered from the retort. The yield obtained ranked from 80 to 90%, depending on the formaldehyde used.

This method proved less profitable than others, and was discontinued by the end of World War II.

4. PREPARATION OF CYCLONITE FROM PARAFORMALDEHYDE, AMMONIUM NITRATE AND ACETIC ANHYDRIDE

This method was worked out by Ebele [38], and known as the "E-method" in Germany. The same method was also invented independently by Ross and Schiessler [58] in Canada in 1940. In this process paraformaldehyde and ammonium nitrate undergo dehydration under the influence of acetic anhydride with the formation of cyclonite according to the equation:

$$3CH_2O+3NH_4NO_3+6(CH_3CO)_2 \rightarrow (CH_2N\cdot NO_2)_3+12CH_3COOH \qquad (44)$$

The studies of Wright *et al.* [59], and Winkler *et al.* [60] led to the conclusion that this method involves two essential steps.

The first is the synthesis of hexamethylenetetramine in acetic anhydride from paraformaldehyde and ammonium nitrate:

$$6CH_2O+4NH_4NO_3+3(CH_3CO)_2O \rightarrow C_6H_{12}N_4+4HNO_3+6CH_3COOK \qquad (45)$$

The second step is the known nitrolysis:

$$C_6H_{12}N_4+4HNO_3 \rightarrow (CH_2N\cdot NO_2)_3+NH_4NO_3+3CH_2O \qquad (46)$$

The detailed mechanism of this reaction will be dealt with later on p. 113.

The advantage of this method lies in the fact that the preparation of cyclonite is accomplished without using hexamine and nitric acid so that the dangers of nitration are avoided. On the other hand acetic anhydride is required, which is rather expensive.

This method is safe on condition that it is conducted as described below, by adding the reactants to the previously warmed acetic anhydride. Otherwise, the exothermic nature of the reaction may cause an explosion. It is therefore inadmissible to mix the reactants and heat up the mixture, since this causes too violent a reaction. Addition of boron fluoride to the mixture promotes the initiation of reaction and increase its safety.

It appears that apart from cyclonite, octogen (XI), a N-acetyl derivative (XXX) and a number of nitramines, mainly chain compounds, less stable than cyclonite, are also formed by this method, in side-reactions. Hence the cyclonite obtained has a relatively low melting point (190–195°C) and may be less stable than that prepared by other methods. The conduct of the reaction in the presence of boron fluoride reduces the number of by-products formed.

Since the majority of the chain compounds formed as by-products are more soluble in acetic acid than cyclonite itself, contamination of the latter with these substances may be partly avoided by filtering off the cyclonite from the spent acid. The by-products can be recycled since some of them may be transformed into cyclonite on treatment with acetic anhydride and ammonium nitrate under the conditions in which the main reaction is conducted.

The by-products obtained during the reaction are discussed more fully on p. 113.

Manufacture at Bobingen [38,61] was on the following lines. A reactor of aluminium or stainless steel (capacity 1.2 m^3) is filled with acetic anhydride and then 0.4% of BF_3 is added. Acetic anhydride is warmed to 60–65°C and at this temperature ammonium nitrate and paraformaldehyde are added gradually. Due to the high temperature and the presence of boron fluoride the reaction starts at once and heat is evolved. The heating is then turned off and the temperature maintained by cooling, within the range 60–65°C. The addition of the reactants requires approximately 6 hr, after which the contents of the reactor are cooled to 20°C. The precipitated cyclonite is separated from the solution on a vacuum filter. The by-products remain in the spent liquor.

160 kg of cyclonite are obtained from each reactor. The output from a number of reactors, amounting to about 800 kg, is stabilized by boiling in an autoclave at 140°C.

The spent acid is distilled in order to separate acetic acid. The paste containing cyclonite and by-products that accumulate on the bottom of the retort is removed continuously, through a syphon overflow. The greater part of this mass (about 80%) is dissolved in acetic anhydride and returned to the reactor while the residue (about 20%) is mixed with ammonium nitrate to make cheap explosives.

Acetic anhydride is prepared from distilled acetic acid by the ketene method with ethyl phosphate as a catalyst. The water from the first cyclonite wash on the vacuum filter contains on an average 20% of acetic acid which is recovered by extraction with ethyl acetate.

The yield of cyclonite on a plant scale is 63–65% calculated as formaldehyde; on a laboratory scale a yield of up to 80% may be obtained.

To produce 1000 kg of cyclonite requires

630–635 kg of paraformaldehyde
1800 kg of ammonium nitrate
and 5000–5100 kg of acetic anhydride containing about 19 kg of boron fluoride.

From the spent acid

about 110 kg of the paste of cyclonite and by-products
and 4150–4200 kg of acetic anhydride

are recovered.

Thus the consumption of acetic anhydride per 1000 kg of cyclonite amounts to *ca.* 800 kg.

According to the German data the product obtained contains:

93.5% of cyclonite
6.0% of octogen
0.5% of the acetyl derivative (XXIX)

5. PREPARATION OF CYCLONITE FROM HEXAMINE DINITRATE, AMMONIUM DINITRATE AND ACETIC ANHYDRIDE

This method is a combination of the first and fourth methods. It was worked out by W. E. Bachmann in the U.S.A. in 1941 and independently by Köffler [38, 62] in Germany in 1943. In Germany it was known as the "KA-method".

Hexamine dinitrate is reacted with ammonium dinitrate in the presence of acetic anhydride. Unlike the E-method no paraformaldehyde is used, all the necessary methylene groups being provided by hexamine, and the additional amino groups (as in the K-method) by ammonium nitrate. Nitric acid enters into reaction in combination with hexamine and as ammonium dinitrate:

$$C_6H_{12}N_4\cdot 2HNO_3 + 2(NH_4NO_3\cdot HNO_3) + 6(CH_3CO)_2O \rightarrow 2(CH_2N\cdot NO_2)_3 + 12CH_3COOH \quad (47)$$

The yield by this method, calculated on the CH_2 groups in hexamine dinitrate, amounts to 75–80%.

The advantage of the KA-method, as compared with the E-method, lies in the fact that the methylene and part of the amino groups required are introduced in a dehydrated form, hexamine being their source, whereas when paraformaldehyde is used, dehydration is essential. Hence less acetic anhydride is used in the KA-method than in the E-method.

At the Bobingen factory hexamine dinitrate is prepared by the action of 50% nitric acid on hexamine at a temperature below 15°C, using spent acid from the nitration of pentaerythritol. $NH_4NO_3\cdot HNO_3$ is obtained by the reaction of equimolecular amounts of ammonium nitrate and concentrated nitric acid.

325 kg of acetic anhydride is mixed in the reactor with 187 l. of filtrate from the previous batch. While maintaining the temperature between 40 and 50°C five portions of 23.9 kg of ammonium dinitrate and of 22 kg of hexamine dinitrate are added to the reactor, after which 271 kg of acetic anhydride are introduced followed by a further 5 portions of ammonium dinitrate and hexamine dinitrate, as above. Experience showed that a small excess of hexamine dinitrate is useful. After the last portions of the reactants have been added, the contents of the reactor are heated to 60°C and this temperature is maintained for 0.5 hr. This procedure requires 4 hr, after which the whole is cooled to 20°C. Cyclonite, crystallized in 70–71% yield, is filtered off. The melting point of the product ranges between 188 and 190°C.

Part of the filtrate is recycled, while most of it undergoes distillation. On distillation, a paste-like residue of highly impure cyclonite (m.p. 160°C — total melting) is obtained. Under the reaction conditions this product may be transformed into cyclonite, after it is returned to the reactor.

The filtered cyclonite is washed with water, to yield a 30% solution of acetic acid from which concentrated acetic acid is recovered by extraction with ethyl acetate.

The consumption of ethyl acetate amounts to 1 kg per 100 kg of cyclonite. From the recovered concentrated acetic acid 85% acetic anhydride is produced by the ketene method.

To produce 1000 kg of cyclonite the KA-method requires

400 kg	of hexamine
430 kg	of ammonium nitrate
680 kg	of 99% nitric acid
2400 kg	of acetic acid (as anhydride)

from which about 1950 kg of acetic acid are recovered, i.e. the net consumption amounts to about 450 kg.

During World War II W. E. Bachmann *et al.* [62, 63, 64] worked out a process of cyclonite manufacture identical in principle to the above. Bachmann's idea was to combine Ross's E-method with hexamine nitration. A semi-plant scale equipment based upon the new "combined" Bachmann process came into operation at the end of 1941. After the procedure for cyclonite production had been worked out, the problem of the regeneration of acetic acid was solved; in the United States cyclonite was produced mainly by this method.

The procedure worked out by Bachmann differs from that described above in that the solution of 117 parts of 98% nitric acid in 508 parts of acetic anhydride is first prepared while maintaining the temperature between 5 and 15°C.

The solution is then heated to 70–75°C and a mixture of 114 parts of ammonium nitrate with 192 parts of hexamine dinitrate is introduced gradually in portions (hexamine dinitrate is prepared beforehand by treating 65 parts of 70% nitric acid with a solution of 40 parts of hexamine in 70 parts of water, at 15°C; the mixture is then cooled to 5°C and the dinitrate is filtered off in 95% yield).

When the mixture of ammonium nitrate with hexamine nitrate is introduced to a solution of nitric acid in acetic anhydride heat is evolved and the temperature rises spontaneously. At that point heating should be stopped and the temperature maintained within the limits of 73–78°C, by cooling. After the reactants have been introduced the whole is stirred for 15 min longer, maintaining the temperature at 75°C by heating. The whole is then cooled to 60°C, and the product is filtered, washed with acetic acid, and then with water. The melting point of the product thus obtained is 203–204°C. 195–202 parts of cyclonite are obtained (61–63% of the theoretical yield). The yield increases to 70–73.5% if the mixture is cooled after the reaction to 25°C, but the product then contains a lot of octogen, hence its melting point is 191–202°C.

The heat of reaction was determined by Gilpin and Winkler [51]. The reaction of a solution of hexamine with Bachmann's reagent to yield cyclonite is exothermic: $-\Delta H = 140$ kcal/mole.

Hexamine mononitrate gives a heat effect of $-\Delta H = 126$ kcal/mole with Bachmann's reagent while hexamine dinitrate with the same reagent gives $-\Delta H = 118$ **kcal/mole.**

At the Elsnig factory the crystallization of cyclonite is accomplished as follows. About 110 kg of cyclonite are introduced into a closed tank, with a capacity of 1000 l., equipped with stirrers and lined with a woollen filter cloth. Approximately 900 l. of acetone heated to 50°C are run into the tank to dissolve the cyclonite, after which the solution filtering through the filter cloth is drained down into a 3000 l. tank. (The filter cloth is changed every 10 hr). Here about 1350 l. of water is added over a period of 5 min, while the temperature is maintained at 25°C, and cyclonite is precipitated from the acetone solution in the form of fairly large crystals: approximately 90% of the total are longer than 0.1 mm. The precipitated cyclonite is separated on a vacuum filter.

Acetone vapour is recovered in an absorber. The aqueous acetone filtered from the cyclonite is purified and freed from water by distillation in a rectifying column. The acetone losses amount to 7–8% per 100 kg of cyclonite.

According to data from German factories, desensitization ("phlegmatization") of cyclonite is carried out as follows. A phlegmatizing tank, equipped with a heating or cooling jacket, is filled with 450–500 l. of hot water (80–88°C). The stirrer (170 r.p.m.) is then started and 120 kg of recrystallized cyclonite is poured in. Molten montan wax is then introduced in the proportion of 5–10% the weight of cyclonite.

If a smaller amount of wax is used, a higher temperature should be maintained, viz. addition of 5% wax requires about 88°C and 10% between 80 and 82°C.

After the wax has been added and incorporated, the cooling should start immediately by introducing cold water into the jacket. The overall procedure requires approximately 2 hr. The phlegmatized cyclonite is filtered on a vacuum filter, dried at 100°C and sieved.

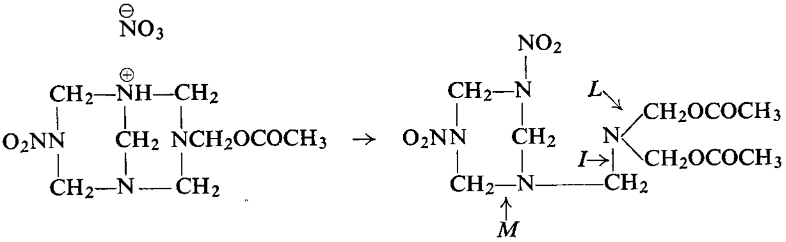
To differentiate phlegmatized cyclonite from the non-phlegmatized product a dye is added during mixing.

THE THEORY OF CYCLONITE FORMATION BY METHODS 4 AND 5

Examination of the mechanism of cyclonite formation has clarified the conditions under which various products similar in structure to cyclonite are formed. These products always accompany cyclonite prepared by method 5 and often that prepared by method 4.

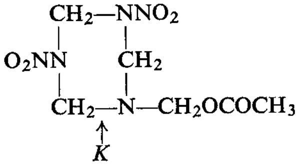
In method 5, as in method 1, nitrolysis of hexamethylenetetramine occurs, the alcohol groups so produced being esterified with acetic anhydride and not with nitric anhydride as in method 1. The most important by-product formed to the extent of nearly 10% by method 5 is octogen (XI). It is produced as outlined above, as a result of hexamine nitrolysis (p. 90).

In the presence of acetic anhydride hexamethylenetetramine dinitrate may be transformed into the product (XIX), and then into (XX). These are the analogues of substances (V) and (VI).

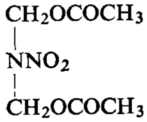


XIX XX

The nitrolysis of the bond *I* in substance (XX) results in the formation of products (XXI) 1-acetoxymethyl-3,5-dinitro-1,3,5-triazacyclohexane and (XXII) bis(acetoxymethyl)-nitramine

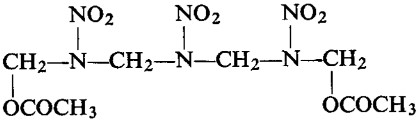


XXI



XXII

Substance (XXI) may subsequently undergo nitrolysis at *K* to form the nitramine ester 1,7-diacetoxy-2,4,6-trinitro-2,4,6-triazaheptane (XXIII) (a chain compound "BSX", m.p. 154–155°C):



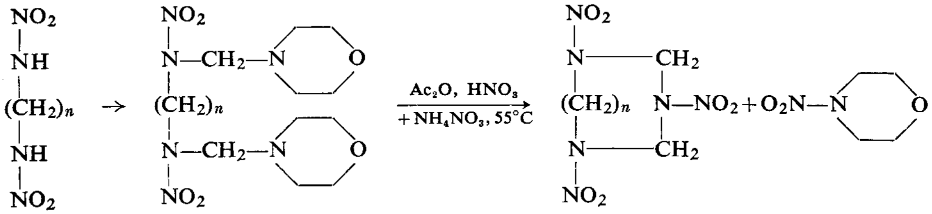
$$\underset{\displaystyle OCOCH_3}{CH_2}-\overset{\displaystyle NO_2}{N}-CH_2-\overset{\displaystyle NO_2}{N}-CH_2-\overset{\displaystyle NO_2}{N}-\underset{\displaystyle OCOCH_3}{CH_2}$$

XXIII

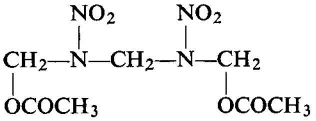
This compound sometimes occurs in an appreciable quantity in cyclonite prepared by methods 4 and 5. It is an undesirable by-product due to its high sensitiveness to impact and to its relatively poor stability, which is lower than that of cyclonite. Bachmann and Sheehan [62] found that stirring the reactants at a low temperature (e.g. 0°C) and subsequently heating the whole to 75°C favours the formation of the product (XXIII).

On the other hand, Wright *et al.* [47] found that the nitrolysis of hexamine with nitric acid in the presence of acetic anhydride but in the absence of ammonium nitrate involves a decrease of the yield of cyclic products. The amount of the chain compound (XXIII) formed is then increased.

The fact that nitramino groups may arise under the influence of ammonium nitrate and nitric acid in the presence of acetic anhydride is shown by the reaction in which aminomethylnitramines (obtained from nitramine, formaldehyde and, say, morpholine) are treated with acetic anhydride in the presence of ammonium nitrate and nitric acid at 55°C (Lamberton *et al.* [65]):



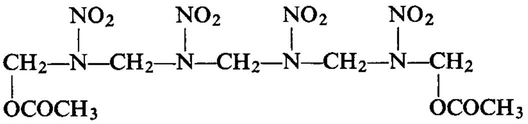
Compound (XXIII) may undergo nitrolysis resulting in the formation of the ester (XXIV) — 1,5-diacetoxy-2,4-dinitro-2,4-diazapentane:



$$\underset{\mathrm{OCOCH_3}}{\mathrm{CH_2}}-\overset{\mathrm{NO_2}}{\mathrm{N}}-\mathrm{CH_2}-\overset{\mathrm{NO_2}}{\mathrm{N}}-\underset{\mathrm{OCOCH_3}}{\mathrm{CH_2}}$$

XXIV

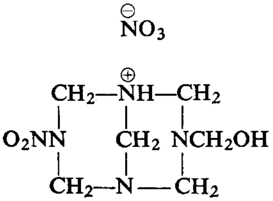
The chain compound XXV, 1,9-diacetoxy-2,4,6,8-tetranitro-2,4,6,8-tetrazanonane m.p. 182.5–183.5°C may also arise from compound (XX) by nitrolysis of the bonds *L* and *M*.



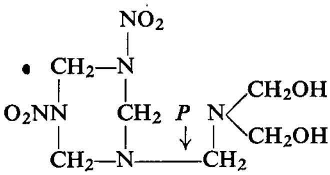
$$\underset{\mathrm{OCOCH_3}}{\mathrm{CH_2}}-\overset{\mathrm{NO_2}}{\mathrm{N}}-\mathrm{CH_2}-\overset{\mathrm{NO_2}}{\mathrm{N}}-\mathrm{CH_2}-\overset{\mathrm{NO_2}}{\mathrm{N}}-\mathrm{CH_2}-\overset{\mathrm{NO_2}}{\mathrm{N}}-\underset{\mathrm{OCOCH_3}}{\mathrm{CH_2}}$$

XXV

It is possible that there may not be time for the free alcohols (XXVI) and (XXVII) to be transformed into esters (XIX) and (XX), but under the influence of ammonium nitrate they will undergo "demethylation" with loss of formaldehyde molecules.



XXVI



XXVII

If compound (XXVI) is "demethylated", the compound (XII) (DPT) will be produced as a result of the additional nitration.

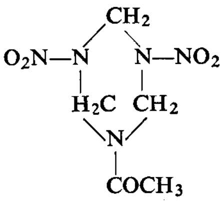
In method 5 ammonium nitrate not only supplies the necessary number of nitramino groups, but also brings about the loss of molecules of formaldehyde from the intermediate products of types (XXV) and (XXVII). If the time is too short for the esterification of the alcohol (XXIII), nitrolysis of this compound occurs first at the bond *P* (not at bonds *L*, *M* and *I* as in the acetylated product (XX)) and cyclonite is formed.

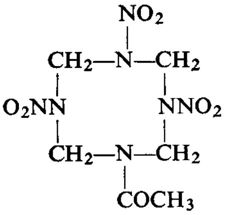
Experiments have shown that the chain compounds of types (XXIII), (XXIV) and (XXV) or the compound (IX) described earlier may also undergo cyclization under the influence of nitric acid, acetic anhydride and ammonium nitrate (Chapman [66]).

On synthesis of cyclonite from paraformaldehyde, ammonium nitrate and acetic acid (method 4), products with cyclic structure, chiefly cyclonite and octogen, may arise due to the polymerization of the transiently-formed, hypothetical methylenenitramine (XXVIII) [67]:

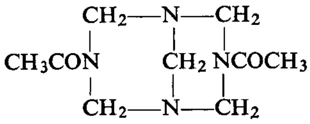
$$CH_2O + NH_4NO_3 \rightarrow \underset{\text{XXVIII}}{CH_2{=}N{-}NO_2} + 2H_2O$$

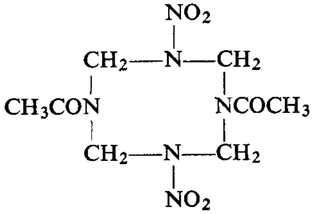
There is an alternative view (e.g. expressed by Wright *et al.* [59]) that hexamethylenetetramine is first formed and then nitrolysed. This assumption is said to be supported by the separation from the reaction products of both methods 4 and 5 of the cyclic products (XXIX) 1-aceto-3,5-dinitro-1,3,5-triazacyclohexane and (XXX) 1-aceto-3,5,7-trinitro-1,3,5,7-tetrazacyclo-octane which may also be obtained from hexamine by treating it with nitric acid and acetic anhydride:


XXIX


XXX

The reaction products (in methods 4 and 5) also include other cyclic N-acetyl derivatives: (XXXI) 1,5-diaceto-3,7-endomethylene-1,3,5,7-tetrazacyclo-octane and (XXXII) 1,5-diaceto-3,7-dinitro-1,3,5,7-tetrazacyclo-octane:


XXXI


XXXII

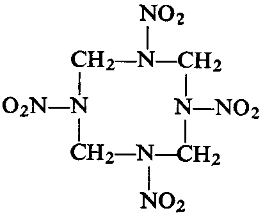
Under the influence of acetic anhydride and nitric acid compound (XXX) gives (XXV) (Marcus and Winkler [68]).

The transient formation of hexamine in method 4 was confirmed by Winkler, Gillies and Williams [60] (see equation (45)) who examined the reaction mechanism of cyclonite preparation by method 4. They found that hexamine dinitrate is formed at 35°C as an intermediate product. At the same time nitric acid is evolved hence nitrolysis of hexamine dinitrate may occur, in other words the mechanism of cyclonite formation would be similar to that of direct nitration of hexamine with nitric acid.

This observation also appears to explain why an excess of paraformaldehyde should have a harmful influence on the yield of cyclonite. In particular, Winkler noticed that the addition of formaldehyde to a hexamine solution in aqueous acetic acid causes the decomposition of hexamine which proceeds at a rate depending on the ratio of formaldehyde to hexamine.

The formation of octogen in method 5 will be discussed below.

OCTOGEN



XI, m.p. 276–277°C

Octogen, known in Britain as HMX, i.e. cyclotetramethylenetetramine, 1,3,5,7-tetranitro-1,3,5,7-tetrazacyclo-octane, is a white crystalline substance which occurs under several polymorphous forms differing from one another in specific gravity and sensitiveness to impact. Usually octogen is obtained in β form, which is the least sensitive to impact (Table 21).

McCrone [69] found that octogen is polymorphic and exists in four forms I (β), II (α), III (γ) and IV (δ). The first three are stable at room temperature, but HMX-IV transforms very readily.

HMX-I can be prepared in different ways. Wright *et al.* [70] recommend preparation by cooling a hot saturated solution of octogen in acetone or acetonitrile. HMX-II was prepared [70] by dissolving HMX in hot 70% nitric acid: crystals of HMX-II precipitate on cooling. When HMX-I was dissolved by warming in 50% acetic acid, HMX-III precipitated on cooling. HMX-III can also be obtained by steam distilling off the solvent from a hot solution of HMX in water-saturated cyclohexanone. When HMX-I was sublimed at 180°C, the product was HMX-IV.

All the crystalline forms were examined by Wright *et al.* [70]. They examined X-ray diffraction pattern, infra-red spectra and dielectric constants. They concluded that the HMX polymorphs are actually lattice-caged conformational modifications.

Octogen, like cyclonite is insoluble in water and non-hygroscopic. Its solubility in organic liquids is similar to that of cyclonite. Octogen and cyclonite are almost alike in chemical reactivity. They differ only in that octogen is more resistant to the action of sodium hydroxide than cyclonite. This reaction forms the basis of one of the methods of separating octogen from cyclonite. It consists in heating the mixture of octogen and cyclonite with a hydroxide solution under such conditions that the latter is decomposed while the former remains unaltered.

TABLE 21

PROPERTIES OF OCTOGEN (ACCORDING TO RINKENBACH [71])

Properties	Form			
	α	β	γ	δ
Specific gravity	1.96	1.87	1.82	1.77
Relative sensitiveness to impact (cyclonite = 180)	60	325	45	75
Stability of crystalline form	metastable	stable	metastable	labile

Another method of separating octogen from cyclonite depends on the difference in solubility of the two substances. Octogen is more easily soluble in 55% nitric acid or 2-nitropropane than cyclonite. The mixture is warmed in nitric acid and filtered and a mixture enriched in octogen is crystallized from the filtrate. Cyclonite, being soluble in 2-nitropropane, is then extracted from the mixture with solvent, while octogen remains undissolved. Octogen can be purified by crystallization from 70% nitric acid.

A mixture of cyclonite and octogen, rich in octogen, is best prepared by method 5, i.e. from hexamine nitrate, ammonium nitrate and acetic anhydride. A particularly large amount of octogen is formed when the product is prepared by Bachmann's method at temperatures ranging from 73 to 78°C and the mixture is then cooled to 25°C and filtered. This mixture m.p. 191–202°, contains approximately 10% of octogen.

The ratio of cyclonite to octogen produced by method 5 was examined by Epstein and Winkler [72]. They found that in general reduction in the amount of ammonium nitrate used for the reaction reduces the yield of cyclonite and increases that of octogen.

The results of these experiments are given in a graph (Fig. 27) which shows that the largest amount of octogen is formed when two moles of ammonium nitrate react with one of hexamine.

Bachmann *et al.* [64] also described the conditions under which the substance (XII) (DPT) can be prepared in a yield of about 20% from hexamine and nitric acid, in the presence of acetic anhydride and acetic acid, at temperatures between 15 and 30°C. On nitrolysis with nitric acid in the presence of ammonium nitrate and acetic anhydride at 60–65°C, this substance gives octogen in 80% yield.

As an explosive octogen is superior to cyclonite in that its ignition temperature is higher (an explosion ensues in 5 sec at 335°C while with cyclonite this occurs at 260°C). The chemical stability of octogen is also superior. In a vacuum, at 120°C in 40 hr octogen evolves 0.4 cm^3 of gas (cyclonite 0.9 cm^3) at 150°C it evolves 0.6 cm^3 of gas (cyclonite 2.5 cm^3). Thus, at 150°C octogen possesses a stability of the same order as trinitrotoluene or picric acid.

According to A. J. B. Robertson [23] decomposition of octogen at temperatures above 280°C occurs as a monomolecular reaction. Activation energy $E = 52.7$ kcal, $\log B = 19.7$.

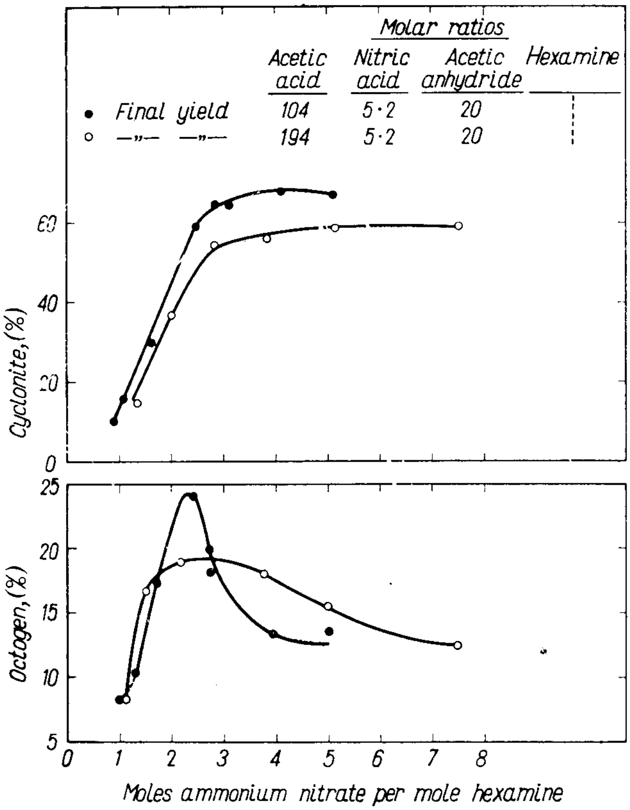
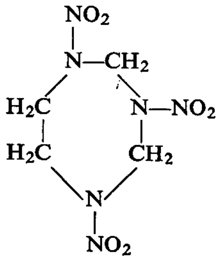


FIG. 27. Effect of ammonium nitrate on relative yields of cyclonite and octogen, according to Epstein and Winkler [72].

In explosive power octogen is somewhat less powerful than cyclonite, its lead block expansion being 450 cm³ whereas that of cyclonite is 500 cm³.

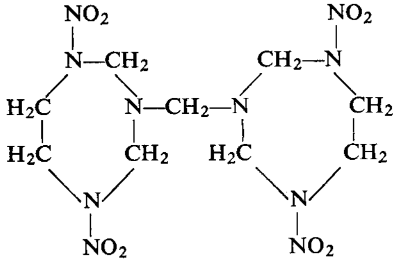
By virtue of these properties, the presence of octogen in cyclonite is not very harmful. Octogen, however, is not used independently as an explosive, being employed solely as a substance accompanying cyclonite.

HOMOCYCLONITE



XXXIII

Homocyclonite (Homohexogen) is an homologue of cyclonite with a 7-membered ring. Wright and Myers [43] prepared it by the nitrolysis of compound XXXIV (which arises as a result of the action of formaldehyde and ammonia on ethylenedinitramine):

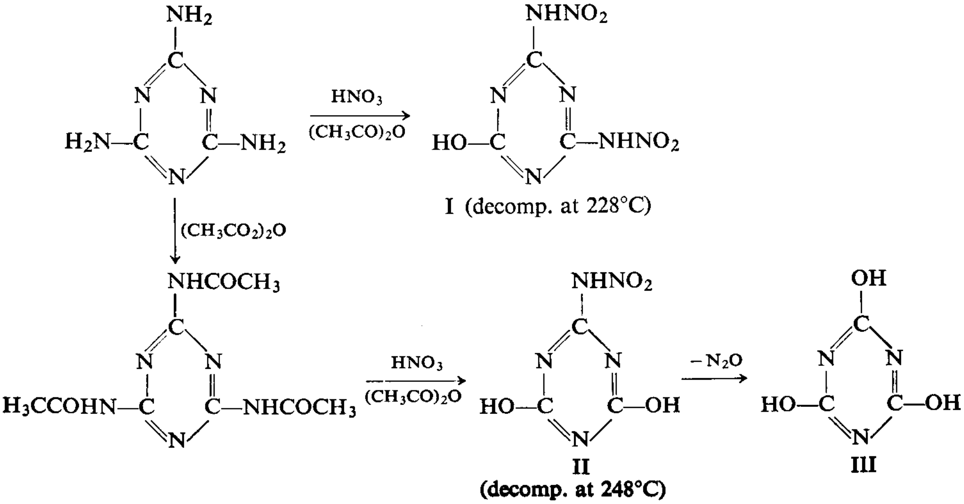


XXXIV
m.p. 205°C (decomp.)

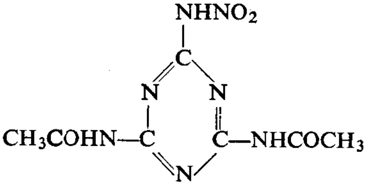
NITRO DERIVATIVES OF MELAMINE

Melamine is now a very important chemical product since it is a starting substance for the manufacture of plastics. The presence in melamine of a triazine ring, as in cyclonite, and of three amino groups induced attempts to nitrate this substance in order to obtain an explosive nitramine.

Whitmore and Cason [73] examined the mechanism of the direct nitration of melamine with nitric acid in the presence of acetic anhydride at 5°C and obtained an explosive product (I). By nitrating a triacetyl derivative of melamine with nitric acid in the presence of acetic anhydride at 20–25°C Cason prepared product (II). This substance hydrolyses, losing N_2O, which results in the formation of a stable compound (III)



Atkinson and Whitmore [74] elucidated the structure of these compounds. They showed that compound (I) is N,N'-dinitroammeline, compound (II) nitroammelide and compound (III) cyanuric acid. The authors also showed that fuming nitric acid at 20–25°C transforms triacetylmelamine into N-nitro-N',N''-diacetyl melamine (IV)

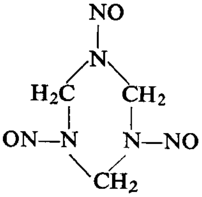


IV
(decomposition at 300°C)

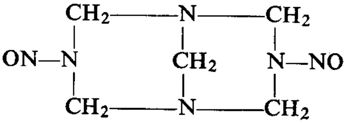
All these substances decompose without melting. Only dinitroammeline (I) has explicit explosive properties.

NITROSAMINES

Trimethylenetrinitrosamine (TMTN) 1,3,5-trinitrosohexahydro-sym-triazine, 1,3,5-trinitroso-1,3,5-triazacyclohexane (I) and dinitrosopentamethylenetetramine (DNPT) or 1,5-endomethylene-3,7-dinitro-1,3,5,7-tetrazacyclo-octane or 3,5-dinitroso-1,3,5,7-tetrazabicyclo [3,3,1] nonane (II)



I
m.p. 105–107°C



II
m.p. 206–207°C

Trimethylenetrinitrosamine (I) was first described in 1881 by F. Mayer [75] who suggested the structure (I). Duden and Scharff [76], Bachmann and Deno [77], and Aubertein [78] gave detailed descriptions of its preparation and chemical properties. Finally, Ficheroulle and Kovache [79] worked out the mechanism of its production on a semi-commercial scale.

Dinitrosopentamethylenetetramine (II) was first obtained by Griess and Harrow [80]. Formulae of these two substances (I) and (II) were proposed by Cambier and Brochet [81] and Duden and Scharff [76].

They are formed by the action of nitric acid on hexamethylenetetramine at a low temperature (max +8°C). Depending on the pH of the solution, the compounds (I) or (II) are obtained, viz.: at pH = 1–2, trimethylenetrinitrosamine (I) is formed whereas at pH = 3–6, dinitrosopentamethylenetetramine (II) is formed.

The yield of both reactions is 65–70%. According to Aubertein [78] substance (I) may be prepared in a yield 84% of theoretical.

The explosive properties of this compound (I) may be of particular interest.

Trimethylenetrinitrosamine

Physical properties. The specific gravity of the substance is 1.508. It is sparingly soluble in water. Šimeček and Doležel [82] report the following figures for its solubility, expressed as the amount in grammes dissolved per 100 g of solvent (Table 22):

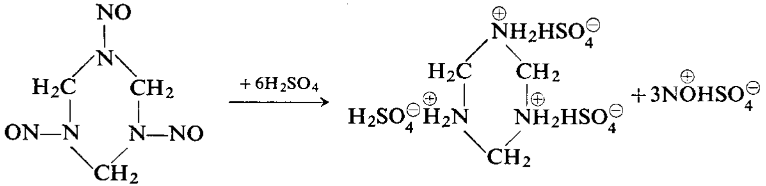
TABLE 22

	20°C	40°C	60°C
Water	0.2	0.3	0.6
Ethyl ether	0.8	1.2 at 34°	—
Toluene	1.4	2.3	4.4
Methyl alcohol	4.3	7.7	18.1
Acetone	68.5	139.7	254.5

According to Médard and Dutour [83] when molten the substance mixes with trinitrotoluene and gives an eutectic consisting of 58% of trinitrotoluene and 42% of trimethylenetrinitrosamine. The eutectic melts at about 55°C.

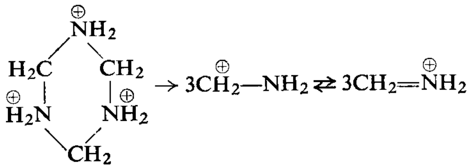
The thermochemical properties of this compound are of great interest. As early as 1896 Delépine [84] determined its heat of formation ($-\Delta H_f$) and found it to be negative. This observation was confirmed in later work by the same author and by Badoche [85] as well as in more recent experiments by Médard and Thomas [86]. According to the latter the heat of combustion of the compound (I) $-\Delta H_v = 557.17$ kcal/mole, hence its heat of formation is $-\Delta H_f = 71.1$ kcal/mole, i.e. 408 kcal/kg. The heat of detonation was found to be 850 kcal/kg.

Chemical properties. Trimethylenetrinitrosamine (I) decomposes explosively under the influence of concentrated sulphuric acid at room temperature. At a low temperature it is hydrolysed to form trimethylenetriamine sulphate (III)



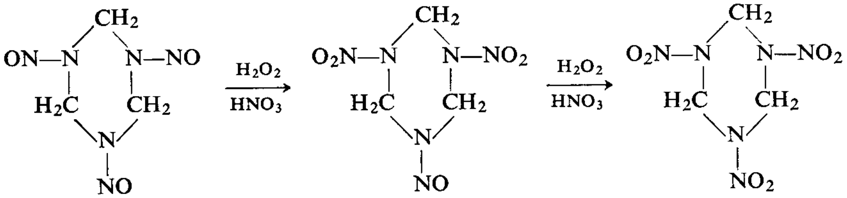
I III

According to Šimeček [87] trimethylenetriamine undergoes further decomposition to a Schiff's base:



Sodium hydroxide causes slow decomposition in the cold and rapid in the hot, with evolution of formaldehyde, nitrogen and ammonia. Rapid decomposition also occurs in boiling water and slow decomposition occurs in water at room temperature.

Oxidation of (I) leads to cyclonite. According to the work of Brockmann, Downing and Wright [12] oxidation with a solution of hydrogen peroxide (30%) in nitric acid (99%) in the ratio of 1 mole (I) to 82 moles of nitric acid, 3 moles of H_2O_2 and 3.7 moles of H_2O, at −40°C, gives dinitro-nitrosamine (IV) as an intermediate:



I IV

The yield of cyclonite in this reaction is 74%.

Explosive properties. The apparent density od trimethylenetrinitrosamine (I) is 0.84, according to Médard and Dutour [83]. The same authors give the following relationship between density and the compressing pressure:

pressure kg/cm^2	density
170	1.10
340	1.23
680	1.37
1020	1.44
1700	1.525
2380	1.57
3000	1.59

Complete detonation is obtained:

at a density of 0.85 by 0.30 g of mercury fulminate
at a density of 1.20 by 0.40 g of mercury fulminate
at a density of 1.40 by 0.50 g of mercury fulminate
at a density of 1.57 by 2.5 g of mercury fulminate

According to these authors sensitiveness to impact is of the same order as that of trinitrotoluene.

Šimeček and Šramek [88] give the following table for sensitiveness to impact in the drop test, using a 5 kg weight:

Weight falling from a height of cm	% of explosions
20	0
30	30
40	67
50	100

The value of the heat of detonation was reported earlier (p. 120).

According to Médard and Dutour the lead block expansion is 125.5 (taking picric acid as 100). The rate of detonation at a loading diameter of 30 mm is as follows:

Density	Rate m/sec
0.85	5180
1.00	5760
1.20	6600
1.40	7330
1.50	7600
1.57	7800

Charges of molten and solidified material at a density of 1.42 give a rate of detonation of between 7000 and 7300 m/sec.

In air the substance takes fire fairly easily and burns regularly.

The same authors examined the rate of detonation of a molten and solidified eutectic comprising 58% of trinitrotoluene and 42% of substance (I), and obtained a value of approximately 7000 m/sec.

Médard and Dutour [83] made a detailed investigation of the stability of the substance (I). At room temperature test samples of the substance remained apparently unaffected for 6 years. Marked decomposition occurred with rising temperature, beginning at about 150°C; at 160°C nitric oxides are evolved. Rapid heating causes immediate decomposition at 300°C and at 200°C decomposition occurs after 2 minutes.

The substance is exceptionally sensitive to the action of acids. When mixed with picric acid, for example, it undergoes violent decomposition after 2 hours' heating at 60°C. At 100°C decomposition ensues in 10–15 minutes. A mixture with trinitrotoluene is decomposed at 85°C.

The molten substance may react with such metals as iron, copper, aluminium. Thus, despite the fact that substance (I) is a powerful explosive, only slightly sensitive to impact, its low stability even in the presence of traces of substances with an acid reaction gives little promise for its practical use.

Dinitrosopentamethylenetetramine

Dinitrosopentamethylenetetramine (II) is used as a gasifiable product for the production of porous plastics and rubber (e.g. Unical ND, Vulkacel BN).

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Part 2

PRIMARY EXPLOSIVES: INITIATORS

CHAPTER I

GENERAL INFORMATION

THE earliest mention of explosives are to be found in the alchemical writings of the first half of the seventeenth century. Basilius Valentinus [1] described "explosive gold" which was a complex explosive salt formed by dissolving gold oxide in ammonia. At that time it was widely known that this substance is easily exploded by heat or direct contact with a flame.

According to Romocki [2], in 1630, the Dutchman, van Drebbel was the first chemist to investigate mercury fulminate, and "explosive gold". The first description of the laboratory preparation of "mercury fulminate" is given in Kunkel's book *Laboratorium Chymicum* published in 1690 [3]. This substance was described again by Howard in 1799–1800 [4]. No further discoveries of other primary explosives were made until the development of modern chemistry.

The invention of percussion compositions for igniting powders is usually attributed to Forsyth [5]. In 1805 he employed pellets composed of a mixture of potassium chlorate and combustible materials, coated with wax to render them safer to handle, but even so they were still dangerous since the mixture was sensitive to friction. The first ignition caps were invented in the early nineteenth century. In these caps the ignitable composition was enclosed in a casing of brass or copper. This invention cannot be traced with any certainty to any individual. The literature on the subject names several chemists including Bellot and Egg in 1815 [5].

The first application of mercury fulminate in ignition caps is attributed to Wright [6] in 1823.

Prior to 1831, straws filled with blackpowder, or fuses, which were cords saturated with a powder mixture, were used for igniting high explosive charges. The rate of burning of these powder timetrains was very irregular and lead to a great many accidents due to premature explosions. In 1831, a considerable advance was made by Bickford [7], who invented slow burning (safety) fuses, which comprised an inner core, filled with blackpowder, surrounded by layers of plaited jute.

Around 1860 Nobel [8] began to use a fuse with a small cartridge of blackpowder at the end which produced a more intense ignition, for detonating nitroglycerine. Subsequently he replaced the cartridges by caps and finally invented the detonator [9], by elongating the cap and considerably increasing the charge of mercury fulminate. Similar work was done by Andreyevskii in Russia [10].

Mercury fulminate is easy to produce, has been known since earliest times and is still widely used. The scarcity of mercury has however led to many attempts to replace this substance by something else, in particular by substances containing a different metal. Some success was achieved as a result of work of Will and Lenze [5] in 1892 on the application of heavy-metal azides as initiating agents.

Primary explosives are a group of substances which are highly sensitive to the action of mechanical shock and are readily ignited by direct contact with flame or electric sparks.

Special care should be taken, therefore, during their manufacture. The danger becomes greatest when the initiating substance is being transferred to the drier after it has been washed with water. From that time onwards all possible safety measures must be taken and strictly observed.

All operations must be handled from an adjacent room or at least from behind a strongly built wall or an armoured shield, progress being observed through a sight-glass or by television. Weighing and pouring materials etc., should also be carried out from behind a shield.

A plant used for drying, grinding, sieving, weighing and stirring primary explosives must be designed to minimize friction, and power units should be located in a separate building.

In such a plant, conditions are particularly favourable for the accumulation of static electricity, due to friction between the crystals themselves, and between the crystals and parts of the plant, even between the crystal and the air, during drying. All the parts of the plant should therefore be well earthed. If they are manufactured of non-conductive material, as for example, plastics, ebonite or leather, these materials should contain conductive substances such as graphite or aluminium dust, to help dissipate the static electricity generated.

If the rule that all the parts of the plant must be earthed is not observed, accumulation of static electricity may occur, and under these circumstances, initiators only need an electric spark to start them burning. Some of them, for instance lead styphnate, are particularly susceptible to ignition by sparks.

It is also desirable to cover the floors of any buildings in which initiators are housed with a conductive material. In order to minimize friction, the flooring material should be soft. Hence polyvinyl chloride or rubber containing aluminium powder or graphite, laid on earthed metallic tapes, are used. A floor that conducts electricity facilitates the escape of static electricity and also removes any danger which may arise from the building up of static charges on operators. According to Freytag [11], a man walking on an insulated floor, covered, for example, with a woollen rug, amasses a static charge of 14,000 volts. It is obvious that a person so charged could, on approaching an earthed instrument, cause a spark capable of igniting a sensitive initiating compound.

Since accumulation of static electricity is favoured by dryness, moderate humidification of the atmosphere increases its conductivity, and thereby decreases the danger in handling initiating materials.

Recent technical literature discusses new methods of minimizing or even preventing the build-up of static electricity by using salts of radioactive elements to ionize the air introduced into the factory buildings.

It is also very important to destroy any explosive substances which may be entrained in liquid wastes and wash-water.

They can be settled out and subsequently precipitated. They should be destroyed by chemicals which decompose them. Mercury fulminate, for example, is decomposed by a solution of thiosulphate, and lead azide by dilute nitric acid plus sodium nitrite.

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CHAPTER II

FULMINIC ACID AND ITS SALTS

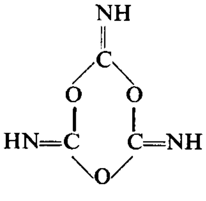
FULMINIC ACID

FULMINIC acid $\mathrm{C}\overset{\leftarrow}{=}\mathrm{NOH}$ is a gaseous, highly toxic substance with an odour resembling that of hydrogen cyanide. It is isomeric with other acids of the same empirical formula HCNO. The chief of these is cyanic acid HCNO, which is obtainable only in the form of its salts; free cyanic acid is unstable. The action of inorganic acids on cyanates leads to the evolution of cyanic acid which hydrolyses to form carbon dioxide and ammonia:

$$\mathrm{NaCNO + HCl \rightarrow HCNO + NaCl}$$

$$\mathrm{HCNO + H_2O \rightarrow CO_2 + NH_3}$$

The treatment of cyanates with organic acids (oxalic acid, for example) in a non-aqueous medium, for instance by grinding the two together, does not result in the decomposition of cyanic acid, but in the formation of a trimer, cyamelide, to which the formula of the trioxymethylene derivative is attributed (I)



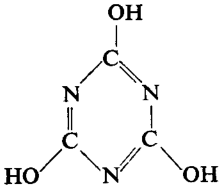
I

When distilled, this substance undergoes depolymerization, and isocyanic acid, a stable liquid with the structure (II), is formed at a temperature of 0°C:

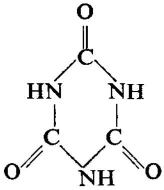
$$\mathrm{NH{=}C{=}O}$$

II

Its salts also exist in the form of a trimer, cyanuric acid (III), which is produced on heating the salts of isocyanic acid with acetic acid. Esters of cyanuric acid undergo isomerization when heated and are converted into esters of isocyanuric acid (IV):



III



IV

The free acid — a trimer of isocyanic acid — probably has the structure (IV). Cyanuric acids are of some importance as sources of initiating materials (cyanuric azide, for example, p. 194).

The salts of fulminic acid differ basically from those of isocyanic acid and its trimers.

The formula (V) attributed originally to fulminic acid, considers it to be an oxime of carbon monoxide [7]; a more recent interpretation suggests the formula (Va):

$$\underset{\text{V}}{C{=}NOH} \qquad \underset{\text{Va}}{C\overset{\leftarrow}{=}NOH}$$

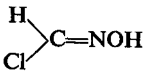
The linear structure of the fulminate ion

$$\overset{\ominus}{C}{\equiv}\overset{\oplus}{N}{-}\overset{\ominus}{O} \quad \text{or} \quad C\overset{\leftarrow}{=}N{-}\overset{\ominus}{O}$$

was recently confirmed by spectroscopic investigation of some salts of fulminic acid.

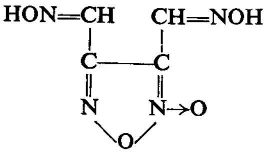
Singh [1] has examined infra-red spectra of mercuric, silver and lead fulminates, and Beck [2] those of sodium and potassium fulminates. The maxima 2147 and 1225 cm^{-1} were found to be characteristic of asymmetric and symmetric vibrations of the O—N—C group, respectively. The maximum 1181 cm^{-1} was assigned to the bending frequency of the same group [1]. Beck also found that the transient formation of an isomeric ion $^{\ominus}N{\equiv}C{-}O$ can occur on thermal decomposition of fulminates.

This kind of structure is also proved by the fact that chemically fulminic acid behaves as an unsaturated compound, adding hydrogen chloride at a temperature of 0°C, to form the crystalline chloroformoxime (VI):



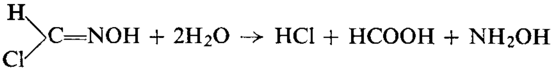
VI

A certain amount of crystalline isocyanylic acid is also produced. This substance has no explosive properties and according to Wieland [3] has the structure of furoxanedialdoxime (VII):



VII

When mercury fulminate is boiled with water, polymerization occurs with the formation of salts of fulminic acid, which is probably a mixture of substances (VII) and (VIII). This compound hydrolyses to produce formic acid and hydroxylamine:



$$\overset{H}{\underset{Cl}{>}}C{=}NOH + 2H_2O \rightarrow HCl + HCOOH + NH_2OH$$

Thus, fulminic acid $C{=}N{-}OH$ (or $C{\equiv}N{-}H$) has been regarded as a substance analogous to hydrogen cyanide $C{=}N{-}H$ (or $C{\equiv}N{-}H$). This analogy is also borne out by the facility with which fulminic acid forms complex compounds with for instance iron–sodium ferrofulminate, $Na_4Fe(CNO)_6 \cdot 18H_2O$, analogous to sodium ferrocyanide.

It must be emphasized that the analogy between fulminic acid and hydrogen cyanide is very deep. Liquefied hydrogen cyanide (b.p. +26°C) has explosive properties. This is explicable by the fact that like acetylene it is a strongly endothermic substance. The explosive decomposition of hydrogen cyanide proceeds theoretically according to the equation:

$$HCN \rightarrow C + \tfrac{1}{2}N_2 + \tfrac{1}{2}H_2$$

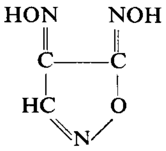
The quantity of heat evolved amounts to 1017 kcal/kg, the volume of gases evolved, V_0, is 830 l./kg, the temperature is 2250°C. This was first reported by Walker and Eldred [4].

Wöhler and Roth [5] proved that liquefied HCN can be exploded by means of a blasting cap.

Wöhler calls attention to the fact that some cyanides of heavy metals, e.g. mercuric cyanide, are highly sensitive to friction and impact and may initiate detonation of liquefied hydrogen cyanide.

Liquefied or solid (m.p. −14°C) hydrogen cyanide is also capable of polymerization, a strongly excthermic reaction which may involve apparent explosion due to local overheating. Local overheating may also induce a genuine explosion, particularly in the presence of the cyanides of some heavy metals.

The unsaturated nature of fulminic acid accounts for its tendency to polymerize and suggests that polymers constitute the brown impurity produced in the manufacture of mercury fulminate. The ability of fulminic acid to polymerize is also proved by the formation of cyamelide (I). It has also been established that an ether solution of fulminic acid is converted into metafulminuric acid on standing:



VIII

MERCURY FULMINATE

Mercury fulminate $(C\overset{\leftarrow}{=}NO)_2Hg$ is an initiating material of the greatest importance. It is obtained very simply by treating a solution of mercuric nitrate with alcohol in nitric acid. A method for preparing it was described in alchemical writings. This reaction, together with its product has been studied by a number of chemists, including Liebig [6], who gave an account of the elementary chemical composition of fulminate in 1823. Nothing was known of its structure until Nef's suggestion [7] in 1894, that fulminic acid is an oxime of carbon monoxide. This structure was subsequently supported for sodium fulminate by Wöhler and Teodorowicz [8]. More recent investigations altered these views, as described above (p. 133). The mechanism of reaction which results in the formation of mercury fulminate was reported by Wieland [9]. Solonina [10] made a detailed examination of its properties and its manufacturing technology.

According to Wieland, reactions between mercury nitrate, nitric acid and alcohol leading to the formation of mercury fulminate proceed as follows:

(1) Oxidation of alcohol to acetic aldehyde

$$C_2H_5OH + HNO_3 \rightarrow CH_3CHO + HNO_2 + H_2O$$

(2) Nitration of acetic aldehyde to nitrosoacetic aldehyde

$$CH_3CHO + HNO_2 \rightarrow NO{-}CH_2CHO + H_2O$$

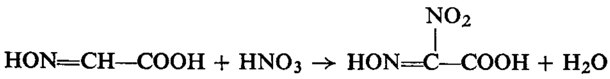
(3) Isomerization of nitrosoacetic aldehyde to isonitrosoacetic aldehyde

$$ON{-}CH_2CHO \rightarrow HON{=}CH{-}CHO$$

(4) Oxidation of isonitrosoacetic aldehyde to the corresponding acid

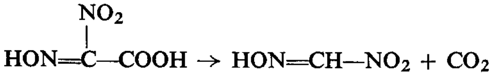
$$HON{=}CH{-}CHO \rightarrow HON{=}CH{-}COOH$$

(5) Nitration of isonitrosoacetic acid to nitrolacetic acid



$$HON{=}CH{-}COOH + HNO_3 \rightarrow HON{=}\overset{\overset{\displaystyle NO_2}{|}}{C}{-}COOH + H_2O$$

(6) Decarboxylation of nitrolacetic acid in methylnitrolic acid



$$HON{=}\overset{\overset{\displaystyle NO_2}{|}}{C}{-}COOH \rightarrow HON{=}CH{-}NO_2 + CO_2$$

(7) Decomposition of methylnitrolic acid into fulminic acid and nitrous acid

$$HON{=}CH{-}NO_2 \rightarrow C{=}NOH + HNO_2$$

(8) Formation of mercury fulminate

$$2C\overset{\leftarrow}{=}NOH + Hg(NO_3)_2 \rightarrow (C\overset{\leftarrow}{=}NO)_2Hg + 2HNO_3$$

This reaction gives the volatile by-products: ethyl nitrate, ethyl nitrite and acetic acid, NO, NO_2 and CO_2.

One hundred and forty-two parts of mercury fulminate can be obtained from 100 parts of mercury. A considerable amount of oxalic acid, produced by oxidation, remains in the solution, hence crude mercury fulminate is washed with distilled water.

Beside this basic method of manufacturing mercury fulminate, which is widely practised, there are alternate processes. Angelico [11] recognized that mercury fulminate is formed by treating a mercury solution in an excess of nitric acid with a concentrated aqueous solution of malonic acid in the presence of a small amount of sodium nitrate. The reaction results in a considerable rise of temperature, CO_2 evolution and the precipitation of the fulminate (L. W. Jones [12]).

Nef [7] showed that the mercuric salt of nitromethane (obtained by the action of $HgCl_2$ on the sodium salt of nitromethane) decomposes when boiled with dilute hydrochloric acid to produce mercury fulminate. In all probability the following reaction takes place:

$$(CH_2{=}NOO)_2Hg \rightarrow (C{\equiv}NO)_2Hg + 2H_2O$$

PHYSICAL PROPERTIES

Mercury fulminate consists of octahedral crystals, belonging to the orthorhombic system with the axial relationship $a : b : c = 0.712 : 1 : 1.353$ (Miles [13]). The pure substance crystallizes into the form of white, silky needles.

Commercial mercury fulminate may be greyish, pale brown or white, the colour depending on the method of its preparation. The reason for these different colours has been the subject of many investigations. A white product is formed when a certain amount of hydrochloric acid or cupric nitrate or chloride is added to the reaction mixture. A pale grey or a pale brown fulminate occurs on the application of pure reagents without the above-mentioned admixtures. The grey fulminate usually consists of very regular crystals (Fig. 28) whereas those of white fulminate are less regular (Fig. 29) due to the presence of impurities of mercuric chloride, or copper salts if copper has been added.

The grey or brown colour is usually uniform throughout the whole mass of crystals, although there are cases when the colour occurs in certain places only, forming stains or dyeing the edges of the crystals.

Kast [14] found that the grey mercury fulminate is the purest and contains 99.7–99.9% of mercury fulminate, soluble in hydrochloric acid. The insoluble residue is composed mainly of mercurous chloride which is probably derived from impurities of the starting substances.

The white fulminate contains 99.3–99.4% of the pure substance. The insoluble residue is again composed chiefly of mercurous chloride, but it also contains substances which turn dark under the influence of ammonia, hence the white product is less pure than the grey one. The more hydrochloric acid is added to the reaction mixture, the higher is the content of mercuric chloride.

It was believed at first that grey fulminate was contaminated with metallic mercury, since it had been observed that when it is dissolved in certain solvents a residue of metallic mercury is obtained. Solonina [10] showed, however, that this residue is produced from both kinds of fulminate and that the mercury which constitutes an insoluble residue in ammonia and potassium cyanide solutions or in pyridine does not occur in the fulminate crystals but is formed as a result of decomposition by reaction with the solvent. Thus the idea that the presence of mercury in the crystals of grey fulminate causes the grey colour cannot be considered proven, although a number of authors still believe in it (Wöhler and Berthmann [15]). In point of fact, a dark grey product, copiously contaminated with mercury, may be prepared by carrying out the reaction in dilute aqueous solution. The formation of mercury fulminate is then accompanied by the reduction of mercuric nitrate to metallic mercury. The same effect can be obtained by using an insufficient amount of nitric acid or too low a temperature of reaction. Such contaminated mercury fulminate cannot be used since it amalgamates with the metal body of the caps, causing their corrosion and may also form copper fulminate by reaction between the amalgam and mercury fulminate. The course of the reaction itself may also influence the colour of the product. According to Wöhler [16] the white coloured product may be obtained if acetaldehyde is used in the reaction instead of alcohol.

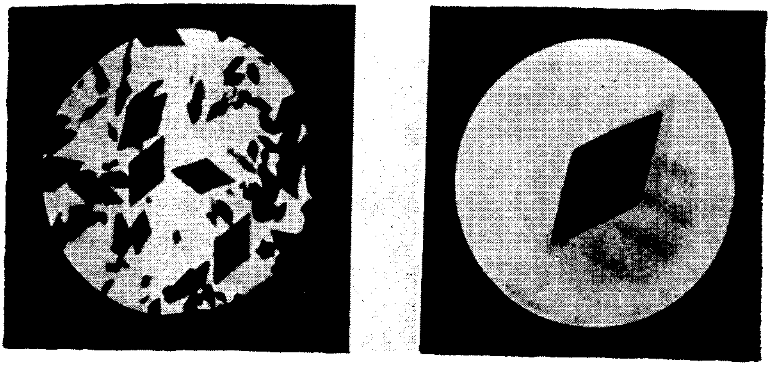


FIG. 28. Crystals of "grey" mercury fulminate, according to Kast [17].

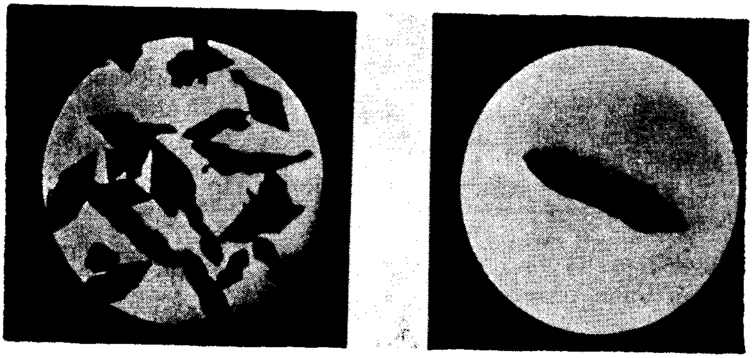


FIG. 29. Crystals of "white" mercury fulminate, according to Kast [17].

On the basis of all these experiments Kast [17] expressed the opinion that different colours are produced by differences in the size and shape of the crystals and not by impurities. This however appears to be incorrect. There seems every reason to believe that the grey and particularly the brown colour of mercury fulminate are produced by the presence of organic impurities, i.e. resinous product of the polymerization of fulminic acid (Marshall [18]). The white product, in Marshall's opinion, contains the same impurities, but in disguised form.

Apart from the impurities that influence its colour, mercury fulminate may contains a trace of mercuric oxalate, the presence of which was discovered by Shishkov [19] as early as 1856. Oxalic acid is always formed during the reaction as a by-product resulting from the oxidation reaction and according to Solonina the amount of oxalic acid formed is larger if hydrochloric acid is present in the reaction mixture.

Nicolardot and Boudet [20] found that mercuric nitrate may also be an impurity of mercury fulminate.

According to various authors, the specific gravity of mercury fulminate is:

4.42	(Berthelot and Vieille [21])
4.394	(Solonina [10], product recrystallized from an aqueous solution of sodium cyanide)
4.307	(Miles [13], product recrystallized from an aqueous solution of ammonia)

According to Patry [22] the crystallized product has a lower specific gravity (4.32) than the crude product (4.40).

The apparent density of loosely-poured fulminate depends to a great extent upon the size and shape of the crystals. According to various authors it may range from 1.22 to 1.60. A fine crystalline product has a low apparent density, a coarse crystalline product a high one. These variations are of great importance when loading caps with fulminate measured volumetrically. In detonators the density is usually as high as 2.5.

The solubility of mercury fulminate in water is low. According to Holleman [23], 100 ml of water dissolve:

at a temperature of	g
12°C	0.07
49°C	0.176
100°C	8

Mercury fulminate crystallizes from water as a yellow coloured product containing $\frac{1}{2}$ H_2O (Shishkov [19]). It was believed at first that the yellow colour is due to the presence of mercuric oxide resulting from the hydrolysis of the fulminate. It is now considered that this colour should be ascribed to the formation of products not fully defined and partly to the mercuric salts of metafulminuric acid (p.134). Furthermore on boiling in water, the hydrolysis of mercury fulminate may be fairly extensive.

Mercury fulminate dissolves in alcohol rather more readily than in water. The best solvent for fulminate is an aqueous solution of ammonia. At 30–35° a concentrated aqueous solution of ammonia dissolves a fourfold amount of mercury fulminate, but at 60°C decomposition ensues with the formation of urea and guanidine. From an ammonia solution fulminate can be crystallized either by evaporating off the ammonia, by diluting the solution with water or by acidifying in the cold with acid (e.g. acetic acid). Mercury fulminate also dissolves in acetone saturated with ammonia.

A good solvent for mercury fulminate is a mixture of a concentrated ammonia solution with alcohol and water (Miles [13]). According to Singh [24] the best results are obtainable by a mixture of the above components in the volume ratio 2 : 1 : 1.

Mercury fulminate dissolves in an aqueous solution of potassium cyanide (Steiner [25], Grigorovich [26]), to form a complex salt. According to Solonina the fulminate is best precipitated from this solution by treatment with dilute nitric acid. Thus, 12 g of mercury fulminate, dissolved in a solution of 6 g of KCN and 30 ml of water is diluted with water to 100 ml and treated carefully with 50 ml of nitric acid, i.e. 10 ml of acid, s.g. 1.40 diluted with water to 50 ml.

Pyridine is also a good solvent for mercury fulminate. 14.5 g of mercury fulminate may be dissolved in a 1 g of pyridine on moderate heating. The fulminate may by recovered if the solution is poured into water. Large crystals, an addition compound of mercury fulminate with pyridine, then separate. This compound loses pyridine on drying.

Mercury fulminate also dissolves in many solutions of various salts, but in some of them (e.g. potassium iodide, sodium thiosulphate) it undergoes rapid decomposition.

Majrich [27] established that ethanolamine or an aqueous solution of ammonia with ethanolamine are good solvents for mercury fulminate. By dilution with water or acidification of the solution, mercury fulminate is precipitated in a highly pure form, suitable for further use.

Mercury fulminate crystals are not so hard as those of lead azide (Todd and Parry [28]).

According to Yuill [29] the specific heat of mercury fulminate is:

at 110°C	0.119 cal/g
at 125°C	0.120 cal/g

Its thermal conductivity according to Belayev and Matyushko [30] is 0.00029.

CHEMICAL PROPERTIES

As previously stated, mercury fulminate is hydrolysed by heating in water; in boiling water hydrolysis is very rapid. Farmer [31] noticed that on heating with water under pressure, mercury fulminate undergoes decomposition to metallic mercury. Marked decomposition also takes place on heating or standing for long periods at room temperature in an aqueous solution of ammonia or potassium cyanide, or in pyridine, i.e. solvents for fulminate. When purifying the fulminate by crystallization, special care must therefore be taken to see that temperatures during dissolution and precipitation are as low as possible and that the latter follows the former with the greatest possible speed.

After a 14 day immersion of mercury fulminate in an aqueous solution of potassium cyanide, precipitation can be inhibited by the addition of nitric acid.

On boiling the solution takes on a violet colour. Dissolved in an aqueous solution of ammonia, fulminate decomposes even after 12 hr. On boiling a pyridine solution of fulminate, complete decomposition occurs.

Mercury fulminate is relatively resistant to the action of dilute acids, in particular to that of nitric acid, but concentrated acids cause decomposition. Thus, under the influence of nitric acid decomposition occurs with evolution of NO, CO, acetic acid and mercuric nitrate. Under the influence of concentrated hydrochloric acid free fulminic acid is evolved (with an odour resembling that of hydrogen cyanide) as well as the decomposition products: hydroxylamine hydrochloride, formic acid, mercuric chloride (Carstanjen and Ehrenberg [32]; Scholl [33]). Mercury fulminate explodes on direct contact with concentrated sulphuric acid.

Strong alkalis decompose mercury fulminate easily. Heating with aniline leads to the formation of phenylurea, diphenylguanidine and metallic mercury (Steiner [34]).

On treatment with phenylhydrazine, mercury fulminate undergoes reduction to free mercury. The phenylhydrazine changes colour from olive, grey (at the moment when mercury is set free) to reddish-brown. Several hours after the addition of alcohol and dilute sulphuric acid, a red-violet colour appears (Langhans [35]). This reaction may be used for the qualitative detection of mercury fulminate.

Mercury fulminate undergoes rapid decomposition by the action of ammonium sulphide to form mercuric sulphide. The fulminate dissolves in sodium thiosulphate, according to the reaction:

$$(CNO)_2Hg + 2Na_2S_2O_3 + 2H_2O = HgS_4O_6 + (CN)_2 + 4NaOH$$

This reaction may be used to determine fulminate quantitatively by back titration of the sodium hydroxide formed. It can also be used to destroy fulminate residues and waste material. The impurities in mercury fulminate (oxalate and nitrate) are insoluble in thiosulphate.

Reactions with metals. When mercury fulminate is boiled with water containing metallic suspensions, the majority of metals (e.g. aluminium, zinc, copper), form their fulminates and mercury is precipitated. Reaction can also occur at room temperature, except with nickel. Other metals may be ranged according to increasing reactivity: silver, tin, bismuth, cadmium, iron, lead, copper, zinc, brass, aluminium. With aluminium, the reaction takes only a few hours, yielding a large amount of Al_2O_3.

A similar reaction was observed when mercury fulminate was kept in contact with metals in a damp atmosphere. Aluminium gave a white bloom after only four days. Iron and brass became slightly corroded in six days and zinc and lead in 14 days. The remaining metals, i.e. copper, cadmium, tin and silver showed no change after 28 days (Langhans [36]).

Chemical stability and behaviour at high temperatures. Mercury fulminate undergoes marked thermal decomposition even at 50°C. Rathsburg [37] found that a sample of the technical product stored at 50–60°C for 6 months in a dry atmosphere lost 3.6% in weight, while in a damp atmosphere 7.6% was lost. A recrystallized sample, however, showed a greater stability, under the same conditions only losing 0.2–0.5% in weight.

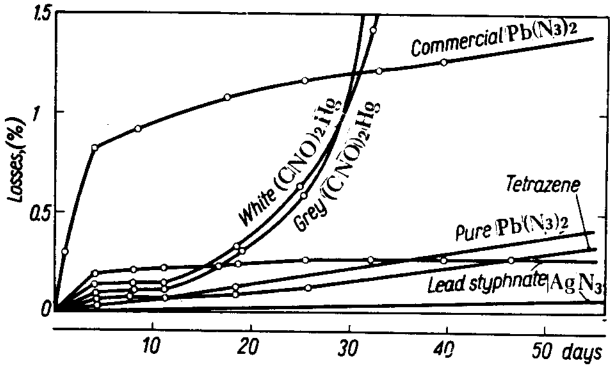


FIG. 30. Comparison of the rate of decomposition of mercury fulminate and other primary explosives at 75°C, according to Wallbaum [38].

Heating mercury fulminate at 75°C causes distinct decomposition. According to Wallbaum [38], during the first 10 days the loss in weight is not significant (*ca.* 0.12%), but after that the rate of decomposition begins to increase. After 46 days the loss in weight reaches 8%. The shapes of the decomposition curve (Fig. 30) clearly shows the increasing rate of decomposition. The curve for mercury fulminate compares unfavourably with that for other initiating materials, i.e. lead and silver azides, lead styphnate and tetrazene.

Hess and Dietl [39] found that 0.5 g samples of fulminate at 90–95°C undergo partial decomposition to form substances with reduced explosive properties after 35–40 hr; they also showed that after 75–100 hr a brown-yellow powder of low inflammability is produced.

Langhans [40] examined the changes which occur in white and grey mercury fulminates during heating at 90°C under reduced pressure. After 100 hr a brown-yellow, non-explosive substance was formed which retained the original crystalline form. This substance was named mercury pyrofulminate by the author. It differs from the starting substance by containing more mercury (76.4%) the empirical formula being $Hg_4C_5O_5N_7$ and by being insoluble in an aqueous solution of ammonia and in pyridine.

Aqueous solutions of organic acids such as formic, acetic, and oxalic, decompose mercury fulminate, forming the corresponding mercuric salts. On the other hand, the action of dilute inorganic acids involves decomposition with formation of CO_2.

The decomposition of fulminate heated at 60–100°C under a reduced pressure (5 mm Hg) was investigated in detail by Farmer [31]. At 80°C the brown fulminate began to decompose with the evolution of gas after the induction period was over, i.e. after 80 hr, whereas decomposition of the white fulminate began after a much longer induction period, lasting 140 to 190 hr, after which it then proceeded with the evolution of gas which was almost exclusively carbon dioxide. The rate of decomposition of the white fulminate was higher at this stage than that of the grey fulminate. The grey fulminate was transformed into a non-explosive product after about 200 hr from the beginning of decomposition.

Farmer quotes the following figures for the time required for the production of 5 cm^3 of gas by heating mercury fulminate (this corresponds to the decomposition of 11% of substance):

Brown fulminate:	at 60.0°C	1227 hr
	at 89.6°C	39 hr
White fulminate:	at 60.0°C	2010 hr
	at 89.6°C	67 hr

The difference in the behaviour of the two modifications was due largely to the differences in crystal size. Fine fulminate, ground under water decomposes more rapidly than a coarse crystalline product.

Farmer's experiments were repeated and extended by Garner and Hailes [41]. They examined the behaviour of mercury fulminate at about 100°C and came to the conclusion that during the initial induction period, decomposition is accompanied by a slow evolution of gas at a constant velocity (linear decomposition). At the end of this phase the main decomposition period begins with an increased rate of gas evolution. The authors noticed that if the fulminate is finely ground, rapid evolution of gas begins at once, without any initial period.

Garner and Hailes believe that decomposition proceeds by a chain mechanism with a constant coefficient of branching.

Grinding increases the number of centres at which the reaction originates. Since the decomposition reaction passes from one grain to another at the points where thin surfaces are in contact, grinding which increases the surface area, would be expected to have the effect described above.

A number of later authors, e.g. Prout and Tompkins [42], Vaughan and Phillips [43] have confirmed that the thermal decomposition of mercury fulminate is a chain reaction.

In a later work Garner and Haycock [44], came to the conclusion that the first 10% of the substance undergoing the accelerated decomposition breaks down according to the cubic equation (1):

$$p-p_0=k_3(t-t_0)^3 \tag{1}$$

where: p is the pressure of gaseous decomposition products during time t, p_0 and t_0 are the pressure of gases and the time at the moment of completion of linear decomposition (initial period) i.e. at the beginning of accelerated decomposition, and k_3 is the constant for the reaction rate.

On the basis of this equation the authors draw the conclusion that after completion of linear decomposition, i.e. at the point p_0, t_0, spherical nuclei of decomposition are formed.

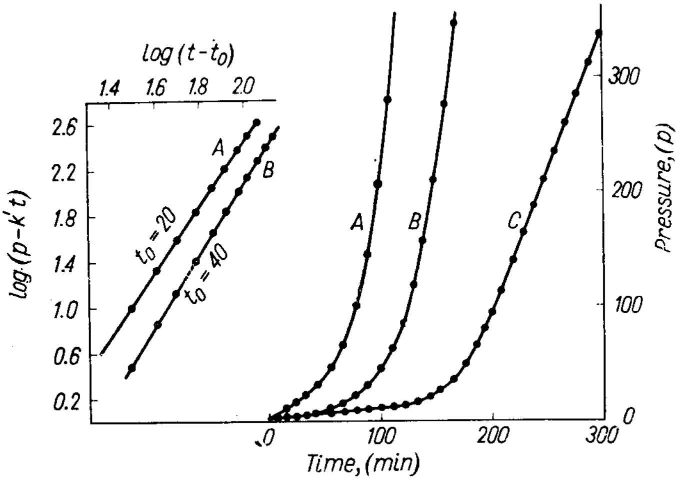


FIG. 31. Influence of various methods of treatment on the thermal decomposition of mercury fulminate, according to Bartlett, Tompkins and Young [45]. *A*—pre-irradiated, *B*—crushed, *C*—aged.

Bartlett, Tompkins and Young [45] suggested a modified (2) equation of Garner and Haycock:

$$p-p_0=k_3(t-t_0)^3+k_1t \tag{2}$$

Here k_1 is the constant for the linear reaction.

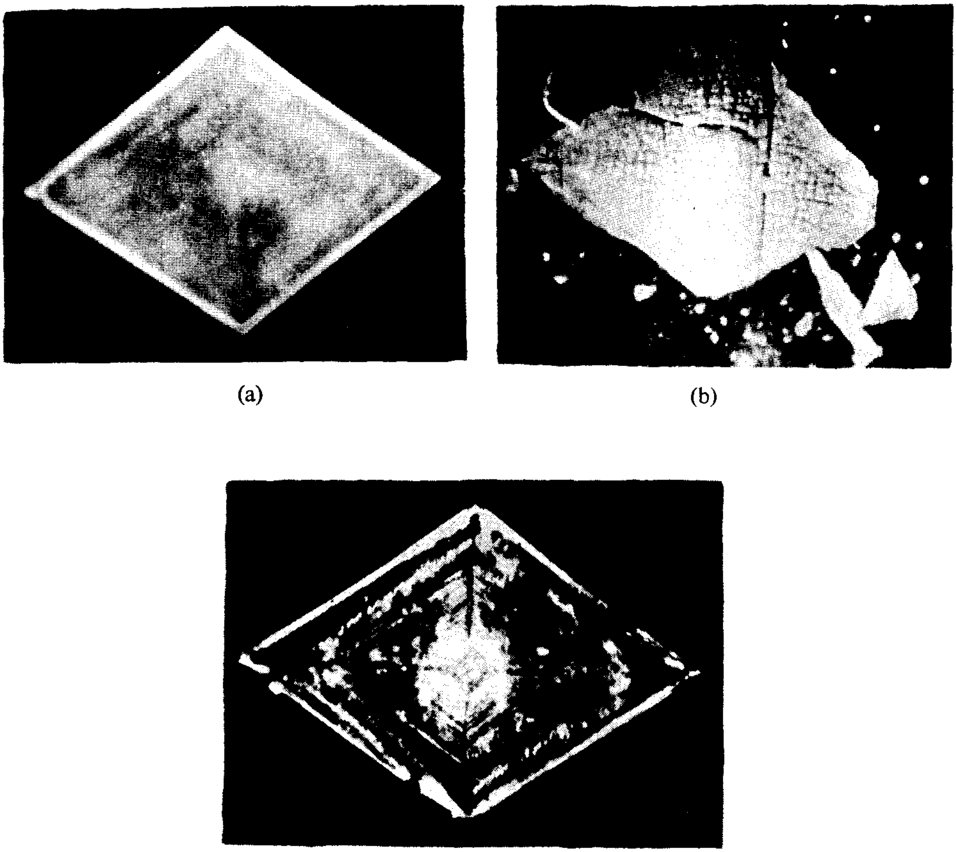
These authors studied the influence of the various methods of treatment on the thermal decomposition of mercury fulminate crystals. This is shown in the graph (Fig. 31).

Curve *A* represents the decomposition of mercury fulminate irradiated with ultra-violet rays, curve *B* the decomposition of ground mercury fulminate, and curve *C* the decomposition of ordinary (freshly-prepared) mercury fulminate.

According to Garner's calculations [44, 46] the activation energy of the accelerated decomposition period is about 32 kcal/mole. Vaughan and Phillips [43] gave the figure 25.4 kcal/mole and log $B=11.05$.

Bartlett *et al.* found for the activation energy the figure of 27 kcal/mole and for linear decomposition the figure of about 5 kcal/mole.

Singh [24] noticed that when heated for a few minutes at a temperature nearing that of immediate decomposition mercury fulminate crystals undergo decomposition first along crystallographic planes (010) and (100) on the surface of the crystals. Thus crystals heated, for instance, for 7 min 36 sec at 160°C undergo the cracking shown in Fig. 32 (b). (The same crystal before heating is shown in Fig. 32 (a)).



(a) (b)

(c)

FIG. 32. Crystals of mercury fulminate: (a) before heating, (b) after heating at 160°C for 7 min 36 sec, (c) after heating at 80°C for 96 hr, according to Singh [24].

Similar behaviour in silver azide crystals was observed by Bowden *et al.* [47].

When crystals of mercury fulminate are heated at lower temperatures the decomposition reaction is localized mainly around lattice defects such as growth marks on the surface of crystals or points where dislocations emerge at the surface (Fig. 32 (c)).

The nuclei formed in crystals of mercury fulminate are yellowish-brown. They probably consist of Langhans' mercury pyrofulminate [40].

The admixture of various substances acts in different ways on the decomposition rate of fulminate: inorganic acids accelerate decomposition; organic acids exert no influence whatever while organic bases sometimes accelerate decomposition considerably. E.g., the addition of 10% of centralite leads to the explosion of fulminate heated for 3 hr at 80°C.

According to various authors, the ignition temperature of mercury fulminate is 187–190°C on rapid heating; on heating at a rate of 5°C/min it is 160–165°C. A test sample, when thrown onto a metallic surface heated to 215°C, explodes after 5 sec, while an immediate explosion takes place on throwing a test sample on a surface heated to 277°C. On a surface heated to 139°C the explosion occurs after 39 min; at lower temperatures there is no explosion at all (data according to Laffitte and Patry [48]).

FIG. 33. Cracks produced in mercury fulminate crystals by exposure to ultra-violet light (500×), according to Tompkins *et al.* [45].

The behaviour of mercury fulminate at high temperatures depends on its purity. The recrystallized substance explodes immediately on a surface heated to 287°C.

Ignition depends on the size of the test sample used. A 10 g sample explodes after about 7 hr of heating at 115°C, while smaller ones decompose completely at 132°C without exploding.

Evans and Yuill [49] investigated the ignition of mercury fulminate by the adiabatic compression of the atmosphere surrounding it. They calculated that a 50% response corresponds to a temperature of 530°C.

The action of light. Mercury fulminate is sensitive to sunlight. Farmer found that on exposure to the sun's rays for 5 weeks in summer a test sample of fulminate showed considerable decomposition with gas evolution.

Berchtold and Eggert [50] and Eggert [51] established that mercury fulminate (like silver fulminate and other primary explosives) is exploded when strongly irradiated. To explode mercury fulminate a light with an intensity of 1.65 J/cm^2 is required (to explode silver fulminate—2.1 J/cm^2).

According to Patry [22] fulminate darkens under the influence of irradiation by a mercury arc. After a month test samples become almost black and the mercury content increases from 70.8 to 71.3. As on heating, the crystalline structure remains unchanged but the optical properties of the crystals undergo alteration.

According to Tompkins *et al.* [45] crystals of mercury fulminate exposed to ultraviolet light (wavelength 2537 Å) develop cracks, roughly parallel and about 10μ apart (Fig. 33). The cracks occur preferentially at points of weakness and high reactivity, i.e. at points where sub-grain boundaries emerge at the surface; it is at such sites that photolysis is most likely to occur. A similar phenomenon of cracking under the action of high temperature was described by Singh [24] (p. 144, Fig. 32).

According to Kaufman [52] strong γ-radiation (on average 10^{5}r per hour) can decompose mercury fulminate. Mercury fulminate evolves large amounts of gas during irradiation and eventually loses its explosive properties.

EXPLOSIVE PROPERTIES

The densities of loading for mercury fulminate obtainable by applying different pressures are tabulated below:

Pressure kg/cm^2	Density
200	3.0
660	3.6
1330	4.0
3330	4.3

Under a pressure greater than 1660 kg/cm^2 mercury fulminate becomes "dead pressed" i.e. takes fire with difficulty and burns without detonation.

According to Gorst [53] mercury fulminate pressed at 500 kg/cm^2 gives 3% misfires following flame ignition, at 600–650 kg/cm^2 it gives 5% and at 3000 kg/cm^2 almost 100% misfires. In detonators, therefore the fulminate is compressed under pressures of 250–350 kg/cm^2.

The sensitiveness of mercury fulminate to penetration by a striker depends upon the pressing pressure. Under pressures up to 750 kg/cm^2 the sensitiveness to perforation rises with the increase of pressing pressure. For pressures between 700 and 750 kg/cm^2 an optimal sensitiveness to perforation is observed, and at still higher pressure, the sensitiveness decreases and finally disappears at about 2000 kg/cm^2.

The most important explosive property of mercury fulminate is that its burning with a moderate rate, started by ignition, impact or friction, is easily converted into detonation. According to Patry [22], a charge of mercury fulminate (of density 1.25) in glass tubes of diameter 3–12 mm, when ignited at one end by the flame of a blackpowder fuse, burns over a certain distance (up to 30 cm at a small diameter of tube, and about 3 cm in one of larger diameter) with a moderate rate, that varies from 10 m/sec in the narrower tube to 20 m/sec in the wider tube. A detonation wave then arises which moves with a rate that ranges between 2250 and 2800 m/sec (the higher rate occurs in the larger diameter tubes). If the tube is very small, with a diameter less than 3 mm, no detonation wave may be produced.

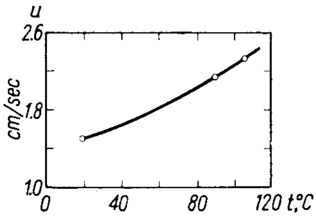


FIG. 34. Rate of burning of pressed mercury fulminate against initial temperature, according to Belayev and Belayeva [54].

Belayev and Belayeva [54] studied the influence of the initial temperature on the rate of burning of mercury fulminate, pressed into pellets. The results are shown in Fig. 34. A 100°C temperature increase in the mercury fulminate accelerated the rate of burning approximately 1.7 times. The authors also investigated the rate of burning of mercury fulminate at various temperatures, and expressed this relationship by the following equations:

at 20°C $u = 0.47 + 1.05\ p$
at 90°C $u = 0.65 + 1.44\ p$
at 105°C $u = 0.71 + 1.60\ p$

where u = the linear rate in cm/sec
p = the pressure in kg/cm^2

The rate of detonation, as reported by various authors, ranges from 2250 to 6500 m/sec, depending on the density and the diameter of loading.

According to Kast and Haid [55] the rate of detonation against the density of mercury fulminate is related as follows:

Density	Rate of detonation m/sec
1.25	2300
1.66	2760
3.30	4480

At the Chemisch-Technische Reichsanstalt [56] the figures given on p. 148 were found for the rate of the detonation of mercury fulminate, pressed into detonators:

Density	Rate of detonation m/sec
3.07	3925
3.96	4740

A mixture of mercury fulminate containing 10% of $KClO_3$ detonates at a density of 3.16 with a rate of 4090 m/sec.

Patry [22] quotes the following rates of detonation in glass tubes (Table 23).

TABLE 23

THE RATE OF DETONATION OF MERCURY FULMINATE (ACCORDING TO PATRY [22])

Diameter of tube in mm	9	9	13	13	13	7.5
Density of loading	0.85	1.25	1.0	1.35	1.45	1.45
Rate of detonation in m/sec	2270	2700	2500	3000	3300	2700

According to other data the rate of detonation is 3975 m/sec at a density of 3.0 and 5400 m/sec at a density of 4.2.

234 cm^3 of gas are formed from the detonation of 1 g of mercury fulminate in an atmosphere of nitrogen. The gas consists of:

CO_2	0.15%
CO	65.7%
N_2	32.25%
H_2	1.9% (Berthelot and Vieille [21])

This conforms to the decomposition equation:

$$(CNO)_2Hg = 2CO + N_2 + Hg$$

The calculated heat of decomposition is 114.5 kcal/mole (mercury as liquid) or 99.1 kcal/mole (mercury as vapour). When based on 1 kg of fulminate the corresponding figures are: 403 kcal and 349 kcal.

Kast [17] reports the following physical constants for mercury fulminate:

heat of formation	-221.5 kcal/kg ($-\Delta H_f = 62.9$ kcal/mole)
heat of explosion	357 kcal/kg
volume of gases (V_0)	316 l./kg
temperature of explosion (t)	4350°C(?)
specific pressure (f)	5530 m

According to the same author expansion in the lead block is 110 cm^3.

The sensitiveness of mercury fulminate to impact and friction is high. The height from which a weight must be dropped to cause explosion is however not the same in reports by different authors. E.g. Stettbacher [57] states that fulminate was exploded by a 2 kg weight from a drop of 4 cm and nitroglycerine by the same weight from a drop of 6 cm. According to R. Robertson [58] fulminate exploded on impact from a drop only 10% of that necessary to explode picric acid.

Fulminate is desensitized by the addition of water. When it contains 5% of water it only partially detonates on impact; at 10% water content it decomposes without explosion and 30% of water prevents its decomposition. These results, however, refer to small scale tests, on a large scale they may be rather different. Substances such as oils, glycerine and paraffin act similarly as desensitizers. Fulminate containing 20% of high-melting paraffin wax was used for the manufacture of a detonating fuse, employed in Austria. Fulminate so phlegmatized is insensitive to moderate impact and friction, but is detonated by a blasting cap.

TOXICITY

Mercury fulminate has a sweetish "metallic" taste. When administered orally it is as poisonous as the majority of mercury compounds. Since, however, it is very sparingly soluble in water its toxicity through contact with the skin is insignificant. Nor is it toxic to lower plants, e.g. moulds often form on the moist bags in which mercury fulminate is stored.

Poisoning from mercury does occur, however, among workers employed in the first stages of production, when handling mercury.

MERCURY FULMINATE MANUFACTURE

There are numerous specifications for the technical manufacture of mercury fulminate. They may be divided into three groups:

(1) methods in which a cold solution of mercury in nitric acid is employed;
(2) methods in which a warm solution of mercury in nitric acid is employed;
(3) methods, in which substances to bleach the product are included in addition to the essential raw materials: a mercury solution in nitric acid and ethyl alcohol.

The most important safety consideration in manufacturing fulminate is to ensure that only very small quantities (usually limited to 500 g of mercury) are produced in each reactor. Since mercury and mercuric nitrate readily react with metals the manufacture has to be carried out in glass reactors (retorts or flasks). A very pure product is thereby obtained and safety is ensured by the absence of metallic parts, against which friction and impact would be dangerous.

(1) One of the earliest descriptions of the manufacture of mercury fulminate given by Chevalier [59] is as follows: 300 g of mercury are dissolved in 3000 g of cold nitric acid (54% HNO_3, s.g. 1.34) and the solution is poured into a flask containing 1900 g of 90% alcohol. After few minutes a vigorous reaction begins and crystals are precipitated. On completion of the reaction 238 g and 158 g of alcohol are added in turn. The fulminate is filtered off through a cloth filter and carefully washed free of acid with water. The yield is 118–128 parts of fulminate per 100 parts of mercury, i.e. 83–90% of theoretical.

Too large a quantity of cold alcohol added during the reaction may cause the formation of contaminated fulminate.

(2) Chandelon's method [60] is more widely used. Here 1 part by weight of mercury is dissolved in 10 parts of nitric acid (65% HNO_3, s.g. 1.40) by moderate heating; the solution, heated to 55%, is poured into a flask or retort with a capacity at least 6 times that of the liquid, containing, apart from the above mentioned solution, 8.3 parts of 87% alcohol. The reactor is connected by a vent pipe with stoneware jars and a cooling tower in which the vapours evolved during the reaction are condensed.

After approximately 15 min the reaction begins, as shown by the evolution of gas. The liquid soon begins to boil, and the reactor fills with white vapour. The violence of the reaction may be suppressed by the addition of cold alcohol, but too large an addition may excessively inhibit the reaction and may lead to the formation of free mercury, which contaminates the product.

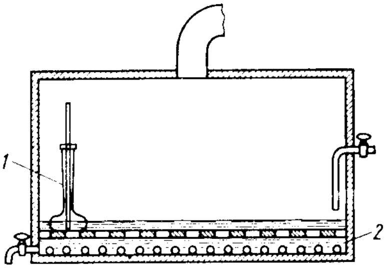


FIG. 35. Fume-cupboard with long necked flask (*1*) and heaters (*2*) for dissolving mercury in nitric acid, according to Budnikov *et al.* [61].

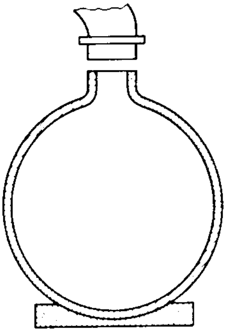


FIG. 36. Reaction flask, according to Budnikov *et al.* [61].

The fulminate is precipitated in the form of greyish needles. When the reaction is complete, the reactor is allowed to stand for approximately 30 min while the contents are cooled. 1–2 l. of water are then poured in and the liquid is decanted from above the precipitated crystals. The precipitate is transferred to a cloth filter and washed with distilled water until completely free of acid. The product is then screened on a silk sieve (approximately 100 mesh/cm^2) which retains the larger crystals. The smaller crystals are collected for direct use. The large ones are ground under water, passed through the same sieve and added to the previous batch. 125 parts of fulminate are obtainable from 100 parts of mercury, which corresponds to a yield of 88%.

The condensate that collects in the jars and tower consists of ethyl nitrate and nitrite, acetaldehyde and unreacted alcohol. The vapours of these substances are noxious so care must be taken that the apparatus is tightly closed.

(3) Solonina [10] gives two methods for the manufacture of mercury fulminate: **the first (a) produces a white fulminate and the second (b) a grey one.**

(a) 500 g of mercury is dissolved in 4500 g of nitric acid (62% HNO_3, s.g. 1.383); 5000 cm^3 of 92–95% alcohol to which 5 g of copper dissolved in 5 g of hydrochloric acid (23% HCl, s.g. 1.115) has been previously added, is poured into the solution.

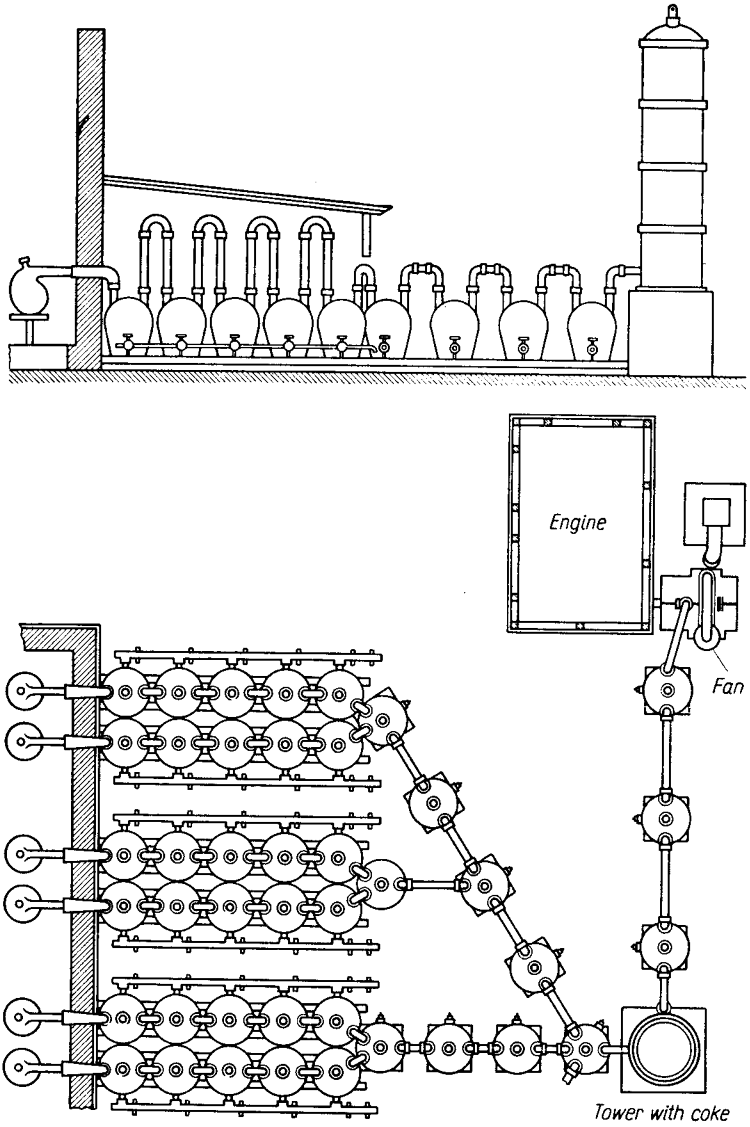


FIG. 37. A lay-out of the manufacture of mercury fulminate, according to Kast [17].

(b) 400 g of mercury is dissolved in 4200 g of nitric acid (62%) and 4000 cm^3 of 96% alcohol is then added.

In both methods the solution of mercury in nitric acid is heated cautiously to 50–56 °C and the added alcohol to 40°C.

(4) According to a method employed in German factories (Kast [17]) 150 g of mercury is dissolved in 1072 cm^3 (1500 g) of nitric acid (65% HNO_3, s.g. 1.40) and 1500 cm^3 of 79.5% alcohol is added.

The temperature of the mercury solution lies between 40 and 55 °C, that of the alcohol between 20 and 35 °C. A grey product is formed. In order to obtain a white product, a little concentrated hydrochloric acid, s.g. 1.185 is added to the alcohol before the reaction.

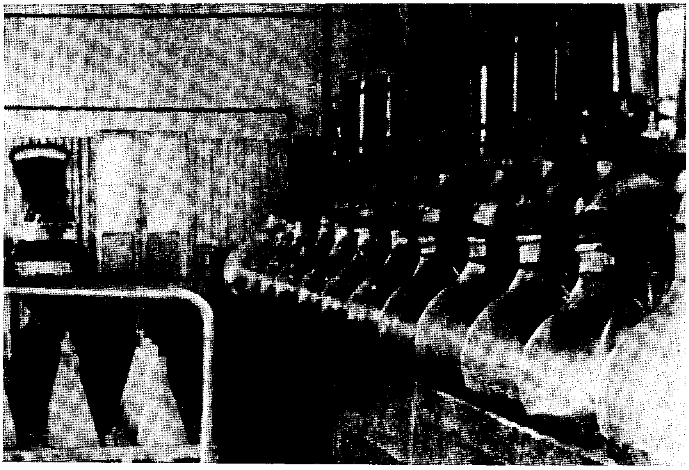


FIG. 38. General view of plant for manufacturing mercury fulminate in Atlas Powder Company, according to Davis [62]. On the left, conical flasks with mercury nitrate in nitric acid. On the right, reaction flasks.

The series of figures explains various stages of the manufacture. Figure 35 shows a fume cupboard with long-neck flask for dissolving mercury (and small amount of copper) in nitric acid with the addition of a small amount of hydrochloric acid. Figure 36 shows a thick walled flask in which mercury fulminate is produced. The lay-out of reaction retorts, condensation jars and a cooling tower is given on Fig. 37, and a general view of the reaction flasks on Fig. 38.

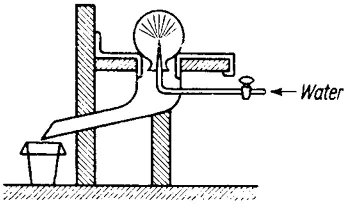


FIG. 39. Removal of mercury fulminate from the reaction flask to a rubber bucket, according to Budnikov *et al.* [61].

Figure 39 shows a method of transferring mercury fulminate from the reaction flask to a rubber bucket. After preliminary washing in a vacuum filter, mercury fulminate can be transferred for final washing in the apparatus shown in Fig. 40 in which water passes upwards through the fulminate layer, until the product is free of acid (this usually requires 40–60 min).

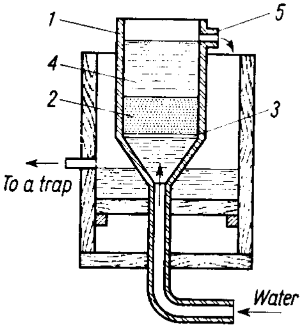


FIG. 40. Washing apparatus, according to Budnikov *et al.* [61]: *1*—glass funnel, *2*—mercury fulminate, *3*—filter plate, *4*—wash-water, *5*—over-flow of wash-water.

Storage and the further processing of mercury fulminate

Mercury fulminate prepared by one of the methods outlined above is tested to check the acid content and the content of other mercury compounds. When tested with litmus paper, the moist product should give a neutral reaction. A 5 g test sample mixed with 2 g of sodium hydrogen carbonate should not give a black or bluish tint.

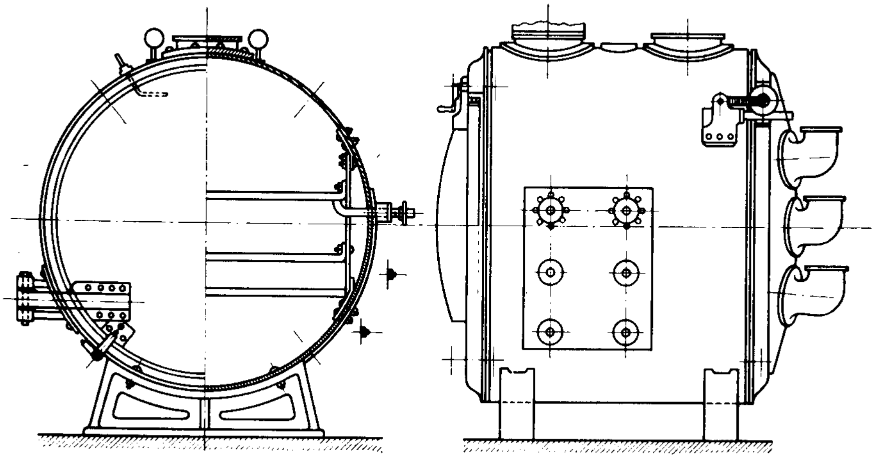


FIG. 41. Vacuum drier of mercury fulminate, according to Budnikov *et al.* [61].

Mercury fulminate containing about 50% of water is stored in glass jars or in linen or linen-rubberized bags placed in bakelite, bakelized cardboard of paraffinized boxes loosely covered with a lid. In this condition it can also be transported.

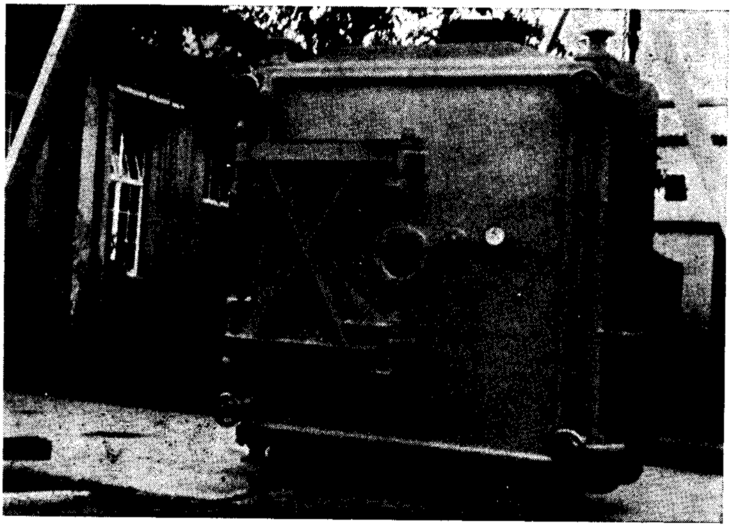


FIG. 42. Vacuum drier. Courtesy H. Orth G.m.b.H., Ludwigshafen-Oggersheim.

After accurate determination of its moisture content the fulminate may be used for the manufacture of mixtures by the so-called wet method. Alternatively it can be dried before mixing.

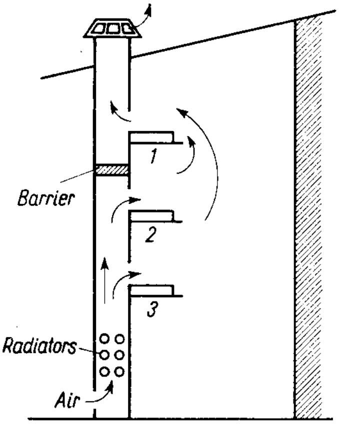


FIG. 43. Diagrammatic view of a drier with natural draught for mercury fulminate, according to Vennin, Burlot and Lécorché [66].

Drying mercury fulminate has always been a difficult problem. For a long time cylindrical vacuum driers (Fig. 41) were used in which the suction effect of the vacuum pressure (100–200 mm Hg), normally held the lids tightly in place.

In the event of an explosion the lids were blown off, and this sometimes prevented the destruction of the drier. The method was not very safe, however, especially when drying other primary explosives. The fulminate was dried at a temperature between 35 and 45°C.

Another former method for drying mercury fulminate in a warm air stream made use of a natural draught (Fig. 43). The fulminate is spread in thin layers over frames wrapped with silk and arranged on shelves (*1*) (*2*) (*3*). Each frame contains approximately 1.5 kg of fulminate.

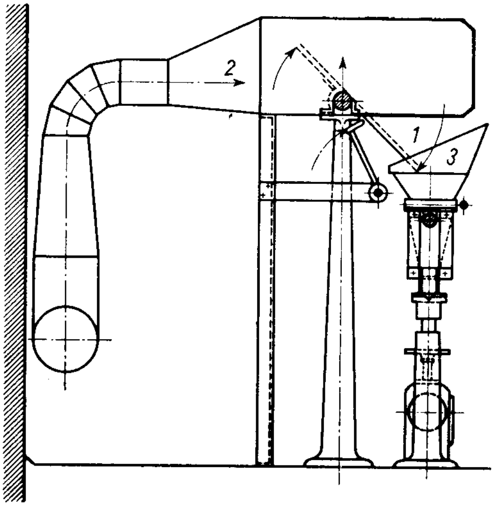


FIG. 44. Diagrammatic view of a German brattice drier for primary explosives with screening of the product [67].

Brattice driers, incorporating a device for removing the dried material (Fig. 44) have been used in Germany. The moist material, spread in a thin layer over cloth stretched on wooden frames (*1*), is dried in warm air supplied via the ducting (*2*) at a rate of about 0.5 m/sec. Next to the frame on which the material is dried there is a tin funnel (*3*) with a built-in sieve in its base. This funnel is connected with the ventilating duct by a flexible tube. Each frame (*1*) contains about 1.2 kg of fulminate (dry substance). To dry a batch of fulminate at 65–70°C takes 1–1.5 hr.

After drying the material is cooled in a current of cold air produced by introducing cold water into the system that normally produces warm air. Since the dried material may become electrically charged even though the frame on which it was dried is earthed, to permit the charge to escape, a certain amount of water is sprayed over it from a water feed nozzle located near the ducting supplying the drying air. These operations take approximately 0.5 hr.

After cooling the frames (*1*) are tilted so that dried material is allowed to run through the funnel (*3*) onto a vibrating sieve. A special device is employed to tap the inclined frame, to ensure that pouring proceeds smoothly. Both the tilting and tapping of the frames is carried out by mechanisms controlled from behind a wall or an adjacent room.

The funnel (*3*) through which the dried material is poured onto the sieves is made of graphitized leather, and the sieves of stainless wire are suspended on belts also made of graphitized leather.

The sifted material is poured into a cylindrical vessel of graphitized plastic, approximately 18 cm high and 6 cm in diameter, loosely covered with a lid of soft, black rubber.

The floors in the building are covered with polyvinyl chloride containing graphite or aluminium powder to make them conduct electricity. The air must not be too dry, since this favours the build-up of static charges so it is kept humid by hanging cloth saturated with water on the walls and by moistening the floors from time to time or by using air-conditioning equipment.

Treatment of waste

Waste substances from the manufacture of mercury fulminate are:

(1) the spent liquor decanted from above the product;

(2) the sediment removed from the mercury fulminate by washing ("slime");

(3) condensed vapours.

(1) The spent liquor contains about 3% of dissolved substances, comprising 90–96% of oxalic acid and 3–6% of mercury in the form of mercurous nitrate. The recovery of mercury in the form of mercurous chloride or mercury proper is usually profitable. This is achieved by adding nitric acid to the spent liquor (1 l. of concentrated hydrochloric acid to 50 l. of liquid). The sediment which is precipitated is separated by decantation and dissolved in concentrated hydrochloric acid, using 10 kg of hydrochloric acid for 10 kg of sediment. Next a solution of pieces of tin (1 kg) in hydrochloric acid (6 kg) is added and pure mercurous chloride is precipitated.

Mercury may also be recovered in a metallic form by neutralizing the liquor with milk of lime and dissolving the precipitated sediment in hydrochloric acid, recovering the mercury by electrolysis or by displacement with zinc.

(2) The "slime" is processed in a similar manner, viz. it is dissolved in hydrochloric acid and the mercury recovered from the solution by one of the methods outlined above.

(3) The liquid in the jars and condenser tower may be distilled over sodium hydroxide. The recovered alcohol can be recycled.

(4) Residues of mercury fulminate are destroyed either by dissolving them in sodium thiosulphate or by covering them with quick lime and treating the mixture with live steam.

OTHER SALTS OF FULMINIC ACID

Among other fulminates, the silver salt, $(CNO)_2Ag$, is of some importance. It is prepared in a way similar to mercury fulminate, by the action of alcohol on a silver solution in nitric acid. Silver fulminate, however, is of little value as an explosive since silver is an expensive raw material. Detonators of silver fulminate were employed only in the Italian Navy.

The other fulminates are of no practical value. They are prepared from mercury fulminate either by reacting the metal amalgam with a suspension of mercury fulminate in water (this is applicable to the majority of metals, including the alkali metals, or simply by the action of the metal itself (e.g. zinc or thallium) which displaces mercury from mercury fulminate (also in water). For example, chips of thallium, zinc, or copper are allowed to stand for some time in a suspension of mercury fulminate in water, the corresponding metal fulminate is gradually formed.

TABLE 24

COMPARISON OF THE PROPERTIES OF FULMINATES

Fulminate	Initiation temperature °C	Sensitiveness to impact, work in kgm/cm²
Sodium	215	–
Potassium	225	–
Calcium	195	165
Strontium	205	170
Barium	220	175
Cadmium	210	110
Copper(II)	205	110
Manganese	215	150
Thallium	110	40
Silver	170	–

Rosenberg [63] investigated the properties of sodium, potassium, calcium, strontium, barium, cadmium, cupric, copper, manganese, thallium and silver fulminates and compared them with mercury fulminate. Some of this results are shown in Table 24.

TABLE 25

Smallest amount which will cause detonation of	Initiated high explosive		
	Tetryl	Picric acid	TNT
Mercury fulminate	0.29	0.30	0.36
Silver fulminate	0.02	0.05	0.095
Cadmium fulminate	0.08	0.05	0.11
Copper fulminate	0.025	0.08	0.15
Thallium fulminate	0.30	0.43	

Martin [64] examined the initiating properties of certain fulminates, and found that silver, cadmium and copper fulminates have stronger initiating properties than mercury fulminate. Table 25 and Fig. 45 show the figures obtained by Wöhler and Martin [65], expressed as the smallest amounts of the fulminate of different metals necessary to produce detonation of various high explosives.

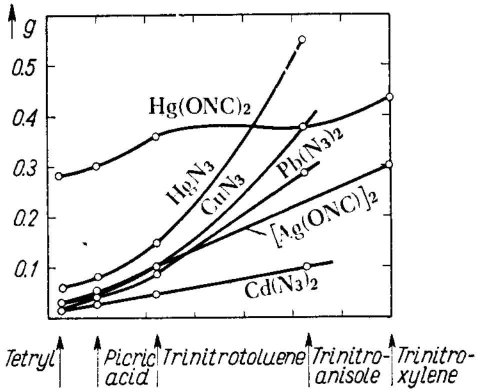
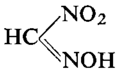


FIG. 45. Initiating ability of various priming explosives, according to Wöhler and Martin [65].

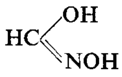
These compounds, however, have not been used in practice (apart from silver fulminate, as mentioned above) due to the high cost of preparing them.

Fulminic acid can be regarded as the simplest oxime. A number of compounds with an oxime group C=NOH can form salts which possess initiating properties, for example salts of nitroformoxime (methylnitrolic acid) (I) which can be obtained in a known way by the action of nitrous acid on nitromethane. Salts of formhydroxamic acid (II), particularly the mercuric salt, also possess initiating properties [66]. Formhydroxamic acid can be obtained by the action of hydroxylamine on formic acid esters or by oxidation of methylamine.



$$\mathrm{HC}\begin{matrix}\diagup \mathrm{NO_2}\\ \diagdown\!\!\diagdown \mathrm{NOH}\end{matrix}$$

I



$$\mathrm{HC}\begin{matrix}\diagup \mathrm{OH}\\ \diagdown\!\!\diagdown \mathrm{NOH}\end{matrix}$$

II

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CHAPTER III

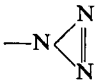
HYDRAZOIC ACID AND ITS SALTS

HYDRAZOIC ACID

HYDRAZOIC acid is a colourless liquid, of sharp, irritating odour with a boiling point of about 37°C and a freezing point of about −80°C. It is highly poisonous, its toxicity being of the order of that of hydrogen cyanide. Even the earliest investigators (Curtius [1]) reported that the vapours of hydrazoic acid irritate the respiratory tract, particularly the nasal mucosa, and that its aqueous solution burns the skin. Stern [2] describes a serious case of poisoning with hydrazoic acid. According to the studies of Pravdin and Shakhnovskaya [3] and Shakhnovskaya [4], hydrazoic acid interferes with the oxidation–reduction processes in the human body. Concentrations in air within the range 0.0005–0.007 mg/l. evoke marked symptoms of intoxication. The toxic effect may be delayed, symptoms appearing the day following exposure. The salts of hydrazoic acid, e.g. sodium azide, are also highly poisonous.

Hydrazoic acid in liquid form is very dangerous to handle owing to the ease with which it explodes.

Its chemical structure has been the subject of many investigations. At first, it was assumed to possess either a ring structure as an acid radical — N_3 (I) (Curtius [1]), or a chain structure (II) (Thiele [5], Franklin [6]):

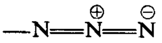


I

$-N=N\equiv N$

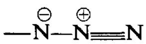
II

X-Ray investigations of the structure of azides by Hendricks and Pauling [7], and Frevel [8] confirmed Thiele's formula (II) and indicated that the chain structure (III) has the extreme forms a and b:



$-N=\overset{\oplus}{N}=\overset{\ominus}{N}$

IIIa



$-\overset{\ominus}{N}-\overset{\oplus}{N}\equiv N$

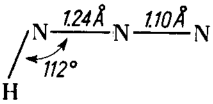
IIIb

The interatomic distances are equal, amounting on average to 1.15 Å.

The more recent investigations by Llewellyn and Whitmore [9] with strontium azide, for example, have confirmed the above findings. The distances between the atoms of nitrogen are 1.12 Å, and between the furthest atoms of nitrogen in the two N_3 groups and the atom of strontium: 2.63 and 2.77 Å respectively.

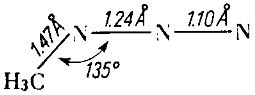
Knaggs [10] found that in the case of cyanuric triazide the distance between the pairs of nitrogen atoms is not the same, being 1.26 and 1.11 Å respectively. Examination of the Raman spectrum of sodium azide solutions has confirmed the chain structure of hydrazoic acid (Langseth, Nielsen and Sörensen [11]). The same conclusion is drawn from investigations of the absorption spectrum in the infra-red (Herzberg *et al.* [12]).

For the gaseous state the interatomic distances and angles



were determined by investigation of the rotational spectrum (Eyster [13]) and the microwave spectrum (Amble and Dailey [14]).

The structure of methyl azide, the simplest organic derivative of hydrazoic acid, is:



i.e. a characteristic bending of valency bond occurs at the end of the N_3 system.

The structure of the $-N_3$ group has also been elucidated by Clusius and Weisser [15], by reacting phenylhydrazine with nitrous acid labelled with the heavy isotope ^{15}N:

$$C_6H_5NHNH_2 + H^{15}NO_2 \rightarrow C_6H_5N_2{}^{15}N$$

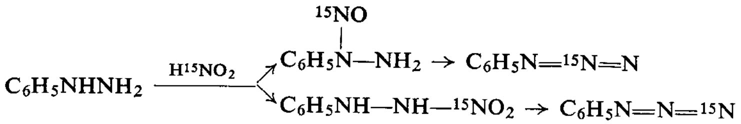
The phenyl azide so obtained was reacted with phenylmagnesium bromide to give diazoaminobenzene, which, in turn, was split into aniline and ammonia. Determination of the isotope content of the reaction products proved that the only linear formula that fits is that in which the extreme nitrogen is the isotope ^{15}N:

$$C_6H_5\overset{\ominus}{N}{=}\overset{\oplus}{N}{=}{}^{15}\overset{\ominus}{N} + C_6H_5MgBr \rightarrow \tfrac{1}{2}C_6H_5N{=}N{-}{}^{15}NHC_6H_5 + \tfrac{1}{2}C_6H_5NH{-}N{=}{}^{15}NC_6H_5$$

The reduction of both of these compounds would give, in all, 1 mole of aniline, 1 mole of labelled aniline ($C_6H_5{}^{15}NH_2$) and 1 mole of ordinary ammonia. This is in agreement with the results of the experiment.

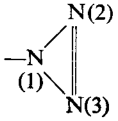
Apart from compound (I) an insignificant amount of product (II) is formed in which the heavy nitrogen occupies a different position $C_6H_5{-}N{=}{}^{15}N{=}N$.

On the basis of their observations, the authors drew up the following reaction mechanism for the formation of phenyl azide:



$$C_6H_5NHNH_2 \xrightarrow{H^{15}NO_2} \begin{cases} C_6H_5\overset{^{15}NO}{N}-NH_2 \rightarrow C_6H_5N{=}^{15}N{=}N \\ C_6H_5NH-NH-{}^{15}NO_2 \rightarrow C_6H_5N{=}N{=}^{15}N \end{cases}$$

If the group N_3 had a ring structure, the equivalence of the nitrogen atoms (2) and (3)



would involve the addition of phenylmagnesium bromide at both positions (2) and (3) with the same probability. The addition products would be the following labelled diazoaminobenzenes:

$$\tfrac{1}{4}C_6H_5N{=}N-\overset{*}{N}HC_6H_5 + \tfrac{1}{4}C_6H_5NH-N{=}\overset{*}{N}C_6H_5$$

$$+ \tfrac{1}{4}C_6H_5N{=}\overset{*}{N}-NHC_6H_5 + \tfrac{1}{4}C_6H_5NH-\overset{*}{N}{=}NC_6H_5$$

The reduction of these compounds would give ½ mole of labelled aniline, 1½ moles of ordinary aniline, ½ mole of labelled ammonia and ½ mole of ordinary ammonia, which is incompatible with the experimental results actually obtained.

Spectrographic analysis of the derivatives of hydrazoic acid

Electronic spectrum. The N_3 group is a chromophore, and may be classified as a chromophore with two cumulated double bonds (Braude [16])

$$N{=}N\Rightarrow N$$

Such chromophores are characterized by absorption bands of low intensity.

Ethyl azide and azidoacetic acid N_3CH_2COOH may serve as examples of compounds in which N_3 is linked to an organic residue by a covalent bond. In an alcohol solution they show the following bands:

285 mμ of very low intensity ($E = ca.\ 20$) and
220 mμ of higher intensity ($E = ca.\ 150$) (V. Henri [17], W. Kuhn and Braun [18], Mohler [19], Sheinker [20]).

Sheinker and Syrkin [21] discovered a difference between the absorption spectrum of the ion $N_3^{\ominus}$ in inorganic and organic azides (salts). They concluded that the transition from the azide ion to the azide linked with alkyl group by a covalent bond involves a change in the symmetry of the N_3 group due to the change in length of the bonds N — N.

According to Jacobs and Tompkins [22] in the reflection spectrum sodium azide and barium azide give a band with the maximum in the vicinity of 240 mμ and 202 mμ respectively. Evans and Yoffe [23] found a value of 248 mμ for potassium azide. Tompkins and Young [24] established that potassium azide gives new absorption bands on irradiation in the ultra-violet at a low temperature (−196°C).

For other azides (in the solid state) the following bands were found in the reflection spectrum:

TABLE 26

Azide	Bands max.	Temperature	Author
TlN_3	275 mμ	room temperature	Evans, Yoffe [23]
	320 mμ	room temperature	Evans, Yoffe [23]
	425 mμ	room temperature	Evans, Yoffe [23]
AgN_3	359 mμ	−175°C	McLaren, Rogers [25]
$Hg_2(N_3)_2$	390 mμ	room temperature	Deb, Yoffe [26]
$Pb(N_3)_2$	400 mμ	room temperature	McLaren [27]

Infra-red spectrum. The spectrum of hydrazoic acid has been examined by a number of authors. Thus, two bands were found by Eyster [28]:

2141 cm^{-1} asymmetric stretching vibrations and
1269 cm^{-1} symmetric stretching vibrations.

Dows and Pimentel [29] present the following table for the frequencies of vibrations of HN_3 and DN_3

TABLE 27

Approximate description	Frequency, cm^{-1}	
	HN_3	DN_3
H—N stretching	3336	2480
N—N—N asymmetric stretching	2140	2141
N—N—N symmetric stretching	1274	1183
H—N—N bending	1150	955
N—N—N bending	672	638
N—N—N bending	522	498

The asymmetric and symmetric vibrations of methyl azide have frequencies of 2141 cm^{-1} and 1351 cm^{-1} respectively (Eyster and Gillette [30]). For a number of aliphatic and aromatic azides Lieber *et al.* [31] found the figures 2114–2083 cm^{-1} for asymmetric vibrations and 1297–1256 cm^{-1} for symmetric ones. Among the other authors who have examined organic azides the investigations of Boyer [32] and Evans and Yoffe [33] are noteworthy.

The most extensive investigations of the infra-red and Raman spectra of metal azides were made by Gray and Waddington [34]. The Raman spectrum of azides was studied by: Kahovec *et al.* [35], Kohlrausch and Wagner [36], and Sheinker and Syrkin [21].

The results of the investigations of Gray and Waddington are tabulated below.

TABLE 28

FUNDAMENTAL VIBRATION FREQUENCIES OF N_3 ION (GRAY AND WADDINGTON [34])

Salt	Frequencies, cm^{-1}			
	Raman		Infra-red	
LiN_3	1369	1277	2092	635
NaN_3	1358	1267	2128	639
KN_3	1344	1273	2041	645
RbN_3	1339	1271	2024	642
CsN_3	1329	1267	2062	635
$Ca(N_3)_2$	1380.5	1267	2114	638
$Sr(N_3)_2$	1373	1273	2096	635
$Ba(N_3)_2$	1354	1278	2123	650
			2083	637
NH_4N_3	1345	–	2041	661
				650

The infra-red spectra of the heavy metal azides, which are the most interesting because of their explosive properties, were investigated by Garner and Gomm [37], Lecomte *et al.* [38], and the Raman spectra have been studied by Kohlrausch and Wagner [36], and by Deb and Yoffe [26]. The results are given in Table 29.

TABLE 29

Salt	Frequencies, cm^{-1}				Author
	Raman		Infra-red		
TlN_3			1941	636	Lecomte *et al.* [38]
AgN_3			2173	644	Lecomte *et al.* [38]
				680	Lecomte *et al.* [38]
CuN_3	1337		2110	615	Deb and Yoffe [26]
		1268		642	Lecomte *et al.* [38]
$Hg_2(N_3)_2$	1300		2080	1322, 1273, 647, 592	Deb and Yoffe [26]
$Hg(N_3)_2$	1313		2070	675, 644, 642 584	Deb and Yoffe [26]
$Pb(N_3)_2$	1352			630	Lecomte *et al.* [38]
	1350	1254	2006	628	Kohlrausch et al. [35, 36]
			2080		Garner and Gomm [37]
	1352		2040		

Summing up the infra-red and Raman spectra data of various authors, Bellamy [39] quotes the following frequencies:

for asymmetric vibrations	2160–2120 cm^{-1}
for symmetric vibrations	1340–1180 cm^{-1}

The first of these bands has a frequency very similar to that of a diazo group and of the C=N group in isocyanates and other compounds.

Hydrazoic acid is a weak acid like acetic acid. Mendeleyev [40] noted its acidic properties. It reacts with zinc, iron, magnesium and aluminium, to form azides with evolution of hydrogen (Curtius and Rissom [41]; Curtius and Darapsky [42]. A small amount of ammonia is also produced, due to the reduction of hydrazoic acid. According to Sofianopoulos [43] heated Al dust reacts with HN_3 to form aluminium nitride

$$6Al + 2HN_3 \rightarrow 6AlN + H_2$$

Hydrazoic acid also reacts with copper, silver and mercury but in a different way: it forms azides without loss of hydrogen and a considerable amount of hydrazoic acid is reduced to ammonia or hydrazine and free nitrogen. The reaction with copper recalls the action of nitric acid on this metal.

$$Cu + 3HN_3 \rightarrow Cu(N_3)_2 + N_2 + NH_3 \tag{3}$$
$$[3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O]$$

Hydrazoic acid, like nitric acid, oxidizes hydrogen sulphide to form sulphur:

$$HN_3 + H_2S \rightarrow S + N_2 + NH_3 \tag{4}$$
$$[2HNO_3 + 3H_2S \rightarrow 3S + 2NO + 4H_2O]$$

When mixed with hydrochloric acid it forms a solution resembling that of nitrohydrochloric acid in its properties and capable of dissolving noble metals, e.g. platinum:

$$Pt + 2HN_3 + 4NHCl \rightarrow PtCl_4 + 2N_2 + 2NH_3 \tag{5}$$
$$[3Pt + 4HNO_3 + 12HCl \rightarrow 3PtCl_4 + 4NO + 8H_2O]$$

Hydrazoic acid reacts with potassium permanganate. They mutually reduce each other to evolve a mixture of nitrogen and oxygen. Nitrous acid oxidizes hydrazoic acid with the evolution of nitrogen.

Hydrazoic acid and its salts give a deep red colour with ferric chloride resembling that of ferric chloride with the salts of thiocyanic acid. This colour fades under the influence of hydrochloric acid.

Liquid hydrazoic acid explodes on heating to 100°C in a tube (Dennis and Isham [44]). According to R. Meyer and Schumacher [45] an explosion may also occur either on rapid cooling, on filtering the liquid acid under vacuum or by passing compressed oxygen into a vessel containing liquid hydrazoic acid. These authors examined the decomposition of gaseous hydrazoic acid at temperatures ranging from 306 to 330°C under pressures between 30 and 200 mm Hg. Decomposition proceeds quantitatively according to the equation

$$3HN_3 \rightarrow NH_3 + 4N_2$$

The reaction is monomolecular. The half-life at 330°C is 12 min. In a dilute aqueous solution hydrazoic acid is stable and not liable to decompose even on long boiling (Curtius [46]). However, a 17% aqueous solution of hydrogen azide can probably detonate [47].

Gaseous hydrazoic acid is liable to non-explosive decomposition at a temperature above 250°C. At 33°C the half-life is 12 min.

Hydrazoic acid is decomposed by ultra-violet radiation. In all probability the decomposition proceeds gradually with the formation of free radicals (Beckman and Dickinson [48]):

$$HN_3 + h\nu \rightarrow HN + N_2$$

$$HN + HN_3 \rightarrow H_2 + 2N_2$$

$$HN + HN_3 \rightarrow H_2N_2 + N_2$$

$$H_2N_2 + HN_3 \rightarrow NH_3 + 2N_2$$

According to Stewart [49] hydrazoic acid decomposes under the influence of active nitrogen to form the NH radical.

A number of investigations have been devoted to the thermal decomposition of hydrazoic acid or to decomposition produced by electric discharge. Thus Rice and Freamo [50] established that its thermal decomposition at 77°K leads to the formation of a blue-coloured sediment. At a higher temperature, 148°K, it changes colour, forming a white substance which has been identified as ammonium azide. They suggested that the blue colour is caused by the presence of the free imino radical NH.

Mador and Williams [51] and Dows, Pimentel and Whittle [52] continued investigations on the subject. According to the former the blue substance contains the radicals NH and NH_2 while the latter believe that the radicals NH and $(NH)_x$ are present. Spectrographic analysis by Pannetier and Gaydon [53] has confirmed the presence of the electronically excited NH radical.

Using Norrish's "flash photolysis method" [54], Thrush [55] examined the decomposition of hydrogen azide in the presence of an excess of inert gas. The absorption spectra characteristic of the radicals NH and NH_2 were observed. He therefore suggested an alternative scheme for the decomposition of hydrazoic acid, different from that proposed by Beckmann and Dickinson [56]:

$$HN_3 + h\nu \rightarrow NH + N_2$$

$$NH + HN_3 \rightarrow NH_2 + N_3$$

$$NH_2 + HN_3 \rightarrow NH_3 + N_3$$

$$2N_3 \rightarrow 3N_2$$

He also observed an absorption band at 2700 Å which he attributed to the N_3 radical. According to Gray and Waddington [57] the initial step in the decomposition of HN_3 is nearly thermoneutral:

$$HN_3 \rightarrow HN + N_2, \quad -\Delta H \cong 5 \text{ kcal/mole}$$

Becker, Pimentel and Van Thiel's [58] equally interesting study of the photolysis of solid hydrazoic acid led to the assumption that the radicals NH, NH_2 and N_3 are formed during decomposition.

Franklin, Herron, Bradt and Dibeler [59] studied the decomposition of hydrazoic acid under a reduced pressure, on ignition by means of Tesla discharges. The reaction products included hydrogen, nitrogen, ammonia and undecomposed hydrazoic acid. Similar results were obtained by Foner and Hudson [60].

Irradiation of an aqueous solution of HN_3 leads to the formation of hydroxylamine according to the reaction.

$$HN_3 + H_2O \rightarrow NH_2OH + N_2 \quad \text{(Glen [61])}$$

According to Alekseyev [62] explosion of a mixture of HN_3 and hydrogen gives ammonium azide and the intermediate compound $N_2H_5N_3$.

The salts of hydrazoic acid, the azides, have solubilities similar to those of the corresponding chlorides. Sodium azide dissolves in water. Silver azide does not dissolve in water or in nitric acid, but dissolves easily in an aqueous solution of ammonia. Lead azide, like lead chloride, is sparingly soluble in cold water but more soluble in hot water; it is also soluble in ammonium acetate.

There are two methods for the manufacture of hydrazoic acid or its salts. One is derived from a number of investigations by Curtius [1] and is based on the action of nitrous acid on hydrazine:

$$NH_2{-}NH_2 + HONO \rightarrow HN_3 + 2H_2O \tag{6}$$

An excess of nitrous acid decomposes hydrazoic acid in accordance with the equation:

$$HN_3 + HONO \rightarrow N_2 + N_2O + H_2O$$

(Seel and Schwaebel [63], G. Stedman [64]).

The reaction is quantitative and is used in practice for destroying waste azides.

Reaction (6) is particularly well suited for use in the preparation of the organic derivatives of hydrazoic acid from the corresponding derivatives of hydrazine. Nitrous esters may be employed, instead of the acid, e.g. ethyl nitrite in the presence of sodium hydroxide

$$NH_2{-}NH_2 + C_2H_5ONO + NaOH \rightarrow NaN_3 + C_2H_5OH + 2H_2O \tag{7}$$

This method is preferable to reaction (6) since the sodium salt is formed instead of the volatile and highly toxic hydrazoic acid.

The other widely used method, that of Wislicenus [65], is based on the action of nitrous oxide on sodium amide. The reaction takes place in the following sequence:

$$2NH_3 + 2Na \xrightarrow{300^\circ C} 2NaNH_2 + H_2 \tag{8}$$

$$NaNH_2 + N_2O \xrightarrow{190-230^\circ C} NaN_3 + H_2O \tag{9a}$$

$$NaNH_2 + H_2O \longrightarrow NaOH + NH_3 \tag{9b}$$

Reactions (9a) and (9b) proceed concurrently: nitrous oxide first reacts with molten sodium amide to form sodium azide and water vapour. The latter then reacts with another molecule of sodium azide, hydrolysing it with the formation of sodium hydroxide and ammonium (9b).

The mechanism of reaction (9a) has been examined by isotope techniques using nitrous oxide labelled with ^{15}N (Clusius *et al.* [66, 67]). The course of the reaction may be summarized by the equations:

$$2NaNH_2 + O^{15}NN \xrightarrow{-NaOH,-NH_3} \begin{array}{l} \nearrow Na^{15}NNN\ (22\%) \\ \searrow NaN^{15}NN\ (78\%) \end{array}$$

Among other reactions leading to the production of hydrazoic acid, the following are noteworthy for theoretical reasons:

The formation of hydrazoic acid and its derivatives together with ammonia from diazo compounds under the influence of hydrazine or its derivatives was explained by Thiele [68]. At an intermediate stage a diazohydrazine, e.g. $C_6H_5N_2NHNH_2$, is formed which then undergoes decomposition according to two parallel reactions:

$$\begin{array}{l} C_6H_5N_2NHNH_2 \rightarrow C_6H_5NH_2 + HN_3 \\ \qquad\qquad\qquad \searrow C_6H_5N_3 + NH_3 \end{array} \tag{10}$$

Hydrazoic acid may be formed from hydrazine under the influence of oxidizing agents. This was first noticed by Sabaneyev [69] who acted hydrazine with nitric acid. According to Jannasch and Jahn [70] chlorates act similarly in an acidic medium while Turrentine and Olin [71] found that hydrazine can be oxidized by electrolysis to hydrazoic acid. On the other hand, according to Tanatar [72] a number of other oxidizing agents such as chromic acid, permanganates, and hydrogen peroxide give hydrazoic acid only in the presence of hydroxylamine. The reaction probably occurs in the following way:

$$N_2H_4 + NH_2OH + 2O \rightarrow HN_3 + 3H_2O \tag{11}$$

The preparation of inorganic azides was reviewed by Audrieth [73] and more recently by Evans, Yoffe and Gray [74].

LEAD AZIDE

Neutral azide

Apart from mercury fulminate, lead azide is the most important primary explosive.

Lead azide can exist in two allotropic forms: the α-form is orthorhombic, the β-form monoclinic. (Miles [75], Garner and Gomm [37]). The crystallographically stable modification is the α-form. It is prepared by rapidly stirring a solution of sodium azide with a solution of lead acetate or lead nitrate.

The β-form is prepared by slow diffusion of sodium azide and lead nitrate solutions. This form has a tendency to revert to the α-form, either on standing at an elevated temperature (*ca.* 160°C), or when crystals of the β-form are kept in water containing a crystal of the α-form (Azároff [76]) or on contact with a lead salt solution (Miles [75]).

The properties of both those forms, as reported by Gray and Waddington [77], together with new figures for the density, are tabulated below.

TABLE 30

Species	Density	Unit cell size			No. of molecules in unit cell	Heat of formation $-\Delta H_f$ kcal/mole
		a	*b*	*c*		
orthorhombic	4.71	6.628	11.312	16.256	12	115.5
monoclinic	4.93	5.090	8.844	17.508	8	115.8

The apparent density of the α-form is 1.2.

The earlier opinion that the β-form is the more sensitive to impact appears to be incorrect. This problem will be discussed more fully in the section on the explosive properties of lead azide.

Lead azide is insoluble in an aqueous solution of ammonia. Acetic acid causes its decomposition but it is soluble in water and concentrated solutions of sodium nitrate, sodium acetate or ammonium acetate. There are fairly big differences of solubility, depending on temperature.

Solonina [78] quotes the following figures for the solubility of lead azide:

in 100 ml of water	at 18°C	0.023 g
	at 70°C	0.090 g
in 100 ml of concentrated solution of $NaNO_3$	at 18°C	0.125 g
	at 80°C	0.487 g
in 100 ml of concentrated solution of CH_3COONa	at 18°C	1.542 g
	at 80°C	2.020 g

Owing to the difference between its solubility in the cold and in the hot, lead azide may be recrystallized from water or from the solutions mentioned above. Under these conditions the crystals are obtained in the form of long, colourless needles.

Majrich [79] reports that lead azide dissolves in ethanolamine, but it is not practicable to precipitate a pure form, suitable for commercial use by dilution of this solution.

According to Wöhler and Krupko's [80] data, recrystallization of lead azide from water or from aqueous solutions is not free from hazard, since the salt often explodes during crystallization. For this reason lead azide is not recrystallized in practice. The phenomenon will be discussed later on p. 173.

The specific heat of lead azide, as reported by Yuill [81], is:

at 100°C	0.100 cal/g
at 200°C	0.117 cal/g
at 250°C	0.116 cal/g

McLaren [82] determined the thermal conductivity of pressed pellets of azides and obtained a value of 4×10^{-4} (c.g.s. units) at 45°C, the density of the pellets being 3.62 g/cm^3.

The V.D.H. hardness values of the crystals, according to Yuill [81] are

for α-lead azide: 114 kg/mm^2 at a load of 50 g
103 kg/mm^2 at a load of 20 g
for β-lead azide: 65 kg/mm^2 at a load of 5 g

Todd and Parry [83] quote figures for the α-form which prove that lead azide is much harder than mercury fulminate.

Lead azide, like hydrazoic acid, is liable to undergo oxidation and reduction reactions. It is partially decomposed by atmospheric oxygen to form free hydrazoic acid, nitrogen and ammonia. This reaction is promoted by the presence of carbon dioxide in the air. When boiled in water, lead azide undergoes slow decomposition with the evolution of hydrazoic acid.

Lead azide is completely decomposed by the action of dilute nitric or acetic acid in which sodium nitrite has been dissolved, and the products pass to the solution. This reaction may be used for the destruction of lead azide wastes and residues, using 15% nitric acid and 8% sodium nitrite.

In an aqueous suspension, lead azide is oxidized by ceric sulphate to form nitrogen:

$$Pb(N_3)_2 + 2Ce(SO_4)_2 \rightarrow PbSO_4 + Ce_2(SO_4)_3 + 3N_2$$

This reaction may be employed for the quantitative determination of azide.

Long experience in the storage of blasting caps filled with lead azide has shown that this substance reacts with copper or brass to form cupric azide, which is highly sensitive to friction and impact. For this reason lead azide is compressed only into aluminium and zinc cases.

When exposed to light lead azide soon turns yellow on the irradiated side. The layer of changed substance protects the deeper layers from further decomposition and thus irradiation does not entail changes in the explosive properties of the substance. However, as Wöhler and Krupko [80] have shown, if the lead azide is subjected to stirring during irradiation, decomposition may proceed too far.

Slow decomposition of lead azide takes place under the influence of ultra-violet irradiation, as demonstrated by the investigations of Garner and Maggs [84] and Tompkins *et al.* [22, 85], but if the irradiation is very intense, explosion may occur, as was shown by Berchtold and Eggert [86] and Meerkamper [87]. In another paper Eggert [88] reported that the light intensity required to cause the explosion of lead azide is 2.0 J/cm^2 when the electrical energy of the flash is 240 J, and the half-life of the flash 0.8 msec.

As shown by the investigations of a number of authors, irradiation of lead azide (and other azides) with α-particles, X-rays and γ-rays does not cause explosion (Haïssinsky and Walden [89]; Günther, Lepin and Andreyev [90]). However, it produces a slow decomposition of lead azide, according to Kaufman [91].

Groocock [92] noticed that lead azide irradiated with γ-rays at an elevated temperature decomposed more rapidly than that which has not been irradiated.

The thermal stability of lead azide is very high. At 75°C it loses approximately 0.8% of its weight during the first 4 days, after which further heating involves a loss of 0.03–0.05% per week (Wallbaum [93] cf. graph in Fig. 30). At 115°C, in the dark, it undergoes no changes for 24 hr unless the temperature reaches 170°C when a distinct loss of weight takes place during that time. At temperatures above 200°C decomposition is quite rapid, ranging from a few hours to several minutes, depending on the temperature, and the substance loses its explosive properties. On the other hand, in the light, decomposition may be observed even at 50°C.

Bowden and Singh [94] and later Bowden and McAuslan [95] using the electron microscope, observed that on heating at a temperature above 120°C the separate crystals of lead azide (like those of cadmium or silver azides), break down into fine particles, approximately 10^{-5} cm in dia. and decomposition reaction takes place chiefly on the newly-formed surfaces. This makes it evident that the thermal decomposition of azides cannot be regarded as a surface reaction or a process occurring within large crystals only; the whole mass is involved, due to crystal breakdown.

According to various authors, the ignition temperature of lead azide ranges from 327 to 360°C. When a test sample is dropped onto a metal plate instant explosion ensues if the temperature of the plate is 380°C or higher. The ignition temperature of lead azide is the highest ignition temperature of an explosive ever to have been observed.

According to Sudo [96] lead azide prepared by the action of sodium azide on an aqueous solution of lead acetate has a lower ignition temperature (332–336°C) than that obtained by the action on a solution of lead nitrate (339–359°C).

According to Garner and Gomm [37] the activation energy of the thermal decomposition of lead azide is 38.0 kcal/mole, assuming that the reaction can be expressed by an equation of the form $p=kt$.

Evans and Yuill [97] investigated the ignition of dextrinated lead azide by the adiabatic compression of air surrounding it, and estimated that the 50% explosion level corresponds to a temperature of 990°C.

Bryan and Noonan [98] carried out similar investigations using helium and estimated the minimum energy required to ignite lead azide with a 3 msec delay to be 0.087 cal/cm^2, i.e. less than that for blasting gelatine, 0.15 cal/cm^2, PETN, 0.25 cal/cm^2 and tetryl, 0.33 cal/cm^2.

Lead azide detonates with a high rate, amounting to 4500 m/sec at a density of 3.8 and 5300 m/sec at a density of 4.6 (Kast and Haid [99]).

According to the Chemisch Technische Reichsanstalt [100] the rate of detonation of lead azide at a density of 2.75 is 3620 m/sec and at a density of 3.65—4700 m/sec.

The rate of detonation of a thin film of lead azide (0.1–0.5 mm thick) is 2100 m/sec (Bowden and Williams [101]). Lead azide is less sensitive to impact than mercury fulminate, but drop test figures quoted by various authors differ widely. Some of them report a negligible difference between the two, while others state it is considerable (e.g. that azide requires 2–3 times the height of drop necessary to explode fulminate). On the other hand, when mixed with pulverized sand lead azide is more sensitive than mercury fulminate, which makes it evident that lead azide is more sensitive to friction than fulminate. Its high sensitiveness to friction has been confirmed by a number of accidents. Nevertheless, lead azide does not necessarily explode when rubbed in a porcelain mortar. On the other hand, numerous cases of spontaneous explosion of lead azide are known, e.g. during pouring, weighing, drying and even when simply left standing or left for crystallizing. It was formerly believed that the β-form is particularly liable to explosion when crystallized in the form of long needles. Hawkes and Winkler [102], however, prepared crystals of the β-form 3–4 mm long which did not explode on being crushed or broken.

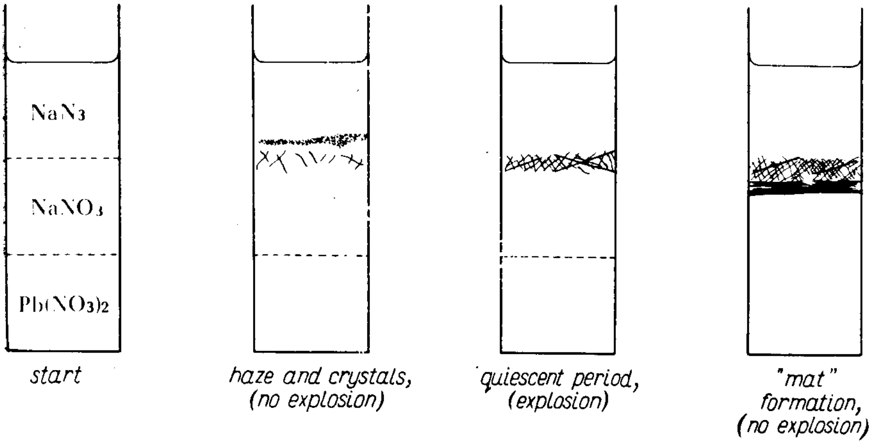


FIG. 46. The diffusion growth of β-lead azide [103].

As stated above, Wöhler and Krupko [80] noticed that lead azide may explode during crystallization. Miles [75] confirmed this and stated that spontaneous explosion could occur during the growth period of crystals of β-lead azide, i.e. when the two solutions forming the crystals diffused slowly. When isolated, however, the crystals (some of which had reached a length of 4 cm) were not found to be particularly sensitive.

Rogers and Harrison [103] tried to determine the conditions governing this phenomenon, i.e. the explosion during the growth of β-lead azide. Their experiments, which are illustrated diagrammatically in Fig. 46, were carried out in a test-tube. Three solutions were carefully introduced so that they did not mix. The bottom layer consisted of 20% lead nitrate (2 cm^3). The middle layer was 20% sodium nitrate (1 cm^3). The top layer was 10% sodium azide (2 cm^3). Crystals of lead azide formed in the sodium nitrate layer after $\frac{1}{4}$–$\frac{1}{2}$ hr. They appeared to start from the walls and spread inwards. A major explosion generally occurred in the system after the crystals had been growing for 6–12 hr. A series of very small explosions accompanied by "clicks" sometimes preceded the major explosion.

Explosion occurred under a number of conditions. For example, if a solution was made up by mixing 5% lead nitrate (0.3 cm^3), 2% sodium azide (0.3 cm^3) and water (2 cm^3) no immediate precipitate was formed. Crystals appeared after *ca.* ½ hr, and spontaneous explosions occurred in certain cases. In all the experiments where crystals exploded the common feature was that the initial concentration of azide in the solution around the crystals was only slightly above the saturation value. No explosions were observed when the azide was precipitated rapidly, using very much stronger solutions. A small rise in temperature e.g. of 10°C appears to increase the probability of explosion.

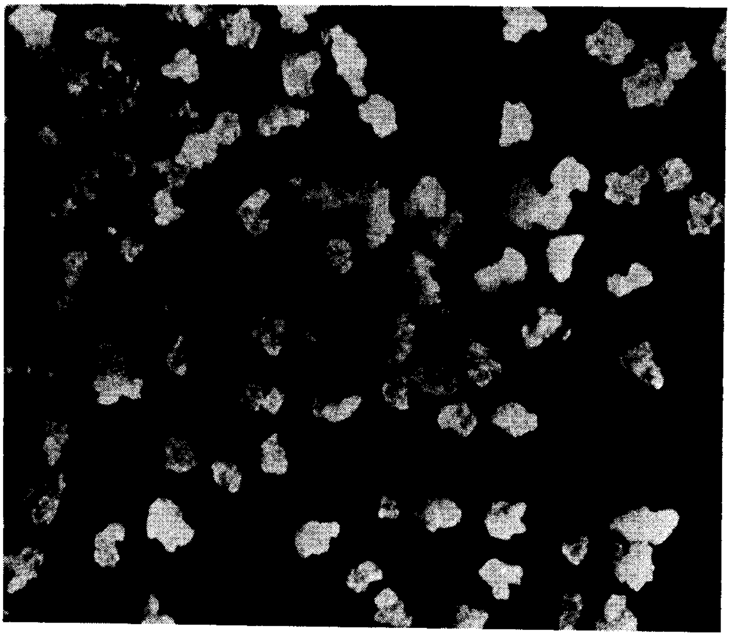


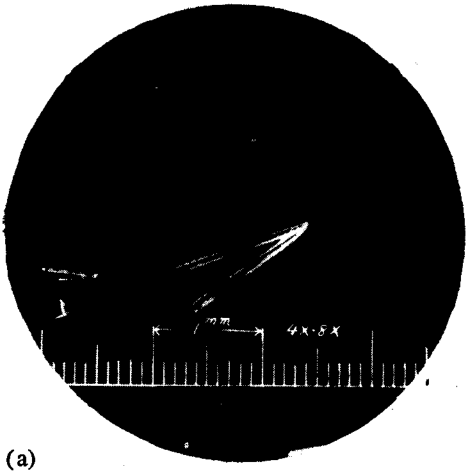
FIG. 47. Lead azide for use in detonators (75 ×) precipitated in the presence of dextrin according to Davis [104].

Spontaneous explosions of lead azide also take place during crystallization from saturated solution in ammonium acetate. A detailed study of this phenomenon has been made by Taylor and A. T. Thomas [105]. When the concentration of the solutions and the temperature and conditions of cooling were carefully controlled, they were able to predict the time at which spontaneous explosions occur. E.g.:

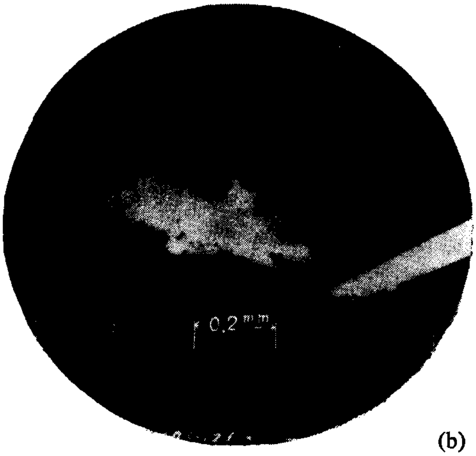
with a 1% lead azide solution in 5% ammonium acetate the explosion may be obtained after 40–45 min,

---

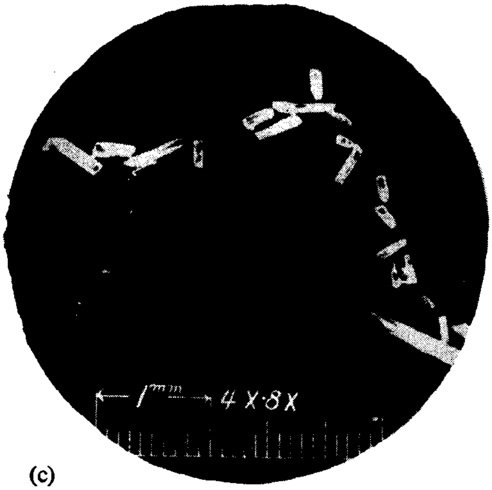
FIG. 48. Lead azide precipitated in different conditions, according to Sudo [96] : (a)—from high concentration of lead acetate (10%) and low of sodium azide (4%); (b)—from low concentration of lead acetate (4%) and high of sodium azide (10%); (c)—from low concentrations of lead acetate (4%) and sodium azide (2%); (d)—from high concentrations of lead acetate (25%) and sodium azide (10%) in the presence of gelatine (5%); (e)—from high concentrations of lead nitrate (25%) and sodium azide (10%) in the presence of gelatine (5%) (very small crystal form).



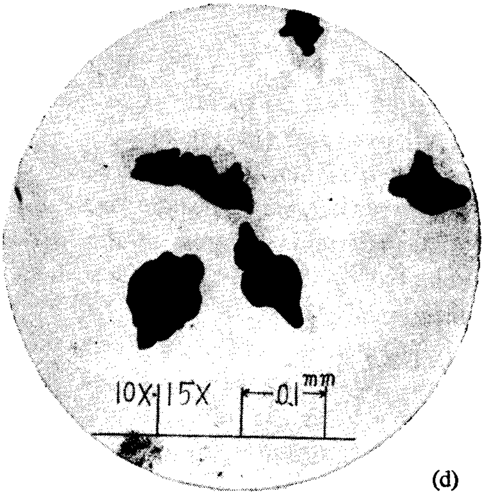
(a)



(b)



(c)



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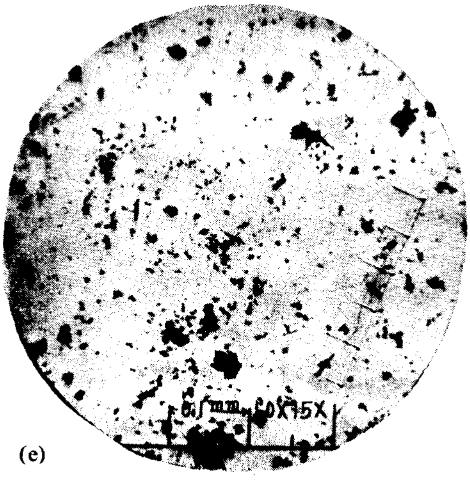


(e)

with a 0.6% and 0.5% lead azide solution, the time is 225–255 min and *ca.* 480 min respectively.

Taylor and Thomas have shown that spontaneous explosions are not associated with the large crystals of lead azide that are formed: they filtered off large crystals *ca.* 30 min before the predicted time of explosion and at the predicted time the mother liquor exploded while the filtered lead azide crystals remained intact.

They also found that by adding small amounts of dextrin, polyvinyl alcohol or other hydrophilic polymers explosion could be prevented. It is known that these compounds are able to alter the crystal habit of several substances, including lead azide.

Clearly, explosion is associated with the very early stages of crystallization.

According to Kaufman [91] spontaneous explosion can also take place during the growth of α-lead azide crystals, e.g. when a supersaturated solution of lead azide in ammonium acetate is seeded with crystals of the α-form. Spontaneous explosions have also been observed with mercuric azide and in some cases with cadmium azide.

According to Sudo [96] spontaneous explosion can occur during the formation of lead azide from sodium azide and lead acetate, when the concentration of reacting solutions is high (10% or more).

When manufacturing lead azide, efforts should be made to precipitate small, highly regular, free flowing crystals of a length not exceeding 0.1 mm.

Considerable progress in the manufacture and application of lead azide was achieved by the addition of dextrin to the solution in which it was produced, as mentioned above.

The presence of dextrin in the solution favours the precipitation of tiny, equal sized, rounded crystals. In Fig. 47 magnified crystals of dextrinated lead azide are shown and in Fig. 48 crystals of ordinary lead azide are shown for comparison. According to Sudo [96] gelatine exerts an influence similar to that of dextrin. In this author's opinion when precipitated from a solution containing gelatine lead azide is less sensitive to friction than that from solutions without added colloids.

The sensitiveness of moist lead azide is not much lower than that of the dry product. According to Wöhler and Krupko [80] a 30% water content does not render the lead azide insensitive.

Yuill [81] investigated the sensitiveness of lead azide to impact at room temperature and at −190°C. He found that 10–15% more energy is required for the initiation of explosion by impact at a low temperature than that at room temperature (Table 31).

The disadvantage of lead azide lies in the difficulty with which it is ignited by a flame. For this reason it is usually mixed with lead styphnate i.e. a substance particularly easy to ignite, or the charge of lead azide in a detonator is covered with a layer of lead styphnate. Such a layer not only facilitates the ignition of the lead azide, but also protects it against the action of carbon dioxide. It is also difficult to ignite lead azide by an electric spark (Brown, Kusler, Gibson [106]).

TABLE 31

INITATION OF EXPLOSION OF LEAD AZIDE PELLETS BY IMPACT

Weight of pellets mg	Specific energy cal/g		Energy difference cal/g
	20°C	−190°C	
0.35	119	134	15
0.42	104	117	13
0.51	93	107	14

Lead azide passes very rapidly from burning to detonation. When used in very small amounts, it is therefore capable of initiating detonation in other explosives, hence it is very suitable for use in detonators though it cannot be employed in caps.

Wallbaum [93] determined the minimum charges of several primary explosives necessary for initiating the explosion of a 0.4 g charge of PETN, loosely poured or pressed. His results are tabulated below.

It is characteristic of lead azide that even under a pressure as high as 2000 kg/cm² it cannot be "dead pressed". This is a great advantage. In practice a pressure of 500–600 kg/cm² is used.

Other data concerning the initiating properties of lead azide, as compared with the other primary explosives, are given in Table 32.

TABLE 32

INITIATION EFFECTS OF PRIMARY EXPLOSIVES

Pressure on PETN, kg/cm²	0	2000	2000	2000	2000
Pressure on initiator, kg/cm²	0	0	500	1000	2000
Primary Explosive	Minimum initiating charge, g				
Lead azide (technical)	0.040	0.170	0.050	0.050	0.040
Lead azide (crystallized)	0.015	0.100	0.010	0.010	0.010
Silver azide	0.005	0.110	0.005	0.005	0.005
Mercury fulminate	0.300	0.330		dead pressed	
Tetrazene	0.160	0.250		dead pressed	
Lead styphnate	0.550	1.000		no detonation	

According to Garner [107] lead azide decomposes in the following way:

$$\tfrac{1}{2}Pb^{2\oplus} + N_3^{\ominus} \rightarrow \tfrac{1}{2}Pb + N_2 + N - 51 \text{ kcal} \qquad (12)$$

$$\tfrac{1}{2}Pb^{2\oplus} + N_3^{\ominus} \rightarrow \tfrac{1}{2}Pb + 2N_2 + 157 \text{ kcal} \qquad (13)$$

According to the equation (12) one atom of nitrogen is expelled from the $N_3^{\ominus}$ ion to form two molecules of nitrogen by reaction with another $N_3^{\ominus}$ ion. Reaction (13) is highly exothermic hence the decomposition of one N_3 group may involve that of

2–3 neighbouring N_3 groups. If these groups decompose simultaneously, the decomposition of 22 ions $N_3^{\ominus}$ may ensue etc. Thus, the rapid transition of lead azide to detonation may be accounted for by the fact that the decomposition of a small number of molecules of lead azide may induce explosion in a sufficiently large number of $N_3^{\ominus}$ ions to cause the explosion of the whole mass.

The decomposition of other salts of hydrazoic acid takes a similar course.

Basic azides

Hydrolysis of lead azide with water or a solution of sodium hydroxide yields basic salts. They are also formed by the treatment of a lead salt solution with sodium azide plus sodium hydroxide solution.

Feitknecht and Sahli [108] found five different basic salts, each of which exists in several crystalline modifications as established by X-ray analysis:

I $Pb(N_3)_2 \cdot PbO$ (3 crystalline modifications)
II $3Pb(N_3)_2 \cdot 5PbO$ (3 crystalline modifications)
III $2Pb(N_3)_2 \cdot 5PbO$
IV $2Pb(N_3)_2 \cdot 7H_2O$
V $Pb(N_3)_2 \cdot n\,PbO$, where n=from 4 to 9.

LEAD AZIDE MANUFACTURE

Lead azide is manufactured on a technical scale by the action of sodium azide on an aqueous solution of lead nitrate. According to a description of manufacture in the Wolfratshausen factory in Germany [109], the reaction is conducted in an open reactor of stainless steel, provided with a jacket warmed by hot water and a stirrer which may be lifted out of the reactor (Fig. 49). The reactor is emptied by tilting. Its upper edge is therefore fitted with a spout so that the contents pour easily. The size of the reactor is such that 4.5 kg of lead nitrate in the form of a 9–10% solution can be used in each batch. This solution is poured into the reactor, warmed to 50°C and neutralized with sodium hydroxide to a pH of about 4.0 (in the presence of methyl orange) and 150 g of dextrin mixed with a small amount of water, is added. The suspension or solution of dextrin in water should be decanted before use to separate mechanical impurities, such as sand.

Next, 1.5 kg of sodium azide is added as a 2.7–3.0% aqueous solution. The solution should be alkaline (50 cm^3 of solution should require 8–10 cm^3 1.0 N H_2SO_4 for neutralization using phenolphthalein as indicator). If the alkalinity is too low, a calculated amount of NaOH should be added to the solution. The above-mentioned quantity of sodium azide is poured into the reactor for 1 hr, maintaining a temperature of 50°C.

After the two solutions have been mixed, stirring is stopped. The lead azide so produced should be allowed to settle after which the liquid above is decanted and the solid is conveyed by a water stream to a cloth filter, stretched on a frame. The azide is washed on the filter with a large amount of water, and then the filter loaded with azide is placed in a bakelite vessel and transferred to the storehouse.

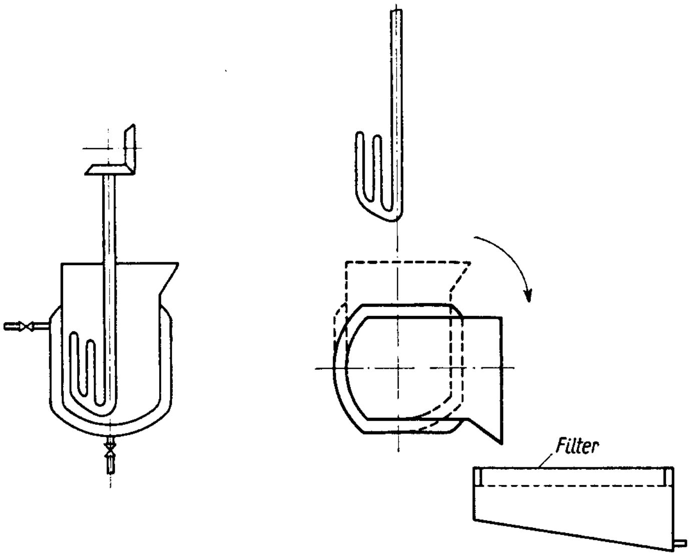


FIG. 49. Diagram of the design and operation of a reactor for the manufacture of lead azide and other primary explosives (tetrazene, lead styphnate and lead picrate).

Drying and sieving is carried out as described in the chapter on mercury fulminate. About 1.2 kg of material is dried at a time on the frame, at a temperature of 65–70°C.

The destruction of azide residues in solutions or suspensions is a matter of great technical importance.

For this purpose the reaction of hydrazoic acid with nitrous acid is utilized (p. 168).

THE CONTINUOUS METHOD OF LEAD AZIDE MANUFACTURE (ACCORDING TO MEISSNER [110, 111])

The method involves introducing a continuous supply of lead nitrate and sodium azide solutions in equivalent proportions into the upper part of the reaction column (Fig. 50) from the bottom of which a suspension of lead azide is removed. The reaction mixture flows down in countercurrent to air blown in.

Lead azide with a purity under 95%

Precipitation. In a dissolving vessel a solution of sodium azide is prepared in distilled water and then aqueous sodium hydroxide is added. The quantity of sodium hydroxide used depends on the amount of lead azide to be produced. The solution thus prepared is conveyed, via a filter, into a receiver standing in the upper floor. Here, it is heated up to the reaction temperature. (According to some information [112] the optimum temperature is 36±1°C. Too high a temperature may cause the precipitation of irregular, small crystals.) In another dissolving vessel a solution of lead nitrate in distilled water is prepared. The solution is filtered and transferred into the receiver. The appropriate amount of dextrin dissolved in water is also added, and the solution is heated up to the reaction temperature. Before the precipitation reaction is begun the precipitation column should be filled with warm distilled water at the desired precipitation temperature, and the air agitation must be switched on. Then the flowmeters for feeding the lead nitrate solution and the sodium azide solutions are opened in turn. After some minutes, the clip of the drain hose is adjusted in such a way that the liquid level in the precipitation column remains at the same height, i.e., the amount of mother liquor discharged with the crystals equals that of the solutions run in. The liquid discharged from the column is led to a vacuum filter.

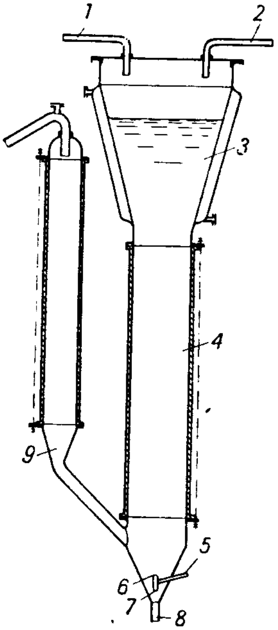


FIG. 50. Column for continuous manufacture of heavy metal azides and lead styphnate, according to Meissner [110]: *1,2*—inflow of reacting solutions, *3,4*—reaction column, *5*—air nozzle with exit openings, *6* and *7* directed up- and downwards, respectively, *8*—outlet, *9*—overflow.

When sufficient lead azide is gathered on one of the suction filters, the liquid from the column is discharged to the second vacuum filter. The lead azide is washed with distilled water until it is no longer alkaline. As soon as sufficient lead azide has been collected on the second suction filter, the liquid discharged from the column is directed once more onto the first suction filter. Each time, the lead azide accumulated on the filter is washed until no alkalinity is shown.

The crystal structure of the lead azide is checked by examination under a microscope at frequent intervals from the beginning of the precipitation. The lead azide is precipitated as spherical crystals (Fig. 51).

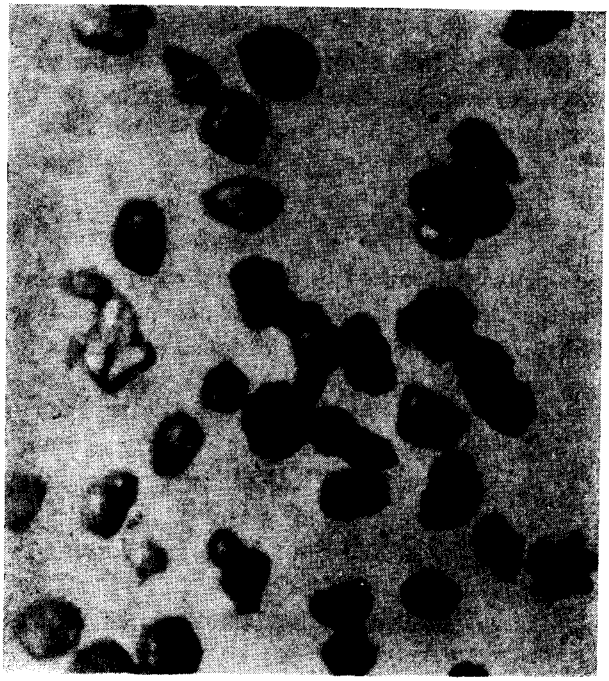


FIG. 51. Lead azide precipitated by Meissner method [111]. Courtesy J. Meissner.

The mother liquor and washing water sucked off from the vacuum filters are led into a destruction vat.

Cleaning and destruction. After the precipitation has been completed, the precipitation column and suction filters should be washed thoroughly with water. For cleaning, the precipitation column is filled with water, nitric acid and sodium nitrite are added, and the air agitation is switched on for half an hour. Then the contents are discharged and the column is rinsed again with water to remove the acid.

The mother liquor and washing waters from precipitation and cleaning carry some lead azide. All the mother liquors and washing waters are therefore collected in a vat, where nitric acid and sodium nitrite are added, and the liquid is stirred for half an hour. After the lead azide has been destroyed, the acid waste waters — which are no longer explosive — are discharged into a sump or the sewerage system.

Drying and sifting. The washed lead azide is removed from the filters while still damp, and carried in a bucket to the separate drying house. There it is laid in a thin layer on trays covered with conductive rubber. The warm air used for drying is supplied from a separate room.

After the drying process, cold air is admitted for a short time into the drying room to cool the lead azide to ambient temperature and bring its humidity to that prevailing at room temperature.

Subsequently, the lead azide is transferred into composition boxes behind a protective wall. Sifting takes place in a separate bulding, on a special vibratory sieve. The explosive is poured out of the composition boxes into the sieve funnel in a safe place behind a protective wall. The sifted lead azide is collected in an empty composition box placed underneath.

Lead azide with a purity of more than 95%

Pure lead azide may be produced in the same equipment, but instead of lead nitrate and dextrin lead acetate is employed. The precipitation temperature is lower than in the manufacture of technical-grade lead azide (having a purity of less than 95%). All other operations are the same as already described.

SILVER AZIDE

Silver azide is slightly hygroscopic — at room temperature in a damp atmosphere it picks up approximately 2% of water.

Silver azide is a very vigorous initiator, almost as efficient as lead azide (cf. Table 32).

The researches of Wischin [113] and those of Garner and Maggs [84] have shown that metallic nuclei are formed during the slow thermal decomposition of silver azide. These researches were carried out by means of an optical microscope.

Sawkill [114] recently confirmed this observation using an electron microscope and found that silver is evolved as the result of slow reactions. In the early stage of decomposition intermediate compounds, richer in silver than azide, are formed. The pure metal, which is evolved only in the final stage of decomposition has a markedly oriented structure and a grain size of $0.1\times0.1\times0.05$ mμ.

Like lead azide, silver azide decomposes under the influence of ultra-violet irradiation. If the intensity of radiation is sufficiently high the crystals may explode (cf. p. 171).

The explosion of silver azide under the influence of brief, intensive irradiation was studied by Berchtold and Eggert [86] and Meerkamper [87]. The intensity of light causing the explosion of silver azide is 2.6 J/cm^2, the el ectrical energy necessary to produce a flash with a half-life of 0.8 m/sec being 310 J.

The same problem was later investigated by Courtney-Pratt and Rogers [115]. They found that the energy required to cause silver azide to explode should be greater than 8×10^{-4} cal per mm^2 of the crystal surface.

Eggert and Courtney-Pratt and Rogers state that the decomposition of silver azide under the influence of irradiation has a thermal character, i.e. that light absorbed by a thin surface layer of the crystal is degraded into heat in a very short time interval (less than 1/50 μsec), whereupon explosion occurs by the normal thermal mechanism.

According to Bowden and Yoffe [116] other possible mechanisms should be considered, including direct photochemical decomposition. A number of experiments have been carried out by members of the Bowden school.

Thus, according to Rogers [117] when the surface of crystals which have been given a flash, but which have not exploded or broken down, is examined by an optical microscope, it can be seen that the crystal is much darkened on the irradiated face, and contains many irregular but parallel cracks. The cracks are not visible on the other side of the crystals suggesting that they penetrate only a short distance into it.

McAuslan [118] and Rogers [117] attempted to measure the time that elapses between the absorption of light by the silver azide and the ignition of the crystals. This proved to be less than 20 μsec.

If silver azide has been sensitized by the dyestuff erythrosin (Rogers [117]) it is about 2.5 times more sensitive to photo-initiation than normal silver azide. Evans [119] examined the sensitization of silver azide by the incorporation of gold powder. He found that the critical light energy necessary for explosion is reduced by incorporating gold powder. The greatest effect was produced when the mixture contained 28% of gold by weight.

According to Bowden and Yoffe [116] these and other results suggest, that the initiation of flash decomposition may be of a true photochemical character.

These authors suggest the following mechanism for the initiation of photochemical decomposition of azides:

$$N_3^{\ominus} \overset{h\nu}{\rightleftarrows} N_3 + e$$

i.e. an N_3 radical is formed.

The spread of the explosion from the decomposed surface layer however depends on thermal factors, i.e. the heat liberated by the reaction is greater than that lost by self heating, conduction etc. The heat liberated during decomposition is sufficient to melt the surface of the azide and give rise to a reaction that will be self-supporting in the thermal sense.

The sensitizing action of gold can be interpreted by postulating that the gold particles act as electron traps.

Gray and Waddington [57,120] examined the physico-chemical properties of silver azide and state that its melting point is 300°C. On the basis of the latest opinion that the explosive decomposition of azides results from processes involving ions and electrons caused by imperfection and deficiencies in the crystal lattice (Jacobs and Tompkins [22]), the authors incorporated silver cyanide, $Ag_2(CN)_2$, into silver azide. The $(CN)_2^{2\ominus}$ ion has the same electron configuration as the $N_3^{\ominus}$ ion and probably has the same linear structure and similar dimensions as $N_3^{\ominus}$ ion.

It is assumed that the presence of silver cyanide increases the sensitiveness of silver azide at elevated temperatures; sensitized AgN_3 explodes at a lower temperature than the ordinary compound and the induction period is shorter.

	Ignition at 260°C after	Minimum ignition temperature
Pure AgN_3	induction 280 min	340°C
AgN_3 precipitated from a solution containing 10% of $Ag_2(CN_2)_2$	induction 10 min	
AgN_3 precipitated from a solution containing more than 10% of $Ag_2(CN_2)_2$	induction 1 min	270°C

The same authors investigated the kinetics of decomposition

$$2AgN_3 \rightarrow 2Ag + 3N_2 + 148 \text{ kcal at } 230\text{–}300°C$$

and found the approximate equation

$$\frac{d(N_2)}{dt} = k(AgN_3)^{2/3}$$

The activation energy is 35 kcal/mole.

The electrical conductivity of AgN_3 at a temperature above 160°C

$$\sigma = 1.60 \exp(-10.7 \text{ kcal}/RT)$$

is therefore very high.

Thus migration of the cation is possible, and the authors presume that this is the cause of the initiating property of silver azide.

Other authors quote the following values for the activation energy of the thermal decomposition of silver azide:

40.0 kcal/mole (Audubert [121])
29.0 kcal/mole (Haycock [122])
44.0 kcal/mole (below 190°C) (Bartlett, Tompkins and Young [123])
31.0 kcal/mole (above 190°C) (Bartlett, Tompkins and Young [123])

The ignition temperature is 273°C and is thus much lower than that of lead azide, although the sensitiveness of silver azide to impact is also lower than that of lead azide. Taylor and Rinkenbach [124] report that with a 0.5 kg weight a 77.7 cm drop is necessary to cause detonation of silver azide, whereas for mercury fulminate a 12.7 cm drop is sufficient.

The rate of detonation of a thin (0.1–0.5 mm) film of silver azide is about 1550 m/sec; that of the same film in an enclosed space about 1700 m/sec (Bowden and Williams [101]).

Silver azide, AgN_3, is manufactured in the same way as lead azide, in aqueous solution, by action of sodium azide on silver nitrate.

CUPRIC AZIDE

Cupric azide, $Cu(N_3)_2$, is of great practical significance since it can be formed in addition to cuprous azide by long term action of lead azide on copper or its alloys.

Curtius and Rissom [41] prepared cupric azide by the action of an aqueous solution of sodium azide on an aqueous solution of cupric sulphate, obtaining the salt in a hydrated form. The anhydrous salt was prepared by Straumanis and Cirulis [125] in the form of dark brown, reddish sediment by reaction of lithium azide on cupric nitrate in an alcohol solution. Another method described by Curtius consists of reacting hydrazoic acid with metallic copper in an aqueous medium.

Green cupric azide has also been described (Dennis and Isham [44]). It is formed by the action of hydrazoic acid on cupric hydroxide or (according to Straumanis and Cirulis) on cupric oxide. It is sometimes grey in colour.

Cupric azide is insoluble in water, but is soluble in dilute acids and in acetic acid. It is decomposed by concentrated sulphuric acid, evolving nitrogen. It dissolves in an aqueous solution of ammonia and aliphatic amines to form a complex compound.

Boiling in water (Wöhler and Krupko [80]) leads to hydrolysis with the formation of basic cupric azide. Long-continued boiling causes complete hydrolysis to cupric oxide and free acid. Black cupric azide, $Cu(N_3)_2$, when exposed to the action of air for 2 months, is completely converted into a yellow basic salt. This is discussed later.

The ignition temperature of cupric azide is 202–205°C. The dry substance is exceptionally sensitive to friction, especially the green modification, and is often exploded by contact. It is also very sensitive to impact; the green modification is exploded by a 2 kg weight falling from a height of less than 1 cm, the black one from a drop of about 1 cm.

Its rate of detonation ranges between 5000 and 5500 m/sec.

Straumanis and Cirulis [125] emphasize its exceptionally strong initiating properties, viz 0.0004 g only of the substance is sufficient to detonate penthrite.

Basic cupric azide, $Cu(OH)N_3$, prepared by Wöhler and Krupko, is yellow coloured. According to Straumanis and Cirulis it is less sensitive to friction and impact. It is exploded by a 1 kg weight falling from a height of 7–8 cm. Its ignition temperature is the same as that of the neutral salt (203–205°C).

Complex salts of cupric azide are also explosive. The salt $Cu(NH_3)_4(N_3)_2$ is much less sensitive to impact than cupric azide itself. The complex lithium–cupric salt $Li_4[Cu(N_3)_6]$ has exceptionally strong initiating properties.

OTHER METAL AZIDES

Martin [126] prepared nickel, cobalt, zinc and manganese azides by the action of an ether solution of hydrazoic acid on the dry metal carbonate. Cuprous azide, CuN_3, was obtained in the form of a light grey sediment by the reaction of sodium azide with a solution of cuprous sulphate.

The preparation of ferric azide failed, however, due to the formation of basic ferric azide. A complex compound was obtained by Martin from chromium hydroxide and hydrazoic acid. It contained no chromium or $N_3^{\ominus}$ ions and has the probable formula of a complex compound $[Cr(N_3)_4]H$.

Martin carried out extensive research into the explosive properties of the azides of various metals (Table 33). The high sensitiveness of cuprous azide to impact is noteworthy.

TABLE 33

EXPLOSIVE PROPERTIES OF AZIDES (ACCORDING TO MARTIN [126]

Azide	Ignition temperature °C	Sensitiveness to impact (work in kgm/cm^2)	Minimum initial charge, g	
			trinitrotoluene	tetryl
Silver	273	13.97	0.07	0.02
Lead	327	4.76	0.09	0.025
Mercurous	281	4.76	0.145	0.045
Cadmium	291	18.54	0.04	0.01
Zinc	289	17.53		
Cuprous	174	2.66	0.095	0.025
Nickel	200	5.46		
Cobalt	148	5.88		
Manganese	203	6.30		
Barium	152	7.70		
Strontium	169	9.10		
Calcium	158	10.14		
Lithium	245	(no explosion)		
Thallium	320	16.18	0.115	0.07

Mercuric azide, $Hg(N_3)_2$, occurs in two allotropic modifications: α (orthorhombic) and β (monoclinic), like lead azide (Miles [75]; Garner and Gomm [37]). The latter is obtained like β-lead azide, by slow diffusion of the solutions. During crystallization spontaneous explosion may occur. Mercuric azide also explodes during crystallization from a hot, aqueous solution.

The physical properties of mercurous azide — $Hg_2(N_3)_2$ — were examined by Evans and Yoffe [33] and its photochemical decomposition by Deb and Yoffe [26]. The activation energy was found to be 8.4 kcal/mole.

Cadmium azide may also detonate spontaneously, but under different experimental conditions, i.e. when a rod of metallic cadmium is immersed in hydrazoic acid and cadmium azide is formed on the surface of the rod (A. T. Thomas [127]).

Gray and Waddington [128] have produced a graph showing changes in the rate of detonation in relation to the heat of formation of various azides (Fig. 52).

The same authors [57] determined the heats of formation and decomposition of a number of azides (Table 34).

TABLE 34

Salt	Heat of formation $-\Delta H_f$ kcal/mole
HN_3 gas	−71.66
HN_3 liquid	−64.37
LiN_3	− 2.58
NaN_3	− 5.08
KN_3	− 0.33
RbN_3	+ 0.07
CsN_3	+ 2.37
NH_4N_3	−26.79
CaN_6	−11.03
SiN_6	− 1.72
BaN_6	+ 5.32
CuN_3	−67.23
CuN_6	−140.4
AgN_3	−74.17
Hg_2N_6	−141.5
TlN_3	−55.78
PbN_6	−115.5
CdN_6	*ca.* −108

The heat of decomposition to metal and nitrogen, ΔH, has of course, the opposite value $\Delta H = -\Delta H_f$.

With regard to their sensitiveness to ignition by light, the azides of monovalent metals may be ranged as follows:

$$KN_3 < TlN_3 < AgN_3 < CuN_3$$

According to Deb [129] the corresponding values are: for TlN_3 — 92; AgN_3 — 39; CuN_3 — 12 J.

The activation energies of azides not mentioned above are shown in Table 35.

TABLE 35

Salt	Activation energy	Author
NaN_3	34.0 kcal/mole	Garner and Marke [130]
KN_3	36.0 kcal/mole	Garner and Marke [130]
$Ba(N_3)_2$	21.0–27.0 kcal/mole	Jacobs and Tompkins [22]
$Sr(N_3)_2$	20.0 kcal/mole	Maggs [131]
$Ca(N_3)_2$	18.0 kcal/mole	Marke [132]
$Cu(N_3)$	26.5 kcal/mole	Singh [133]

The properties of thallous azide have been examined in detail by Gray and Waddington [120].

Thallous azide is a yellow, crystalline substance, m.p. 334°C. The crystal structure as determined by X-ray analysis points to the isomorphism of TlN_3 with KN_3 and RbN_3 azides.

Thallous azide is sensitive to the action of light and decomposes under its influence to evolve metallic thallium.

The ignition temperature, as determined by throwing a test sample on a heated metallic surface, is 490°C. The activation energy of its pre-explosive state as calculated by the authors is said to be approximately 40 kcal/mole.

The introduction of a thallium salt with a bivalent anion, e.g. thallous sulphide, Tl_2S, produces defects in the crystal lattice. According to a recent view (Jacobs and Tompkins [22]), the explosive decomposition of azides is caused by imperfection and deficiencies of the crystal lattice. Due to defects produced artificially with thallium sulphide, the ignition temperature is reduced, e.g. the ignition temperature of thallium azide containing 18% of Tl_2S is reduced to 420°C.

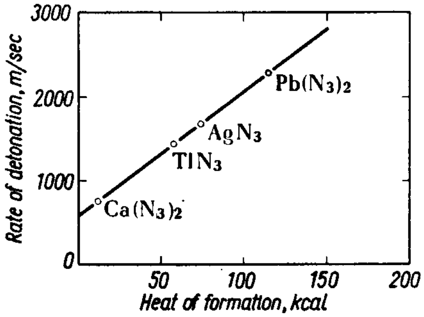


FIG. 52. The variation of the rate of detonation with heat of formation of azides, according to Gray and Waddington [128].

Deb and Yoffe [134] examined the decomposition of thallous azide under the action of ultra-violet light in the wavelength region 3200–3800 Å. Two exciton bands 3415 and 3348 Å have been observed in thallous azide by low-temperature spectroscopy (Nikitine and Gross's method). The refractive index has been measured by the Brewster angle method, the electron energy levels have been estimated and the results of the photochemical decomposition have been related to the electron energy level and to measurement of photoconductivity [33].

The overall reaction is

$$2TlN_3 \rightarrow 2Tl + 3N_2,$$

where nitrogen gas is formed by the reaction at the surface

$$2N_3 \rightarrow 3N_2$$

The activation energy was found to be 3.2 ± 0.1 kcal/mole. The suggested mechanism of photochemical decomposition is as follows:

$N_3+h\nu \rightarrow \overset{*}{N_3}$	(exciton formation)
$\overset{*}{N_3} \rightarrow N_3+q$	(reversion of the exciton to the ground state)
$\overset{*}{N_3} \rightarrow N_3+e$	(thermal dissociation of the optically formed exciton)
$N_3+e \rightarrow N_3$	(recombination of electron and positive hole)
$2N_3 \rightarrow 3N_2+Q$	(combination of two positive holes)
$Tl_n+Tl^{\oplus}+e \rightarrow Tl_{n+1}$	(electron trapping and metal formation)

The electrical conductivity of TlN_3 is very high: $6–5\times10^{-5}/275°C$ (i.e. a million times higher than that of KN_3).

The explosive properties of sodium, calcium, strontium and barium azides have been investigated at the Chemisch-Technische Reichsanstalt [135]. These azides differ markedly from lead, silver and cupric azides in that they show none of the properties of primary explosives. All three may be ignited by a spark, a glowing wire or the flame of blackpowder. Calcium azide burns most rapidly and has distinctly marked explosive properties. Larger quantities of it may explode when ignited in a closed tin, while strontium and barium merely burn violently. Calcium azide detonates under the influence of a detonating cap. The sodium azide does not decompose in these conditions. The other azides show weak decomposition under the influence of a standard (No. 3) detonator. Their most important properties are tabulated below.

TABLE 36

Azide	Ignition temperature °C	Lead block expansion cm³	Heat of decomposition kcal/mole
Sodium	no ignition up to 300	0	–
Calcium	171–176	120	–
Strontium	190–202	30–90	–
Barium	190–200	25–30	13–14

Tompkins *et al.* [22, 85] studied the photochemical decomposition of potassium and barium azide. Originally they found that the rate of photolysis was proportional to the square of the intensity of the radiation.

In more recent studies, Jacobs, Tompkins and Young [136] examined the rate of evolution of nitrogen from barium azide as a criterion of the rate of photolysis, and have shown the reaction to be more complex than was previously indicated. A mechanism for the photolysis involving the production and reaction of both excitons and positive holes has been formulated.

According to Ficheroulle and Kovache [137] barium azide has a low sensitiveness to impact (a 2 kg weight falling from 100 cm causes 14% of explosions) but it is very sensitive to friction. It does not possess the properties of a primary explosive, but in large quantities may burn very violently. The toxicity of BaN_6 is negligible, but in the presence of strong acids it decomposes to evolve strongly poisonous hydrazoic acid.

Strontium azide possesses similar properties, but is highly sensitive to the action of even weak acids (e.g. with CO_2 it forms $SrCO_3$) and easily is hydrolysed.

Barium and strontium azides are used in the manufacture of valves in radio technology.

Ficheroulle and Kovache recommend two methods for the manufacture of barium azide. One of them is based on the reaction of ethyl nitrite with hydrazine in the presence of barium hydroxide: 19.5 kg of ethyl nitrite is cooled with brine to −15°C when a mixture of 31 kg of $Ba(OH)_2$ in 100 l. of the 10% hydrazine hydrate previously cooled to −15°C is added at a rate of 4 l. per hr. The whole is strirred for 10 hr while room temperature is attained gradually. A stream of CO_2 is allowed to pass through the liquid to precipitate excess barium. Barium carbonate is then removed by filtration. The filtrate is greatly concentrated and BaN_6 precipitated by the addition of alcohol. Thus 12.6 kg of BaN_6 is obtained i.e. 44% of the theoretical yield. A yield up to 55% may sometimes be obtained. The other method is based on the double decomposition of $Ba(ClO_4)_2$ and KN_3. Sparingly soluble $KClO_4$ is precipitated while BaN_6 passes into solution. This method gives a product which is less pure and not suitable for valve manufacture.

Sodium azide (see above, p. 189 and Table 36) can be decomposed on heating but it is of low sensitiveness to impact or friction and is not listed as an explosive in transport regulations. According to Günther *et al.* [138] rubidium azide is much more sensitive to impact and friction than sodium azide. Günther believes this to be due to the fact that the radius of the orbit of nitrogen atoms in rubidium azide is much shorter than that in sodium azide.

Curtius [1] who prepared ammonium azide did not notice its explosive properties. They were reported by Berthelot [139] who found ammonium azide to be an endothermic substance with a heat of formation $-\Delta H_f$ of −19.0 kcal.

Berthelot and Vieille [140] reported that the explosive decomposition of ammonium azide proceeds according to the following equation:

$$2NH_4N_3 \rightarrow 3N_2 + H_2 + 2NH_3 + 502 \text{ kcal/kg}$$

Volume of gases (V_0) is 1148 l./kg
Temperature of explosion t, 1350–1400°C
Specific pressure (f), 7290 m

A low explosion temperature together with a great amount of gaseous products and a high specific pressure suggested the used of ammonium azide as a propellent explosive. In practice the use of the substance, however, is prevented by its high volatility.

Azides of complex salts with ammonia ("ammines") are described below (p. 231).

Among other inorganic azides those prepared by Wiberg *et al.* [141] i.e. boron, $B(N_3)_3$, and silicon, $Si(N_3)_4$, azides are of interest. Grundman and Rätz [142] obtained highly explosive "phosphorous azide", P_3N_{21}. As early as 1915 Curtius and Schmidt [143] described the preparation of $SO_2(N_3)_2$ from SO_2Cl_2 and NaN_3. By the action of SO_3 on KN_3 Lehman and Holznagel [144] obtained an addition compound, $KN_3 \cdot 2SO_3$, which is transformed on heating into disulphuryl azide, $S_2O_5(N_3)_2$, a highly explosive substance. Sundermeyer [145] described recently silily-azides, e.g. $(CH_3)_2Si(N_3)_2$.

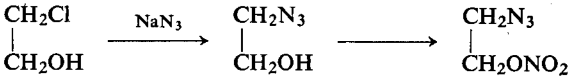
Halogen azides, e.g. IN_3, BrN_3, ClN_3, FN_3 are also known. They are, however, highly unstable.

An extensive review of physics and chemistry of inorganic azides is given by Evans, Yoffe and Gray [74].

ORGANIC AZIDES

In the search for powerful explosives, attempts have been undertaken to introduce the $—N_3$ group into organic molecules. Generally this so enhances their sensitiveness to friction and impact that they cannot be used. Moreover, the increase in explosive power is not always commensurate with the rise in the manufacturing costs of the substance.

Triazoethanol nitrate $N_3 \cdot CH_2CH_2 \cdot ONO_2$ (II) is an example of an organic aliphatic azide and nitric ester. It was prepared by T. Urbański and Rusiecki [146] by the following steps:

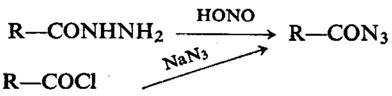


$$\begin{array}{c}CH_2Cl\\|\\CH_2OH\end{array}\xrightarrow{NaN_3}\begin{array}{c}CH_2N_3\\|\\CH_2OH\end{array}\longrightarrow\begin{array}{c}CH_2N_3\\|\\CH_2ONO_2\end{array}$$

I II

Compound (I) was obtained by Forster *et al.* [147]. Substance (II) is a liquid explosive resembling nitroglycerine in its properties: it gives the same lead block expansion and a rate of detonation ranging from 2000 to 6550 m/sec (in a lead pipe 17/21 mm diameter). Mixtures with ammonium nitrate give an even larger expansion and a higher rate of detonation than analogous mixtures with nitroglycerine. Triazoethanol nitrate has a higher sensitiveness to impact than has nitroglycerine. The ignition temperature is 190°C in a closed vessel. According to Urbański and Rusiecki the alcohol itself, triazoethanol (I), is an explosive substance and gives a lead block expansion of 130 cm^3.

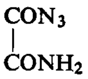
Azides containing the $—CON_3$ group have received little attention, and have poor prospects for practical use. They are formed either by the action of nitrous acid on hydrazides or by the action of sodium azide on acid chlorides:



$$R—CONHNH_2 \xrightarrow{HONO} R—CON_3$$
$$R—COCl \xrightarrow{NaN_3} R—CON_3$$

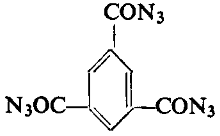
Some azides are capable of the so-called Curtius rearrangement, which results in the formation of isocyanates with loss of nitrogen.

Organic azides with initiating properties may be exemplified by the following substances (Curtius [148]): oxamidoazide (III) and triazide of trimesic acid (IV):



$$\begin{array}{c} CON_3 \\ | \\ CONH_2 \end{array}$$

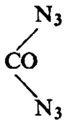
III



IV

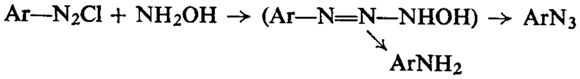
The first of these is obtained by the action of nitrous acid on oxamidohydrazide. It is unstable and decomposes explosively at 115°C. The second is formed by the action of nitrous acid on the trihydrazide of trimesic acid. The explosive properties of neither of these azides have been reported.

Diazide of carbonic acid (V) is exceptionally sensitive to friction: it explodes on contact with a glass rod (Curtius and Heidenreich [149]) Succinyl azide [150] and other acyl azides [151] behave similarly.



V

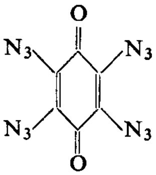
Organic azides in which the N_3 group is combined with an aromatic radical may be prepared by a general method based on the action of hydroxylamine on a diazo compound (Mai [152]):



$$Ar{-}N_2Cl + NH_2OH \rightarrow (Ar{-}N{=}N{-}NHOH) \rightarrow ArN_3 \quad \searrow ArNH_2$$

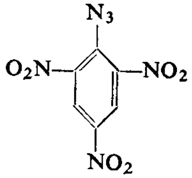
The initial amine is formed again, together with azide.

Tetra-azido quinone (VI) was obtained by Šorm [153], by the action of sodium azide on chloranil. This explosive is powerful but of no practical use due to its inadequate stability; its ignition temperature is low: 91°C.



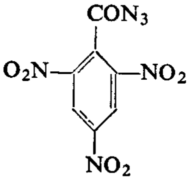
VI

The organic derivatives of hydrazoic acid which contain an aromatic ring with nitro groups comprise an important group of initiators. Picryl azide (VII), m.p. 89–90°C is a typical example. It has been prepared both by the action of nitrous acid on trinitrophenylhydrazine (Purgotti [154], Schrader [155] and Korczyński [156]) and by the action of sodium azide on picryl chloride. Rathsburg [157] suggested the use of picryl azide as an initiator but its initiating properties proved to be too weak and the compound has not found practical application.



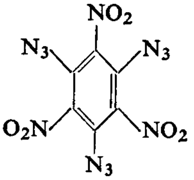
VII

Trinitrobenzoyl azide (VIII) was prepared by Vasilevskii. Blokhshtein and Kustria [158] by the action of sodium azide on trinitrobenzoyl chloride



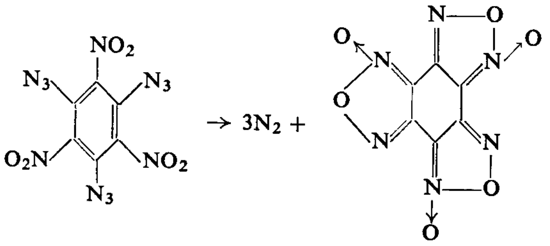
VIII

Trinitrotriazidobenzene (IX) is the only representative of organic azides possessing properties of primary explosives which has some prospect of practical use. Turek [159] prepared it by the action of sodium azide on sym-trichlorotrinitrobenzene (Vol. I. p. 469) and on the basis of its properties which he himself determined he suggested its use as an initiator.



IX

Trinitrotriazidobenzene is insoluble in water, easily soluble in acetone and moderately soluble in chloroform and alcohol. It is not hygroscopic and is moisture-resistant. In the presence of moisture it has no effect on iron, steel, copper or brass. At its melting point, 131°C, it undergoes decomposition to evolve nitrogen and to form benzotrifuroxane ("hexanitrosobenzene") also an explosive substance (Vol. I, p. 603).



m.p. 159°C

IX X

The same reaction also occurs at a lower temperature. 0.665% of the substance decomposed at 20°C to form benzotrifuroxane in 3 years; 2.43% at 35°C in one year; 0.65% at 50°C in 10 days; and at 100°C the substance underwent complete change in 14 hr. This decomposition is not, however, autocatalytic. This reaction — the formation of furoxane derivatives from aromatic azides with nitro group in the *ortho*-position — is of a general character (Boyer *et al.* [160]). Despite the ease with which it decomposes trinitrotriazidobenzene has not been rejected for use as an initiator. In some countries large scale experiments are in progress to examine the possibilities of developing its practical application.

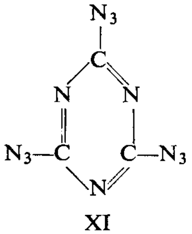
Trinitrotriazidobenzene is less sensitive to impact and friction than mercury fulminate.

As an explosive the substance is very powerful. Its expansion in the lead block is about 500 cm^3, i.e. its explosive strength is midway between that of tetryl and penthrite. At a density of 1.54 it detonates at a rate of 7500 m/sec.

The specific gravity of trinitrotriazidobenzene is 1.8054. Under a pressure of 3000 kg/cm^2 it gives a density of 1.751 and under 5000 kg/cm^2 the density achieved is 1.7526. A pressure higher than 300 kg/cm^2 may make it "dead pressed". 0.02 g of the substance compressed under the pressure of 300 kg/cm^2 detonates trinitrotoluene, and 0.01 g detonates tetryl. It is therefore one of the most vigorous initiators.

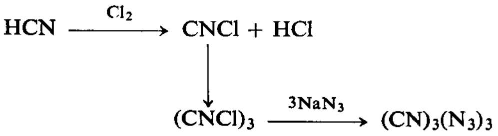
As a starting material for the preparation of sym-trinitrotriazidobenzene, 1,3,5-trichlorobenzene is used. It is obtained by the chlorination of aniline and the removal of the amino group. Nitration to the trinitro derivative is described in Vol. I. The final reaction is simple: powdered 1,3,5,-trichloro-2,4,6-trinitrobenzene is added to an aqueous alcohol solution of sodium azide. The precipitated product is washed with alcohol and water and dried at a moderate temperature. The product so obtained may be purified by crystallization from chloroform.

A powerful initiator in which azido groups are combined with a heterocyclic ring is cyanuric triazide (XI)



XI
m.p. 94°C

It was obtained by Ott and Ohse [161] in the following way:



$$\begin{tikzcd}
\mathrm{HCN} \arrow[r, "\mathrm{Cl_2}"] & \mathrm{CNCl} + \mathrm{HCl} \arrow[d] & \\
& \underset{\mathrm{XII}}{(\mathrm{CNCl})_3} \arrow[r, "3\mathrm{NaN_3}"] & \underset{\mathrm{XI}}{(\mathrm{CN})_3(\mathrm{N_3})_3}
\end{tikzcd}$$

On reaction with chlorine, hydrogen cyanide gives cyanogen chlorides, forming a trimer—cyanuric chloride (XII). The latter is a liquid with a melting point of 146°C and a boiling point of 196°C. Next, cyanuric triazide (XI) is obtained by the action of sodium azide in an aqueous solution, at room temperature on compound (XII).

Cyanuric triazide is insoluble in water, sparingly soluble in cold alcohol and readily soluble in hot alcohol, acetone, benzene, chloroform, ether, and molten trinitrotoluene, It is slightly hygroscopic and slightly volatile. It irritates the skin causing dermatitis. Its heat of formation $-\Delta H_f$ is 219 kcal/mole (H. Muraour [162]).

Much attention has been devoted to this substance as an initiator since it was found that its initiating properties are stronger than those of mercury fulminate. However it proved to be highly dangerous to handle and sensitive to impact and friction; it has been known to explode during manufacture, e.g. during drying. Large crystals, which explode even under the pressure of a rubber cork, are particularly dangerous. Attempts to press it into capsules often resulted in explosion. This accounts for the fact that the substance has found no practical application. It is nevertheless very interesting from the theoretical point of view. The following data are characteristic of its properties.

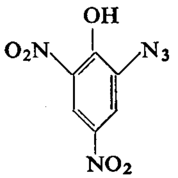
The ignition temperature, when heated at the rate of 20°C/min, is 205–208°C i.e. higher than that of fulminate, but decomposition becomes evident on heating at a temperature slightly exceeding 100°C. The substance is exploded by a drop three times less than that of mercury fulminate.

The rate of detonation at a density of 1.15 is 5545 m/sec (Kast and Haid [99]), it is therefore an initiator that detonates extremely fast.

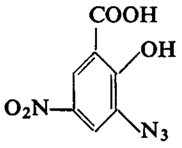
The initiating properties of the substance are characterized by the following figures (Taylor and Rinkenbach [163]) which indicate the amounts of primary explosive required to initiate different high explosives compressed under a pressure of about 14 kg/cm^2.

Trinitrotoluene	0.10 g of cyanuric triazide 0.26 g of mercury fulminate
Picric acid	0.05 g of cyanuric triazide 0.21 g of mercury fulminate
Tetryl	0.14 g of cyanuric triazide 0.24 g of mercury fulminate

A new type of initiator containing the azido group has recently been described by Głowiak [164]. These are salts of heavy metals (e.g. lead), phenols of phenolic acids containing nitro groups and azido group, e.g. the plumbous salt of dinitroazidophenol (XIII) and 5-nitro-3-azidosalicylic acid (XIV):



XIII



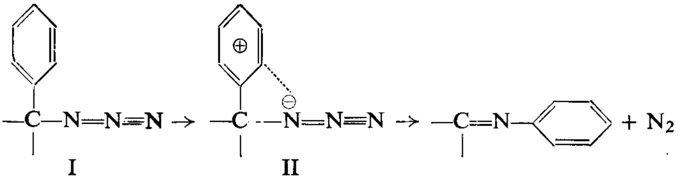
XIV

Plumbous salts of these compounds are very sensitive to mechanical and thermal impulses but have no distinctly marked ability to initiate secondary explosives and are similar to lead styphnate in their properties.

Interesting material with which the mechanism of decomposition of organic azides was investigated is triphenylmethyl azide

$$(C_6H_5)_3CN_3$$

Saunders and Ware [165] examined its thermal decomposition in the molten state at 170 – 200°C and found it gives a benzophenone anil $(C_6H_5)_2C{=}NC_6H_5$. They suggest the following mechanism for the decomposition



The transition state is represented as the resonance hybrid of (I) and (II).

The same product was obtained by Deb and Yoffe [26] as the result of photochemical decomposition of the substance. The activation energy of this reaction was found to be 8.82 kcal/mole. See also [33].

The chemistry of organic azides has been the subject of many theoretical and practical investigations. Apart from their application as explosives some organic azides possess interesting pharmacological and bacteriostatic properties.

A new group of azides containing silicon of general formulae

$$R_3SiN_3$$
$$R_2Si(N_3)_2$$
$$RSi(N_3)_3 \quad (R = C_6H_5 \text{ or } CH_3)$$

were recently prepared by Reichle [166]. He also described similar compounds with other group IV elements: Ge, Sn and Pb, e.g. $(C_6H_5)_3PbN_3$.

The compounds are remarkably stable.

An extensive review of the chemistry of aliphatic and aromatic azides is given by Boyer and Canter [167] and Gray [168]. Organic azides are subject to various reactions such as the Bergmann degradation and the synthesis of peptides, the well known Curtius rearrangement, the Darapsky synthesis of α-aminoacids [169], for synthesis of triazoles [170], tetrazoles ("Schmidt reaction") [169] and [171] etc. These reactions lie beyond the scope of the present book.

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CHAPTER IV

OTHER INITIATING EXPLOSIVES

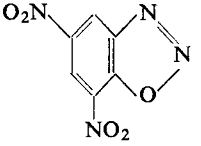
DIAZO COMPOUNDS

Berthelot and Vieille [1] examined the explosive properties of diazobenzene nitrate $(C_6H_5N=N)^{\oplus}NO_3^{\ominus}$. Later Wöhler and Matter [2] demonstrated that it is unsuitable for use as an initiator due to its very weak initiating properties and very high sensitiveness to friction and impact. Herz [3] suggested the use of *m*-nitrodiazobenzene perchlorate. This, however, is hygroscopic and insufficiently stable (it explodes at 154°C).

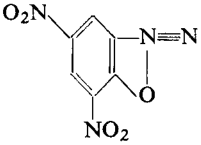
DINITROBENZENEDIAZO-OXIDE
(DINITRODIAZOPHENOL)

The only diazo compound of practical value is dinitrobenzenediazo-oxide (dinitrodiazo-oxide, or less correctly dinitrodiazophenol). In technical literature it may be denoted as DDNP or Dinol.

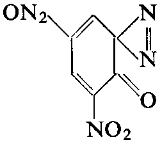
The following formulae have been ascribed to this substance: cyclic (I) (Bamberger [4]), diazonium (II) (Hantzsch and Davidson [5], Klemenc [6]) or quinonoid (III) (Wolff [7]).



I

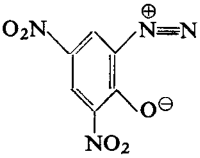


II

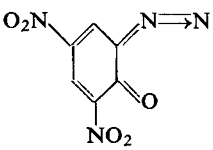


III

In modern transcription formulae (II) and (III) take the forms (IIa) or (IIIa) (Hodgson and Marsden [8], Anderson and Le Fèvre [9]):



IIa



IIIa

Recently from a comparison of the infra-red absorption spectrum of this compound with that of *o*-benzoquinone Głowiak [10] came to the conclusion that dinitrobenzenediazo-oxide has a quinonoid structure. Both substances show the presence of the strong absorption band of the carbonyl group: 1666 cm^{-1} for dinitrobenzenediazo-oxide and 1680 cm^{-1} for *o*-benzoquinone. In addition dinitrobenzenediazo-oxide gives a band with a frequency of 2190 cm^{-1}, characteristic of a double bond between nitrogen atoms. (Some derivatives of this compound may also have the diazo structure (IIa), which is discussed later on.)

This substance was the first diazo compound to be discovered. It was prepared by Griess [11] by diazotizing picramic acid. Its explosive properties attracted the attention of Lenze [12] who found it to be as valuable as mercury fulminate in spite of its higher sensitiveness to impact. This compound is also of interest as being the first initiator containing no heavy metals. It has now been utilized in the United States of America and Japan as a component of initiating charges in detonators and caps.

Physical properties

Dinitrodiazophenol has a specific gravity of 1.63, and occurs as yellow needles which decompose without melting on heating to 188°C.

Its crystalline form is of great importance from the practical point of view.

The needle-like shape of the crystals prevents their being easily poured (into the capsule) making them liable to felt so the aim is to produce short crystals either by a suitable selection of conditions for the reactions of diazotization and precipitation of the product (D. Smoleński and Pluciński [13]) or by the addition of certain substances to the solution from which the product is to be precipitated; Garfield [14], for instance, suggests for this purpose the addition of triphenylmethane dyestuffs to the solution.

The physical and explosive properties of dinitrodiazophenol were investigated by Clark [15] and by D. Smoleński and Pluciński [13]. The solubility of dinitrodiazophenol at 50°C (in 100 g of solvent) is: 2.45 g in ethyl acetate, 1.25 g in methyl alcohol, 2.43 g in ethyl alcohol, 0.23 g in benzene, 0.11 g in chloroform.

The substance is also soluble in concentrated hydrochloric acid, acetone, acetic acid, nitrobenzene, aniline, pyridine, and nitroglycerine, at room temperature. In water its solubility is only 0.08% at 25°C.

Chemical and explosive properties

Dinitrodiazophenol is not decomposed by concentrated acids at room temperature, but on the other hand a dilute (e.g. 0.5%) solution of sodium hydroxide causes its decomposition with the evolution of nitrogen even at room temperature. This property finds application in the destruction of residues.

Dinitrodiazophenol is more stable than mercury fulminate. It may be stored without change at 50°C, in dry condition, for 30 months (under these conditions fulminate is stable only for 9 months) and under water for 12 months.

Vaughan and Phillips [16] investigated the decomposition of dinitrodiazophenol at temperatures between 111 and 120°C *in vacuo*. The gaseous products of decomposition contain: 61.5% of N_2, 3% of NO, 4.0% of NO_2, 2.5% of CO, 28% of CO_2. This is evidence of the fact that decomposition consists not only in the loss of diazo group nitrogen, but also in the decomposition of the benzene ring.

Smoleński and Pluciński [13] examined the effect of sunlight and found that signs of decomposition are perceptible after only 40 hr of irradiation. A sample so irradiated shows a somewhat lower ignition temperature.

Kaufman [17] found that γ-radiation produces gas evolution from dinitrodiazophenol. Partial decomposition occurred after 45 days of irradiation (on average 10^5 r per hour) and the explosive power of the irradiated substance was reduced and irregular.

Dinitrodiazophenol explodes [13] on a metal plate at 180°C after 10 sec; at 185°C after 5 sec; at 190°C after 2.5 sec; at 200°C after 1 sec.

In spite of its high specific gravity the apparent density of the needle-shaped crystals, according to Clark [15], is only 0.27; under a pressure of 240 kg/cm^2 it is 0.86. The crystals may be obtained in the form of pellets whose apparent density is about 0.8. The effect of the conditions of preparation have been thoroughly examined by Smoleński and Pluciński [13]. They found that at a diazotization temperature as recommended by Clark, i.e. 15°C, the product pours with difficulty. Conversely, diazotization at a higher temperature (25–45°C) results in formation of a product with a density of about 0.82.

Smoleński and Pluciński prepared dinitrodiazophenol in the form of free-flowing crystals by applying the following reaction conditions:

A solution of 320 g of sodium nitrite in 2 l. of water is added to a suspension of 1000 g of the sodium salt of picramic acid in 8 l. of water. Next, 6 l. of 5.5% hydrochloric acid is added dropwise for 2 hr, stirring continuously. The initial temperature of 20°C rises to 25°C. Completion of the reaction is determined by means of starch–iodide paper. The product is filtered off, washed with cold water and dried at 35–40°C. Its yield amounts to 80% of the theoretical.

T. Urbański, Szyc-Lewańska *et al.* [18] have recently found that dinitrobenzene-diazo-oxide can be prepared by oxidation of picramic acid with chromium trioxide in the presence of sulphuric acid at 55–60°C. One part of picramic acid is fully oxidized by chromic acid to yield gaseous products: CO, CO_2, NO_2, NH_3 and H_2O. Nitrogen dioxide acts further as a diazotizing agent on undecomposed picramic acid to yield the diazo compound. The yield of this reaction does not exceed 31% of theoretical calculated on the picramic acid used.

Clark confirmed that dinitrodiazophenol does not become "dead pressed" even under a pressure of 9140 kg/cm^2 which is a great advantage in an initiating material. Smoleński and Pluciński quote the following figures which are characteristic of its explosive properties. The substance is endothermic. Its heat of formation is about 365 kcal/kg. The reaction proceeds according to the following equation:

$$C_{28.57}H_{9.52}O_{23.8}N_{19.0} = 20CO + 1.2CO_2 + 1.4H_2O + 1.5H_2 + 3.65C + 3.72HCN + 7.64N_2 + 955.3 \text{ kcal/kg}$$

The volume of gases (V_0)	876 l./kg
The temperature of explosion	3700°C.

Owing to the great volume of gases, high heat of formation and high explosion temperature this substance is a much stronger explosive than those initiators which contain metal in the molecule.

According to Clark [15] 1 g of dinitrodiazophenol on being pressed at a pressure of 240 kg/cm^2 into a copper capsule gives an expansion of 25 cm^3 in a small lead block (mercury fulminate 8 cm^3, lead azide 7 cm^3). Using 0.75 g of the substance, Smoleński and Pluciński obtained a lead block expansion of 17–23 cm^3.

Clark found dinitrodiazophenol less sensitive to impact than mercury fulminate, lead azide or lead styphnate; it is exploded by a drop of 375 g weight from a height of 22.5 cm, whereas mercury fulminate is exploded by a drop of 15 cm.

Smoleński and Pluciński also disclosed that a fine crystalline product is more sensitive (15 cm drop) and coarse crystalline less sensitive (30 cm drop).

A. Belayev and A. Belayeva [19] found its linear rate of burning to be 2.15 cm/sec.

The initiating properties of dinitrodiazophenol were investigated by Clark [15] and Smoleński and Pluciński [13]. According to Clark the initiating power of the substance is approximately twice as great as that of mercury fulminate, but a little less than that of lead azide.

Thus to initiate picric acid the following quantities of priming explosives are required:

0.115 g of dinitrodiazophenol
0.225 g of mercury fulminate
0.12 g of lead azide

For trinitrotoluene the corresponding figures are as follows:

0.163 g, 0.240 g, 0.16 g

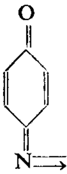
and for tetryl:

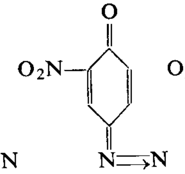
0.075 g, 0.165 g, 0.03 g.

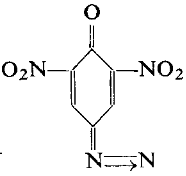
In Smoleński and Pluciński's opinion dinitrodiazophenol alone is not suitable as an initiating material for detonators since it requires too long a path for burning to change into detonation, hence it is necessary to add another initiating substance e.g. lead azide. Nevertheless it is suitable for filling caps.

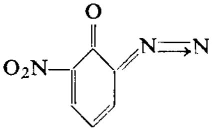
The properties of benzenediazo-oxides

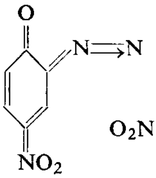
Vaughan and Phillips [16] studied the decomposition of 4-diazo-1-oxide (III) and nitro derivatives of this compound (IV, V) and of the nitro derivatives of 2-diazo-1-oxide (VI, VII, VIII).

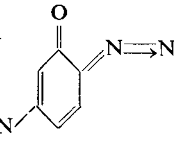

III


IV


V


VI


VII


VIII

Their experiments showed that the nitro derivatives of 4-diazo-1-oxide are more stable than the corresponding derivatives of 2-diazo-1-oxide.

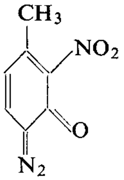
The introduction of a nitro group at the *ortho*-position to the oxygen atom in 4-diazo-1-oxide (IV) increases the stability. Great stability is also demonstrated by the *o*- and *p*-substituted nitro derivatives of 2-diazo-1-oxide (VI and VII). On the other hand, the *m*-substituted compound (VIII) has a lower stability than compounds (VI) and (VII). Dinitro substituted derivatives, *ortho–ortho* (V) and *ortho–para* (IIa), are distinguished by a higher stability than the mononitro derivatives of the same oxides (IV) or (VI) and (VII).

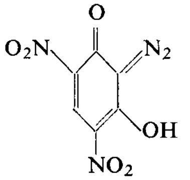
Głowiak [20] examined the properties of the diazotization products of numerous nitro derivatives of *o*-aminophenol, viz.:

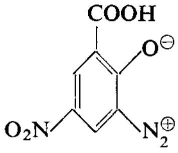
2,6-dinitro-4-amino-*m*-cresol
4,6-dinitro-2-amino resorcinol
5-nitro-3-aminosalicylic acid
4,6-dinitro-2-amino-*m*-hydroxybenzoic acid.

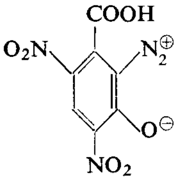
From them he prepared the diazo compounds (IX), (X), (XI), and (XII).

From their infra-red absorption spectra he ascribes a quinonoid structure to the first two compounds and a diazo structure to the last two and to their plumbous salts:


IX


X


XI


XII

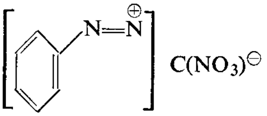
The compounds with a quinonoid structure differ from those with a diazo structure by their darker colour and lower chemical stability. They are for example easily decomposed by light and concentrated acids; they are less resistant to heat and show a higher sensitiveness to impact, friction and flame than compounds with a diazo structure.

Phenyldiazonium nitroformate. Nitroform derivative (XIII) is of particular interest among derivative diazonium salts. It was prepared by Ponzio [21] who reacted the potassium salt of trinitromethane (nitroform) with an aqueous solution of phenyldiazonium acetate:

$$(NO_2)_2C{=}NOOK + CH_3CO\overset{\ominus}{O}\,\overset{\oplus}{N}_2C_6H_5 \rightarrow \underset{\text{XIII}}{(NO_2)_2C{=}NO\overset{\ominus}{O}\,\overset{\oplus}{N}_2C_6H_5}$$

Quilico [22] questioned the formula (XII), assuming the substance to be an azo compound with the structure $(NO_2)_3C—N{=}NAr$, but in a later paper Ponzio [23] insists that in principle his formula is correct, while modifying it into $(NO_2)_3CN_2C_6H_5$ (XIIIa).

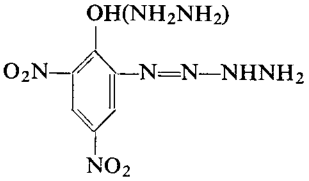
On the basis of its infra-red absorption spectrum Głowiak [20] deduced an ionic structure (XIIIb), confirming, in principle, the formula (XIIIa):



XIIIb

According to Głowiak's researches this substance has the following properties Its ignition temperature with an induction period of 1 sec is 124°C. To initiate 0.5 g of tetryl, compressed under a pressure of 500 kg/cm^2, the minimum charge of the phenyl diazotate of nitroform, loosely poured or compressed under a pressure of 100 kg/cm^2, is 0.3 g. When compressed at higher pressure (300 kg/cm^2) the charge must be increased to 0.5 g.

Dinitrobenzene diazo-oxide reacts with hydrazine hydrate to yield 2,4-dinitro-6-[tetrazene-(1)]-phenolhydrazine salt (XIV)

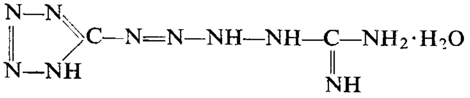


XIV

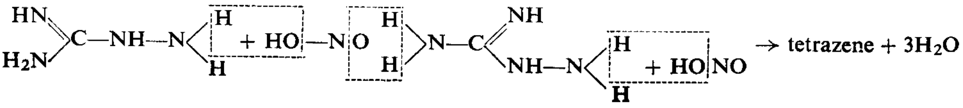
The product (XIV) can form metal salts. Some of them (e.g. potassium salt) possess initiating properties [24].

THE DERIVATIVES OF AMINOGUANIDINE

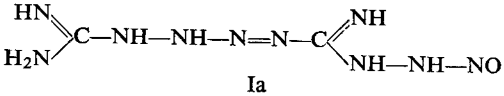
TETRAZENE



Tetrazene or tetrazolylguanyltetrazene hydrate was first prepared by Hoffmann and Roth [25], by the action of a neutral solution of sodium nitrite on aminoguanidine salts (without an excess of inorganic acid). According to these authors the reaction proceeds as follows:



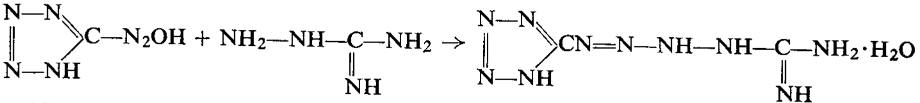
The course of the reaction in the presence of inorganic acids is different from that in the presence of acetic acid.



$$\mathrm{(HN{=})(H_2N)C{-}NH{-}NH{-}N{=}N{-}C({=}NH){-}NH{-}NH{-}NO}$$

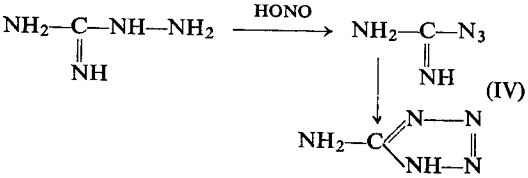
Ia

Hoffmann *et al.* [26] suggested the structural formula (Ia) for tetrazene, i.e. 1-guanyl-4-nitrosoaminoguanyltetrazene. The correctness of this formula was later questioned by Patinkin, Horwitz and Lieber [27]. The synthesis of tetrazene by the action of tetrazolediazonium hydroxide (II) on aminoguanidine salts (III) at 0°C, suggested that tetrazene has the structure of 1-(5-tetrazolyl)-4-guanyltetrazene hydrate (I):



II III I

The formation of guanyl azide (IV) at the first stage may account for the formation of tetrazene by the action of nitrous acid on aminoguanidine, i.e. by Hoffmann synthesis.



(IV) (V)

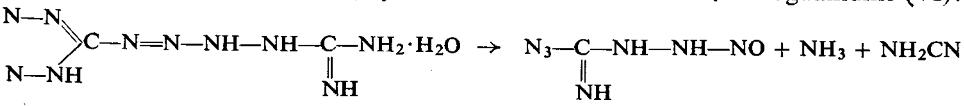
Guanyl azide is then isomerized to aminotetrazole (V) which undergoes diazotization and couples with aminoguanidine as stated above.

Rathsburg [28] suggested the use of tetrazene in explosive technology.

Tetrazene is a light, crystalline substance, s.g. 0.45, colourless or pale yellow, practically insoluble in water and in the majority of organic solvents. It is only slightly hygroscopic (it absorbs 0.77% of moisture, at 30°C, in an atmosphere with a relative humidity of 90%). It has basic properties and is soluble in concentrated hydrochloric acid. Tetrazene hydrochloride may be precipitated from such a solution with ether. Free tetrazene is evolved from the hydrochloride by reaction with sodium acetate or ammonia. With an excess of silver nitrate, tetrazene gives a precipitate of the double salt $C_2H_7N_{10}OAg \cdot AgNO_3 \cdot 3H_2O$.

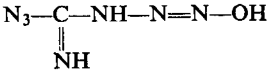
It is stable at ordinary temperatures, whether wet or dry, but hydrolyses on being boiled in water with the evolution of 2 N_2 per molecule.

Under the influence of sodium hydroxide, tetrazene undergoes decomposition with the evolution of ammonia, cyanamide and triazidonitrosoaminoguanidine (VI):



VI

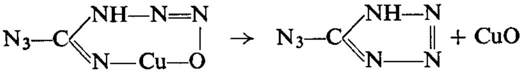
Substance (VI) reacts in an enol form (VIa):



$$N_3{-}\underset{\underset{NH}{\|}}{C}{-}NH{-}N{=}N{-}OH$$

VIa

On the addition of copper acetate to a solution of compound (VI) the copper salt (VII) is formed which on treatment with acid decomposes to form 5-azidotetrazole (VIII):



VII VIII

Tetrazene is stable at temperatures up to 75°C. At 100°C it undergoes marked decomposition. The ignition temperature of tetrazene is lower than that of mercury fulminate. On a metal plate, heated to 160°C, it explodes after 5 sec (mercury fulminate behaves in the same way at 190°C). According to Wallbaum [29] tetrazene explodes at 140°C on being heated at the rate of 20°C/min.

The explosion heat of tetrazene is rather low, i.e. 663 kcal/kg. This is characteristic of explosive substances containing a guanyl group in the molecule.

According to some authors tetrazene is rather more sensitive to impact than mercury fulminate. Others consider it to be equally sensitive.

The ease with which tetrazene is detonated by ignition depends to an exceptionally great extent on its density. It has been shown that tetrazene detonates most easily when it is poured freely into the capsule; when pressed it gives a much weaker detonation. Rinkenbach and Burton [30] obtained the following data in a sand test, using a 0.4 g charge of tetrazene:

TABLE 37

Tetrazene charge pressed under a pressure of kg/cm^2	Crushed sand, g
0	13.1
16.7	9.2
33	7.5
200	2.0

Thus, at a pressure of 200 kg/cm^2 the substance nears the condition of being "dead pressed". In spite of the fact that burning under this condition passes to detonation with difficulty, when greatly compressed the material maintains its ability to be detonated by a cap. Thus, 0.4 g of tetrazene, pressed under a pressure of 200 kg/cm^2, develops its maximum power, i.e. 21.1 g of sand crushed, when initiated with 0.4 g of mercury fulminate. The difficulty in passing from burning to detonation makes tetrazene unsuitable for detonators and its application is thus limited to ignition caps, where even 2% in the composition results in improved uniformity of percussion and friction sensitiveness and makes it suitable as a sensitizer for friction compositions.

The explosive properties of tetrazene perchlorate are also of interest.

Tetrazene manufacture

In the Wolfratshausen factory [31] in Germany, an 8% solution of sodium nitrite and a 12.5% solution of aminoguanidine sulphate, slightly acidified with acetic acid in the presence of litmus, were used for the reaction.

Into a reactor of the type used for the manufacture of lead azide (cf. Fig. 49) 50 l. of a solution of sodium nitrite (4 kg of $NaNO_2$) were introduced and heated to a temperature of 50–55°C. To the warm solution 40 l. of a solution of aminoguanidine sulphate, containing 5 kg of the dry substance, was added during a period of 1–2 hr. The rate at which the solution was introduced influences the dimensions of the crystals formed. If the solution was introduced rapidly, small crystals resulted, if it was introduced slowly, the crystals were large.

In some factories (e.g. at Stadeln [32]) dextrin was added to the reacting solutions to obtain more uniform crystals. After a solution of aminoguanidine sulphate has been added, the contents of the reactor were stirred for a further 30 min, when the stirrer was stopped. The precipitate of tetrazene settled on the bottom, the liquid from above the precipitate was decanted, the precipitate itself was covered with water, agitated, allowed to stand, decanted and finally transferred by a powerful stream of water onto a cloth filter. The product was washed first on the filter with water and finally with alcohol. The tetrazene, containing alcohol, was then transferred in a bakelite vessel together with the filter. Washing with alcohol is necessary for uniform drying of the product. If tetrazene containing only water is dried, the crystals are liable to stick together due to the low solubility of tetrazene in water. The presence of alcohol completely prevents this. Tetrazene was dried in the usual way (cf. p. 155) at a temperature from 45 to 55°C.

From the above-quoted amounts of raw material 2.6–2.7 kg of product is obtained.

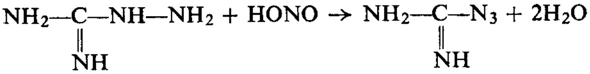
The waste tetrazene, collected in settling tanks (vessels), is destroyed by injection of live steam.

Other reactions of aminoguanidine with nitrous acid

During the reaction of tetrazene preparation care should be taken that the solution contains neither free inorganic acid nor an excess of acetic acid.

When guanidine sulphate is treated with sodium nitrite, a molecule of sulphuric acid combined with guanidine is sufficient for the liberation of nitrous acid from sodium nitrite in an amount necessary for the reaction.

In the presence of an excess of inorganic acid, the reaction proceeds differently and the formation of azidoguanidine (IV) as a final product takes place

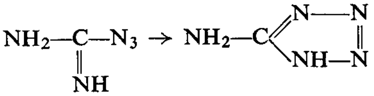


$$NH_2{-}\underset{\underset{NH}{\|}}{C}{-}NH{-}NH_2 + HONO \rightarrow NH_2{-}\underset{\underset{NH}{\|}}{C}{-}N_3 + 2H_2O$$

IV

This substance forms salts with acids. The nitrate, perchlorate and picrate of (IV) have explosive but not initiating properties.

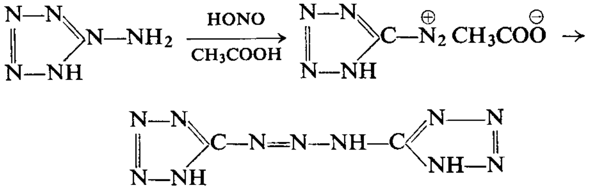
Azidoguanidine is not decomposed by boiling in water. It is, however, hydrolysed on treatment with concentrated sodium hydroxide to form sodium azide. Under the influence of a dilute solution of sodium hydroxide or of dilute acids it is isomerized to 5-aminotetrazole (V):



V

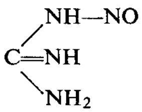
Attempts have been made to employ aminotetrazole as a constituent of smokeless and flashless propellants.

The reaction of aminoguanidine with nitrous acid in the presence of an excess of acetic acid gives also 1,3-ditetrazyltriazine (IX). It is possible that 5-aminotetrazole first arises, which then undergoes diazotization and the diazo compound thus formed couples with the remaining aminotetrazole:

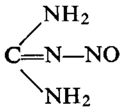


IX

NITROSOGUANIDINE



or



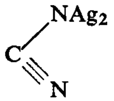
Davis and Rosenquist [33] suggested the use of nitrosoguanidine as a weak initiator. This compound occurs in the form of pale yellow crystals which explode on being heated to 165°C.

According to these authors, nitrosoguanidine is prepared by the reduction of nitroguanidine with zinc dust in a neutral medium, in the presence of ammonium chloride at room temperature (below 20–25°C). The product is filtered off together with a precipitate of zinc oxide and zinc salt, from which it is then extracted with hot (65°C) water. Nitrosoguanidine crystallizes when the solution is cooled to 0°C. The yield is about 50%.

Nitrosoguanidine decomposes explosively on contact with sulphuric acid. When dry, it is very stable, but it decomposes in the presence of water and in a moist atmosphere. Its lack of stability prevents its practical application.

CYANAMIDE SALTS

Silver cyanamide



Chretien and Woringer [34] described the preparation of silver cyanamide from calcium cyanamide by the action of silver nitrate and also described its explosive properties. Montagu-Pollock [35] described a method for growing large crystals of the salt from its aqueous solution in the presence of ammonium nitrate, ammonia and a surface active agent. Bowden and Montagu-Pollock [36] and Montagu-Pollock [35] studied the slow decomposition of the crystals when heated at temperatures from 150 to 360°C. The course of decomposition was studied by electron microscope.

The main conclusions from this work were:

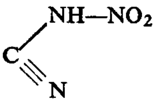
(1) Nucleation by metallic decomposition products was observed only in the special cases involving the initiation of holes of crystallographic shape.

(2) In general, decomposition was found occurring everywhere on the crystal surface.

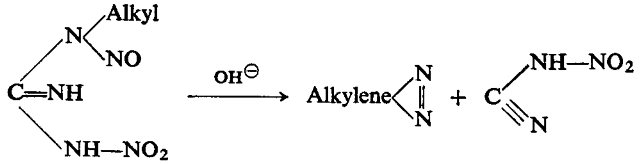
(3) The silver produced by the decomposition was very mobile on the crystal surface.

(4) Boundaries appeared separating areas of greater and lesser decomposition.

NITROCYANAMIDE SALTS



The explosive properties of the potassium salt of nitrocyanamide first attracted McKay's [37] attention. He separated this potassium salt as a by-product from the preparation of aliphatic diazo compounds by the hydrolysis of N-alkyl-N-nitroso-N′-nitroguanidines with an aqueous solution of sodium hydroxide at temperatures from 0°C to room temperature:



The same author *et al.* (McKay, Hatton, G. W. Taylor [38]) prepared a number of nitrocyanamide salts by the action of the chlorides of various metals on the silver salt in suitable solvents or the by reaction of the carbonates of various metals with a solution of nitrocyanamide in acetonitrile, and found that some of these salts have initiating properties. The majority, however, cannot be recommended for practical use, their sensitiveness to impact being too low (they are not exploded by a 5 kg weight falling from a height of 300 cm).

Harris [39] reports that only the following nitrocyanamide salts possess greater sensitiveness and may be considered to be of practical use: potassium, tin, lead, barium and silver nitrocyanamides.

Comparing with the experiments of Grant and Tiffany [40] Harris states that silver and barium nitrocyanamides show an initiation capacity the same as that of an 80 : 20 mixture of mercury fulminate and potassium chlorate, but weaker than that of a mixture of lead azide and lead styphnate. This can be seen from Table 38 quoted by Harris:

TABLE 38

Primary explosive	Minimum initiating charge necessary for explosion of 1.25 g of tetryl	Sand crushed per g
Lead azide–lead styphnate (80:20)	0.15	110
Diazodinitrophenol–potassium chlorate (75:25)	0.25	103
Mercury fulminate–potassium chlorate (80:20)	0.40	83
Silver nitrocyanamide	0.45	91
Barium nitrocyanamide	0.50	80

In spite of their fairly promising initiating properties, nitrocyanamide salts are of no practical use due to their high hygroscopicity.

For instance, due to its hygroscopicity, the air-dried tetrahydrated lead salt is not exploded by a 5 kg weight falling 325 cm. Only after being dried over magnesium perchlorate it is exploded with 100% probability by a 15 cm drop, whereas the anhydrous lead salt is exploded by a 10 cm drop.

NITROPHENOL SALTS

LEAD PICRATE

A number of salts of picric acid have been described already (Vol. I). Some salts of polynitrophenols and of heavy metals have initiating properties. One of the earliest known substances of this kind is lead picrate. Its high sensitiveness to the action of mechanical impact, however, raised difficulties in its practical utilization.

T. Urbański and Kruszyńska [41] made a comparative study of the sensitiveness to impact of lead picrate and other initiating explosives. They found lead picrate to be more sensitive than any other substance. They also examined the decomposition of lead picrate on hot metal plates. On contact with a metal surface heated to 341°C it explodes after 3 sec, and on one heated to 370°C after 1 sec.

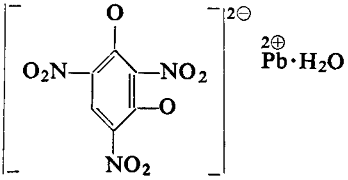
From their results the authors calculated the activation energy of the thermal decomposition which leads to explosion of this substance, and obtained a value of 55.6 kcal/mole.

During World War II the Germans employed, on a small scale, cap compositions containing lead picrate for the manufacture of electric fuses giving few gaseous products.

The lead picrate for this purpose was produced in the following way [42]. Into a stainless-steel reactor equipped with a stirrer of the type used for the manufacture of lead azide and other initiators (cf. Fig. 49) 8 l. of a solution containing 1.44 kg of lead nitrate and 15 l. of ice water were poured. Fifteen litres of a solution containing 1.5 kg of picric acid were then added. During the reaction the temperature should be maintained between 6 and 10°C. Since the temperature rises with the precipitation of lead picrate, 7–8 more litres of ice water must be poured into the reactor, usually a few minutes after the picrate has begun to precipitate. After 4 hr the liquid was decanted from above the precipitate; the latter was transferred to a cloth filter and washed with alcohol (10 l.) to which an aqueous solution of lead nitrate (500 ml of a 30% solution) has been added to avoid the dissolution of lead picrate during washing. 2.2 kg of product was obtainable from one batch.

The very fine crystalline percipitate of lead picrate which with water takes the form of a paste, was then dried for 4 days, first at 40°C and finally at 60°C. The product so dried was sieved through a silk screen of 600 mesh per cm^2. The lead picrate was then mixed with silicon and lead chromate.

LEAD STYPHNATE

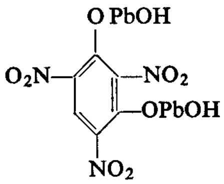


I

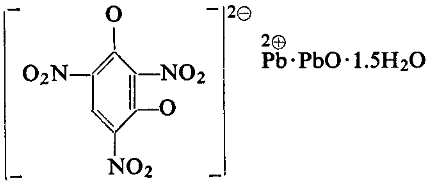
Lead trinitroresorcinate or lead styphnate is also known under the names: Bleitrizinat, Trizinat in Germany and Teneres in the U.S.S.R.

It is usually prepared by adding a solution of lead nitrate to one of magnesium styphnate. The latter is an easily soluble and weakly basic salt of trinitroresorcinate. The use of suitable salts and conditions (pH, temperature, rate and sequence in adding the raw materials) is of great importance, since unsuitable salts and conditions may easily lead to the formation of basic lead styphnate, which has considerably weaker initiating properties.

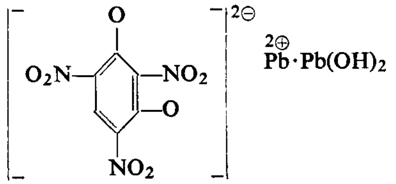
The basic salt is formed by the reaction of lead acetate with sodium or magnesium styphnate. The chemical composition of the basic salts formed depends upon the reaction conditions. The basic salt is usually credited with the structural formula (II), corresponding to the dibasic salt:



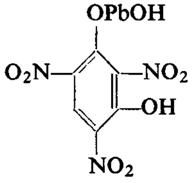
II



III



IV



V

Griess [43], who possibly dealt with the same salt, ascribed to it the structure III.

According to Zingaro [44] the dibasic salt (II) may be prepared by slowly adding a solution of styphnate in a 2% solution of sodium hydroxide at 65–70°C to an aqueous solution of lead nitrate. Zingaro also reports that structure (IV) is possible for this salt.

Finally there is the possibility of the formation of monobasic salt, probably with the structure (V). Basic salts may be converted into neutral ones by the carefully controlled action of nitric acid.

The neutral salt has a characteristic reddish-brown colour, whereas the basic salts are yellow.

Lead styphnate (neutral salt I) is practically insoluble in water (0.04 g in 100 ml of water, at 15°C) and in the majority of organic solvents. It is very stable at room and elevated temperatures (e.g. 75°C) and is not hygroscopic. In a moist atmosphere, at room temperature, it absorbs only 0.05% of water. Its specific gravity is 3.1, its apparent density, 1.0–1.6.

A method of preparation of the neutral salt (I) has been given by Herz [45]. He claims that the anhydrous salt crystallizes from an aqueous solution. In the light of other authors' works (e.g. Zingaro), it is doubtful whether in such conditions, an anhydrous salt can really be formed. The dehydration of neutral lead styphnate (I) was investigated by Zingaro who found that complete dehydration may be effected by heating the substance at 115°C for 16 hr. At higher temperatures (135–145°C) dehydration takes place more quickly (Fig. 53). Stettbacher [46] reported that in a moist atmosphere anhydrous lead styphnate absorbs water to reform the hydrate. This observation was confirmed by Zingaro [44]. The hydration curve at 30°C, according to Zingaro, is represented in Fig. 53.

Zingaro has also shown that the neutral lead styphnate, which is orange in colour, reacts with pyridine at 50°C, to form pale yellow needles after approximately 1 hr. This is a molecular addition product of ½ pyridine molecule to 1 mol. of basic lead styphnate:

$$C_6H_5(NO_2)_3OH(OPbOH)\cdot\tfrac{1}{2}C_5H_5N$$

The neutral salt crystallizes with one molecule of water (according to some authors, e.g. Rinkenbach [47]), or with half a molecule of water, which exerts a favourable influence on the substance's sensitiveness to impact. This sensitiveness is relatively small. Wallbaum [29] reports a drop test figure of 23 cm for a 1 kg weight, whereas mercury fulminate is exploded by an 8–10 cm drop and the corresponding figure for lead azide is 23 cm.

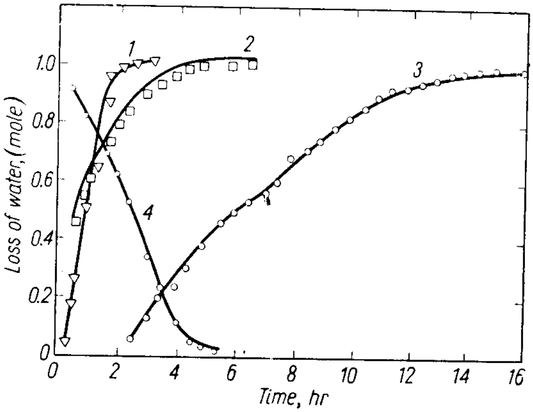


FIG. 53. Loss of water of crystallization by the neutral salt of lead styphnate at various temperatures: *1*—145°C, *2*—135°C, *3*—115°C, *4*—hydration curve at 30°C, according to Zingaro [44].

Research by T. Urbański and Kruszyńska [41] showed that lead styphnate (neutral salt) is exploded in the drop test by a 2 kg weight performing work of 5.0 kgm/cm², whereas lead picrate is exploded by work of 0.04 kgm/cm².

The ignition temperature of lead styphnate is 267–268°C.

A number of authors have investigated the thermal decomposition of lead styphnate: Hailes [48] examined the decomposition of this substance within the temperature range 200 to 228°C, and Garner, Gomm and Hailes [49] derived the following equation for the decomposition curve:

$$p=ct^m \quad \text{where}$$

p — pressure developed by the decomposition products,
c — constant,
t — temperature,
m — exponent with values ranging from 0.88 to 4.43.

Tompkins and Young [50] investigated the decomposition of the substance at temperatures between 195 and 229°C. Explosive decomposition begins at a temperature above 235°C. Decomposition curves as a function of time at various temperatures are reproduced in Fig. 54, the kinetic equation taking the form:

$$p = k(\tau - \tau_0)^2 \qquad \text{where}$$

p — pressure developed by the decomposition products,
k — the rate constant,
τ — time,
τ_0 — time of about 10 min, denoting the end of the process.

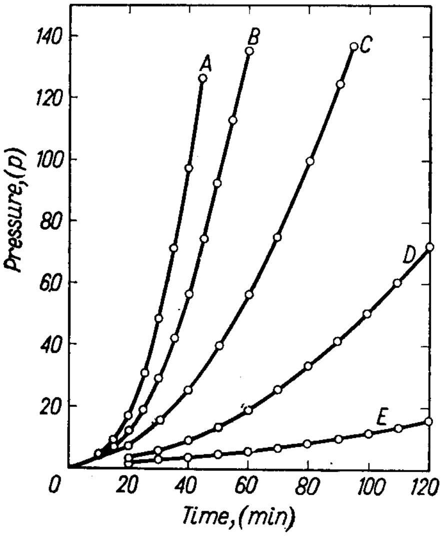


FIG. 54. The decomposition of lead styphnate monohydrate. Pressure developed with time at various temperatures: A— at 229.3°C, B—at 224.4°C, C—at 216.9°C, D—at 214.5°C, E—at 194.9°C, according to Tompkins and Young [50].

The activation energy of decomposition, according to Hailes, is 46.7 kcal/mole, according to Tompkins and Young 33 kcal/mole and according to T. Urbański and Kruszyńska [41] 42.2 kcal/mole.

Tompkins and Young confirmed Zingaro's [44] figure for the activation energy of the dehydration of lead styphnate as 13 kcal/mole.

The inflexion in curves (A) and (B) occurs after a decomposition of about 30% of substance. The plots of the acceleratory period are approximately parabolic. The mechanism of the decomposition probably consists of nucleation of sub-grains at the edges and progression of the reaction into the grains with a non-coherent interface.

Evans and Yuill [51] showed that lead styphnate may be ignited by adiabatic compression of air, the calculated temperature amounting to 660°C, whereas Bryan and Noonan [52] using helium as the gas surrounding the styphnate, found that the energy to obtain the necessary compression for igniting this substance is 0.046 cal/ /cm^2.

McAuslan [53] examined the ignition of lead styphnate by irradiation with the intense light of a spark from an electric discharge. The light energy required to initiate lead styphnate to explosion was 29 J. This author also studied the relationship between the light energy required to initiate lead styphnate and the temperature of the substance. He obtained a straight line graph (Fig. 55). Extrapolation gives a temperature of 480°C for zero light energy. This value is higher than the ignition temperature of non irradiated lead styphnate.

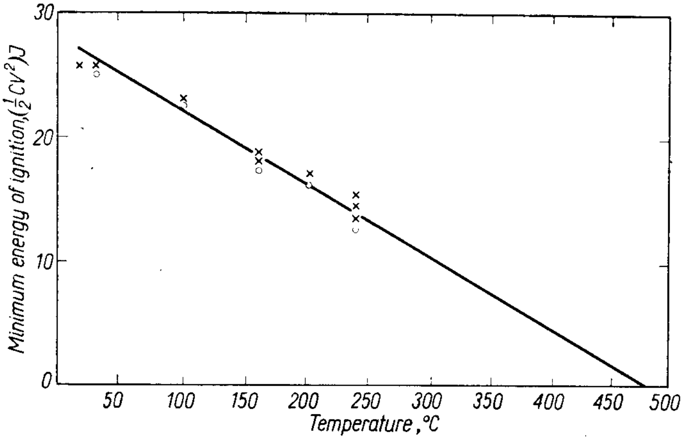


FIG. 55. Variation of the minimum light energy for ignition of lead styphnate with ambient temperature, according to McAuslan [53]. × —ignition; ○—no ignition.

Kaufman [17] found lead styphnate to be exceptionally resistant towards nuclear radiation. After 90 days strong γ-radiation from ^{198}Au (an average irradiation of 10^5r per hour) produced practically no change in the substance. The volume of gas evolved after 90 days was only 0.12 ml/g.

High ignitability by direct action of a flame or electric spark is a characteristic feature of lead styphnate. The salts enormous sensitiveness to the discharge of static electricity was first disclosed in 1938 by Barcikowski, Dobrzyński and Kiełczewski [54].

This property has since been confirmed by many authors (Hartmann, Nagy and Brown [55]; Morris [56]; and Taylor and Hall [57]). It became clear that numerous accidents due to the ignition of lead styphnate during drying, pouring, moving, stirring etc. had been caused by the discharge of accumulated static electricity. Attempts to reduce its sensitiveness by the addition of graphite have been unsuccessful, and lead styphnate continues to be very dangerous to handle.

Special attention is now paid to the careful earthing of all parts of the plant in which dry lead styphnate is handled. Floors in factory buildings should be made of asphalt or of a soft material (plastic) containing graphite or aluminium to make them conduct electricity. When manual work with lead styphnate is unavoidable, the operator should stand on a felt-cloth sheet saturated with a solution of calcium chloride.

To prevent excessive dryness of the working atmosphere, which favours the build up of static electricity, wet cloths should be hung about the building or air-humidifying equipment used.

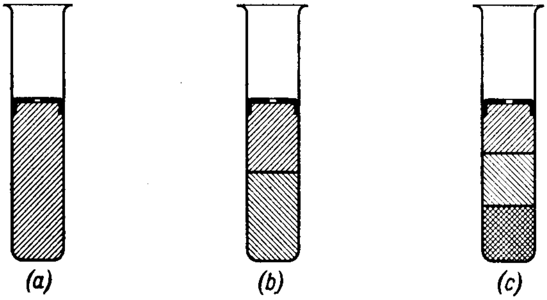


FIG. 56. Blasting caps: (*a*)—charged with a single explosive (mercury fulminate or lead azide); (*b*)—charged with a primary explosive and a high explosive; (*c*)—charged with three layers: a primary explosive and two high explosives.

A more modern procedure is to introduce by means of radioactive salts ionized air into the premises.

Lead styphnate is a fairly weak explosive because of its high metal content (44.25%).

The rate of detonation is:

at a density of 0.93	2100 m/sec
at a density of 2.6	4900 m/sec
at a density of 2.9	5200 m/sec

It is also very weak as a primary explosive. Even 1.0 g of it fails to initiate penthrite compressed under a pressure of 2000 kg/cm^2. It is therefore not used for filling detonators, and its applications are limited to use in

(a) non-corrosive ignition caps (so called "Sinoxyd");
(b) addition to lead azide in detonators to facilitate ignition;
and (c) as a covering layer to protect lead azide against carbon dioxide and to facilitate ignition (Fig. 56).

Lead styphnate manufacture

In the method employed at Wolfratshausen [31] a solution of magnesium styphnate was first prepared, adding to 20 kg of magnesium oxide a suspension (partly solution) of 120 kg of trinitroresorcinol in 350 l. of water. The temperature rose spontaneously due to the reaction, but should be raised further by heating to 60°C. The solution so obtained was filtered through a cloth filter, diluted with water to s.g. 1.043 (6°Bé) and poured into a vat, in which it was allowed to stand for 10 hr. The temperature then fell to 25–30°C.

From the magnesium styphnate solution so prepared, 86.4 l. of liquid was decanted, leaving the lower layer in which the sediment was collected. This solution was heated to 60°C, while stirring, and 22.7 l. of 34% solution of lead nitrate, s.g. 1.274 (31°Bé) was then poured into it during a period of 20–30 min, while stirring continued and the temperature was maintained at 60°C. When the solutions were mixed, the contents of the reactor were cooled as quickly as possible to 25°C; when this temperature has been reached the stirrer was stopped and the precipitated sediment of lead styphnate was allowed to settle. The liquid from above the sediment was then decanted, and the latter was first washed out of the reactor by a stream of water, and transferred onto a cloth filter, where it was washed again as is the custom with other primary explosives. From the above mentioned amounts of raw material about 8 kg of lead azide was obtained.

The product was dried in a drier (as described for mercury fulminate) at temperatures from 65 to 70°C in batches of 1.2 kg at a time; it was then sieved as described above. A sieve analysis of the product showed, for example, the following sizes of crystals:

on sieves with a clearance of 0.1 mm	8% of the substance was retained
on sieves with a clearance of 0.075 mm	33% of the substance was retained
on sieves with a clearance of 0.060 mm	32% of the substance was retained
on sieves with a clearance of 0.040 mm	18% of the substance was retained
and	9% of the substance passed through.

Waste lead styphnate was destroyed by adding an excess of sodium carbonate; most of the lead was then precipitated as a carbonate and a solution of sodium styphnate was formed. This solution was then treated with iron filings and acidified with sulphuric acid, reduction of the nitro groups took place, and the substance ceased to be dangerous.

The continuous method for the manufacture of lead styphnate (according to Meissner [58, 59])

The continuous preparation of lead styphnate can be carried out in the same equipment as for the manufacture of lead azide (Fig. 50) after previous cleaning of the apparatus and exchanging the flowmeters.

For this production, the starting materials are needed: trinitroresorcinol and magnesium oxide to form magnesium styphnate and lead nitrate, all disssolved in distilled water.

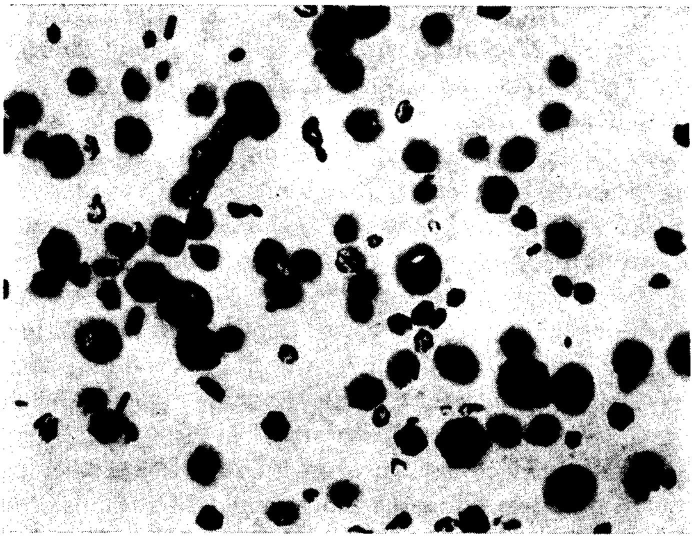


FIG. 57. Lead styphnate precipitated by Meissner method [59]. Courtesy J. Meissner.

The precipitating temperature is, in this production, somewhat higher than in the manufacture of technical-grade lead azide.

All other operations are similar to those already described before.

Lead styphnate crystals obtained by this method are sphere-shaped (Fig. 57).

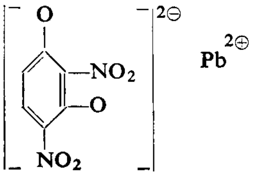
OTHER STYPHNATES

Tompkins and Young [50] examined the thermal decomposition of barium styphnate and found it to be similar to that of lead styphnate hydrate (Fig. 54).

The point of inflexion of the decomposition curve occurs after 50% of the substance has decomposed. The energy of decomposition is 36.5 kcal/mole.

According to T. Urbański and Kruszyńska [41] thallium styphnate has similar properties to those of lead styphnate. The former, however, is much more sensitive to impact than the latter. Their sensitiveness to temperature is similar: contact with a metal surface heated to 351°C causes explosion after 1 sec. The activation energy of thermal decomposition is nearly 80 kcal/mole.

LEAD DINITRORESORCINATE



This substance is prepared by the action of a hot solution of lead nitrate on a solution of sodium dinitroresorcinate. The lead salt is precipitated as the solution cools. Lead dinitroresorcinate ignites from a direct flame readily and burns with great velocity. Its initiating action is weaker than that of lead styphnate and it is less sensitive to impact and friction than styphnate. It has therefore recently found application as a component of cap compositions. It is valuable because it is safer to handle than styphnate. The preparation of dinitroresorcinol is discussed in Vol. I, p. 536.

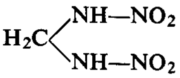
NITROSOPHENOL SALTS

Nitrosophenols are formed very easily by the action of nitrous acid on phenols. Some salts of heavy metals have weak initiating properties. These are: lead dinitrosophenate and lead trinitrosophloroglucinate.

Due to the readiness with which it ignites under the direct influence of flame, lead dinitrosophenate has found a certain application in the manufacture of cap compositions for ignition by spark or flame. Its disadvantage lies in its relatively low stability; heating to 120°C causes explosion after 2 hr, and after 10 days of heating at 80°C marked decomposition occurs.

NITRAMINE SALTS

T. Urbański, Piskorz and Mazur [60] prepared a number of methylenedinitramine salts



$$H_2C\begin{cases}NH{-}NO_2\\NH{-}NO_2\end{cases}$$

and found that the silver and lead salts have initiating properties. Their ignition temperatures and sensitiveness to impact are shown in the following table:

TABLE 39

Salt	Ignition temperature	50% of explosions by 2 kg weight dropped from
Silver	195°C	10 cm
Plumbous	213°C	12 cm

"ISONITRAMINE" (NITROSOHYDROXYLAMINE) SALTS

T. Urbański, Zacharewicz and Pietrzyk [61] suggested the use of some methylenedi-isonitramine salts $(CH_2)(N_2O_2H)_2$ as primary explosives.

The sodium salt of methylenedi-isonitramine was prepared by Traube [62] from acetone and nitric oxide in the presence of sodium alcoholate according to the following chain of reactions:

$$CH_3COCH_3 + 4NO + 2C_2H_5ONa \rightarrow \underset{\text{I}}{CH_3COCH(N_2O_2Na)_2} + 2C_2H_5OH \qquad (14)$$

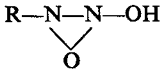
Product (I) so produced undergoes hydrolysis in water:

$$CH_3COCH(N_2O_2Na)_2 + H_2O \rightarrow CH_3COOH + \underset{\text{II}}{CH_2(N_2O_2Na)_2} \qquad (15)$$

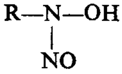
The sodium salt of methylenedi-isonitramine (II) is formed. In an aqueous solution this precipitates with the salts of heavy metals. Some of these salts (e.g. the thallium salt) have the properties of weak initiators.

The structure of these compounds remained obscure for a long time. Traube originally assigned the structure —N—N—OH to the isonitramino group, but in further researches he found that isonitramines and the derivatives of nitrosohydroxylamine which he prepared by the action of nitrous acid on *β*-derivatives of hydroxylamine were identical. He did not, however, draw from this any definite conclusions as to the structure of isonitramines in spite of the fact that by the synthesis of isonitraminoisobutyric acid, Gomberg [63] had confirmed the nitrosohydroxylamine structure of the isonitramino group.

Hantzsch [64] described isonitramines as compounds which have either the structure reported by Traube (I) or that of nitrosohydroxylamine (IIa):



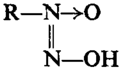
I



$$\mathrm{R{-}\underset{\displaystyle NO}{\underset{|}{N}}{-}OH}$$

IIa

for which the tautomeric formula (IIb) is also possible:



$$\mathrm{R{-}\underset{\displaystyle N{-}OH}{\underset{\|}{N}}{\rightarrow}O}$$

IIb

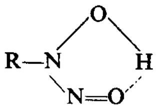
Hantzsch expressed the opinion that the active hydrogen in isonitramines is always combined with the oxygen atom whereas in nitramines it may be combined, in different tautomeric modifications, either with the nitrogen or the oxygen atom.

In the light of Angeli's [65] investigations, which led to the conclusion that the azoxy group has an unsymmetrical structure $(-\mathrm{N}{=}\underset{\displaystyle O}{\underset{\downarrow}{\mathrm{N}}}-)$, and not as formerly assumed the symmetrical one of $(-\underset{\diagdown_{O}\diagup}{\mathrm{N}{=}\mathrm{N}}-)$, it did not seem possible to accept a symmetrical structure for the isonitramine group (I).

Hantzsch and Strasser [66] came to this conclusion and assigned the structure of nitrobenzyl-N-nitrosohydroxylamine to esters of nitrobenzylisonitramine:

$$O_2N\cdot C_6H_4CH_2N(OR)NO \quad \text{(thus IIa)}$$
$$\text{or } O_2N\cdot C_6H_4CH_2(NO)NOR \quad \text{(thus IIb)}$$

However, on investigating the ultra-violet absorption spectra of methylenedi-isonitramine, R. N. Jones and Thorn [67] failed to detect a band characteristic of the nitroso group. This was accepted as evidence against the nitrosohydroxylamine structure of these compounds. On the other hand, the methyl ester of methylenedi-isonitramine has a spectrum typical of a nitro compound. Carmack and Leavitt [68] confirmed the absence of the NO group band in the ultra-violet spectrum of nitrosohydroxylamine derivative prepared by Cason and Prout [69] and ascribed this to the existence of a hydrogen bond:



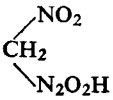
III

This bond cannot, of course, exist in an ester, in which a band characteristic of the nitroso group does occur.

Urbański and Piskorz [60] found that the properties of methylenedi-isonitramine salt differ markedly from those of methylenedinitramine salt. They also established that methylenedi-isonitramine is not a tautomeric modification of methylenedinitramine. In their most recent work [70] they have confirmed the nitrosohydroxylamine structure of isonitramines by examining the infra-red absorption spectra.

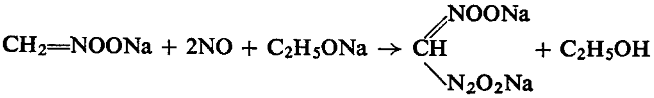
Under the influence of aqueous solutions of the water soluble salts of heavy metals the sodium salt of methylenedi-isonitramine gives precipitates of the salts of these metals. T. Urbański, Zacharewicz and Pietrzyk [61] suggested the use of certain heavy metal salts as initiators. Particularly interesting properties were demonstrated by the thallous salt $CH_2(N_2O_2Tl)_2$.

In another investigation, T. Urbański and Wesołowski [71] studied the salts of nitromethylisonitramine:



$$\begin{matrix} & NO_2 \\ CH_2 & \\ & N_2O_2H \end{matrix}$$

According to Traube [62] the sodium salt of the aci-modification of this compound is obtained by the action of nitric oxide on the sodium salt of nitromethane in the presence of sodium alcoholate:



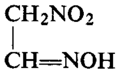
$$CH_2{=}NOONa + 2NO + C_2H_5ONa \rightarrow \begin{matrix} & NOONa \\ CH & \\ & N_2O_2Na \end{matrix} + C_2H_5OH \qquad (16)$$

III

Some of the heavy metal salts of nitromethylisonitramine appear to have initiating properties, which are however considerably weakened by the presence of a nitro group. The salts of type III are therefore weaker initiators than the corresponding metal salts of methylenedi-isonitramine.

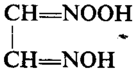
SALTS OF METAZONIC ACID

Metazonic acid is a nitroacetaldoxime:



$$\begin{array}{l} CH_2NO_2 \\ | \\ CH{=}NOH \end{array}$$

The aci-modification has the form



$$\begin{array}{l} CH{=}NOOH \\ | \\ CH{=}NOH \end{array}$$

It is produced by the action of sodium hydroxide on nitromethane at an elevated temperature (Friese [72]; Steinkopf and Kirchhoff [73]). Urbański and Kowalczyk [74] found that some heavy metal salts of this compound have weak initiating properties and that metazonic acid itself is a fairly weak explosive. Its expansion in the lead block is 240 cm^3.

SALTS OF OXALIC ACID

As early as 1883 Berthelot [75] noticed that some salts of oxalic acid (e.g. mercuric or silver oxalates) have the properties of primary explosives.

This group of initiators has no practical application. Nevertheless it is interesting from the theoretical point of view, due chiefly to the fact that the general equation for the decomposition of oxalates is:

$$\text{A solid} \rightarrow \text{B solid} + \text{C gas}$$

Thus it is similar to the decomposition of azides. There have been several papers on silver oxalate — $Ag_2C_2O_4$. Macdonald and Hinshelwood [76] confirmed the Berthelot equation, according to which the only products of decomposition of silver oxalate are metallic silver and CO_2.

Benton and Cunningham [77] found that the rate of thermal decomposition of silver oxalate may be increased by previously exposing it to ultra-violet radiation.

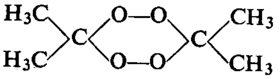
During the thermal decomposition of silver oxalate, fragments of metallic silver are formed. This has been confirmed by conductivity measurements (Macdonald and Sandison [78]) or by X-ray examination (Griffith [79]).

Tompkins [80] investigated the thermal decomposition of silver oxalate at 110–130°C. Its decomposition, in his opinion, is similar to that of barium azide.

Mercuric oxalate appears to undergo decomposition by a somewhat different mechanism with the formation of mercury and mercurous oxalate as intermediate products before full decomposition occurs (Prout and Tompkins [81]).

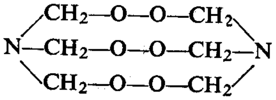
PEROXIDES

The explosive properties of peroxides have attracted attention for a long time, mainly because of their initiating properties: namely, in a confined space burning readily passes into detonation. In spite of this, virtually none of the peroxides has found practical application. Some are rather unstable, others are very volatile and all are highly sensitive to friction and impact: e.g. acetone peroxide, very easily prepared by the action of potassium persulphate on acetone in the presence of sulphuric acid (Baeyer and Villiger [82]) possesses, according to T. Urbański's [83]

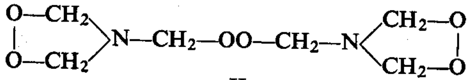


studies, a very high vapour pressure and is highly volatile at room temperature. In an open vessel a thin layer of the substance loses half its weight in approximately 3 months. The Chemisch-Technische Reichsanstalt [84] determined the rate of detonation of acetone peroxide in a tube of 6.3 mm diameter: the rate was found to be 5190 m/sec when the s.g. was 1.6 and 5290 m/sec when the s.g. was 1.2.

A peroxide which might have practical importance and which has been the subject of fairly extensive studies, is hexamethylenediamine peroxide, so-called HMTD, a substance with a m.p. 145°C with the probable formula:



I



II

I, according to Baeyer and Villiger [82] or II, according to Girsewald and Siegens [85].

Legler [86] was the first to prepare this substance by the action of hydrogen peroxide on ammonium salts in the presence of formaldehyde. Later, Girsewald [87] obtained it by the treatment of hexamethylenetetramine with hydrogen peroxide.

At present, it is rather difficult to decide between these two formulae, but it seems certain that the substance contains methyleneamino groups $N-CH_2$ and peroxy groups, —O—O—. This view is supported by the observation of T. Urbański and Szyc-Lewańska [88] that the action of nitric acid on hexamethylenediamine in the presence of ammonium nitrate leads to the formation of cyclonite and formic acid.

Hexamethylenediamine peroxide is prepared by dissolving 14 g of hexamethylenetetramine in 45 g of 30% hydrogen peroxide, in a beaker chilled with a mixture of ice and common salt. 21 g of powdered citric acid is then poured into the solution while maintaining the temperature below 0°C. When all the citric acid has been added, the whole is agitated for 3 hr at 0°C and allowed to stand for 2 hr at room temperature. The white, crystalline product is filtered off and washed with water and alcohol to aid drying at room temperature.

The same compound was prepared by Leulier [89] by the action of hydrogen peroxide on hexamethylenetetramine in the presence of nitric acid, but in a lower yield than that in the Girsewald method. Leulier ascribed an incorrect formula to the substance as pointed out by Girsewald and Siegens [85].

Hexamethylenediamine peroxide is practically insoluble in water and in the majority of organic solvents. According to Taylor and Rinkenbach [90] it is volatile at a temperature higher than room temperature and at 75°C it decomposes markedly losing methylamine. At 100°C it is totally decomposed after 24 hr. When boiled in water it decomposes, and passes into solution with evolution of oxygen, the aqueous solution contains ammonia, formaldehyde, ethylene glycol, formic acid and hexamethylenetetramine.

When thrown onto a metallic surface heated to 200°C it explodes instantly, or on a surface at 149°C after 3 sec. It is a very powerful explosive. Its rate of detonation at a density of 0.88 in a pipe 5.5 mm in diameter is 4510 m/sec.

It is less sensitive to impact than mercury fulminate (a 3 cm drop is necessary to cause explosion, with a 2 kg weight, whereas for mercury fulminate a 2.5 cm drop is sufficient), but as an explosive it is much powerful than the latter.

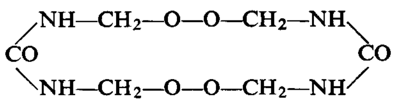
As an initiator it is also much more powerful than mercury fulminate. Thus, trinitrotoluene is detonated by as little as 0.08 g of hexamethylenediamine peroxide compressed under a pressure of 67 kg/cm^2, whereas with mercury fulminate 0.26 g is required. For picric acid and tetryl 0.05 g of peroxide is sufficient to produce detonation as compared with 0.21–0.24 g of fulminate.

Its specific gravity is 1.57, but its apparent density only 0.66. A density of 0.91 can be obtained under a pressure of 170 kg/cm^2. It is not liable to become dead pressed even under a pressure of 730 kg/cm^2.

In spite of its initiating qualities, hexamethylenediamine peroxide is of no practical use due to its doubtful stability.

Recently Lefevre and Baranger [91] recommended it as a chemotherapeutic agent against cancer. They obtained positive results from oral treatment of cancer of the prostate gland.

Another peroxide, i.e. tetramethylenediperoxidodicarbamide has similar properties. It probably has the following structure:



This compound was obtained by Girsewald and Siegens [92] by the action of hydrogen peroxide and nitric acid on an aqueous solution of urea and formaldehyde.

Spaeth [93] suggested its application as an initiator, but without practical success for the same reasons as with other peroxides, i.e. insufficient stability and a very high sensitiveness to mechanical stimulus.

Peroxides and ozonides are a wide group of compounds which are receiving a growing amount of attention for both theoretical and practical reasons. Particularly in the polymer industry peroxides have found wide application as catalysts and intermediates.

This subject is outside the scope of this book. Those interested should consult monographs and review articles and books by Rieche [94], Davies [95] and others [96–98].

ACETYLENE AND ITS SALTS (ACETYLIDES)

It has long been known that acetylene explodes under the influence of compression. Experiments by Rimarski and Metz [99] showed that at a temperature below 500°C acetylene does not explode if the pressure is lower than 3 kg/cm^2. An explosion may occur at 510°C under a pressure of 2.05 kg/cm^2. At room temperature acetylene may explode provided it is compressed adiabatically with a pressure of 170 kg/cm^2.

Acetylene is an endothermic compound, its heat of formation ($-\Delta H_f$) being -54.9 kcal/mole. Its heat of explosion is therefore very great, viz. 1870 kcal/kg, although the explosion is not connected with an oxidation reaction:

volume of gases (V_0) is 60 l./kg

temperature of explosion approximately 2700°C

Solid acetylene (m.p. about -83°C) is insensitive to impact, but at a density of 0.64 it can be detonated by a number 8 detonator, showing a rate of detonation of 2500 m/sec and a lead block expansion of 300 cm^3.

Gaseous, compressed acetylene also detonates. According to Penny [100] when compressed to 8 atm in a pipe $\frac{1}{2}$ in. in diameter, it detonates with a rate of 1817 ± 7 m/sec and in a pipe 1 in. dia. with a rate of 1870 ± 22 m/sec. According to Mayes [101] when compressed to 3–6 atm in a pipe $1\frac{1}{2}$ in. dia., it detonates with a rate of 1848 m/sec.

The heavy metal salts of acetylene have the properties of primary explosives, but only cuprous acetylide was found to be satisfactory for practical use.

CUPROUS ACETYLIDE

Cuprous acetylide was prepared by Berthelot [102] as early as 1866 by the action of acetylene on an ammonia solution of cuprous chloride. Cuprous acetylide takes the form of a russet or reddish-brown powder, insoluble in water and in the majority of organic solvents.

Much research was necessary in order to establish the chemical composition of cuprous acetylide. Blochmann [103] and Scheiber and Reckleben [104] showed that the freshly precipitated and dried product has the approximate composition $Cu_2C_2 \cdot H_2O$. According to Keiser [105] drying this salt over sulphuric acid or calcium chloride (Scheiber and Reckleben [104]) gives an anhydrous product.

Küspert [106] drew attention to the fact that cuprous acetylide may form a colloidal solution. The colloidal state is favoured by the use of diluted ammonia solutions of cuprous salts.

The substance is stable at ordinary temperatures and up to 100°C. Like cupric acetylide it decomposes on being heated in hydrochloric acid (Berthelot [102], Sabaneyev [107]). A solution of potassium cyanide also causes decomposition with the loss of acetylene. Makówka [108] showed that aldehyde-like compounds are formed from cuprous acetylide on reaction with a 30% solution of hydrogen peroxide.

Cuprous acetylide explodes in air at 120–123°C, but in an acetylene atmosphere, under a pressure of 5 atm it decomposes without explosion at 250°C. According to Morgan [109] it is very easily exploded by an electric spark.

Apart from cuprous acetylide, with the formula Cu_2C_2, there are complex cuprous salts prepared by the action of acetylene on certain cuprous salts in a neutral or slightly acidic medium; e.g. Bhaduri [110] obtained a cuprous acetylide containing a thiosulphate group by the action of acetylene on cuprous thiosulphate, and in the presence of potassium iodide Scheiber and Reckleben [104] precipitated an acetylide containing iodine.

Care should be taken that cuprous acetylide is not contaminated with cupric acetylide which may occur if the cuprous chloride used for the reaction contains cupric salt. This is of importance since cupric acetylide is unstable and explodes on heating even between 50 and 70°C. It is also more sensitive to impact and friction than cuprous acetylide. The pure cupric acetylide is black or brown.

Many authors recommend the precipitation of cuprous acetylide in the presence of reducing substances such as hydroxylamine (Ilosvay [111]), SO_2 (Rupe [112]), hydrazine sulphate (Cattelain [113]), so as to avoid contamination with cupric acetylide.

The precipitation of cuprous acetylide was introduced into analytical chemistry for the quantitative determination of copper. Since cupric acetylide was dangerous to handle, Makówka [108] worked out a method in which cupric salts are previously reduced, e.g. with hydroxylamine, to cuprous salts, when the acetylide is precipitated. Cuprous salts in a solution of hydroxylamine are employed as reagents for acetylene (e. g. Pietsch and Kotowski [114]).

Cuprous acetylide is used as the chief component of match heads in electric fuses, being particularly susceptible to ignition by sparks or a glowing wire to give a sharp, hot flame.

SILVER ACETYLIDE

Silver acetylide, Ag_2C_2, is a white powder formed when acetylene is passed through an ammoniacal solution of silver chloride. It has even stronger explosive properties than cuprous acetylide due to its exceptionally large negative heat of formation ($-\Delta H_f = -87.15$ kcal/mole). Its ignition temperature is 200°C. It is of no practical value.

VARIOUS INITIATORS

NITROGEN SULPHIDE

Nitrogen sulphide, N_4S_4, m.p. 178°C, was prepared by Soubeiran [115] by the action of ammonia on sulphur chloride dissolved in benzene

$$6SCl_2 + 16NH_3 \rightarrow N_4S_4 + 2S + 12NH_4Cl$$

It is prepared by dissolving 1 volume of sulphur chloride in 8–10 volumes of carbon disulphide, cooling and passing in dry ammonia until the dark brown precipitate, first formed, has redissolved, producing an orange-yellow solution containing, flocks of ammonium chloride. The latter is filtered off and the filtrate is evaporated to dryness. The dry residue is extracted with boiling carbon disulphide to remove the sulphur. The undissolved material is crude nitrogen sulphide. On cooling the hot extract deposits a further quantity of the substance. The combined crude product is recrystallized from carbon disulphide.

Nitrogen sulphide is insoluble in water, slightly soluble in alcohol and ether, somewhat soluble in carbon disulphide and benzene. At room temperature it is hydrolysed to some extent by water to form free sulphur, sulphur dioxide and ammonia. Its specific gravity is 2.22.

Nitrogen sulphide is less sensitive to friction and impact than mercury fulminate. It is a weaker initiator than mercury fulminate, its rate of acceleration being considerably less than that of the latter. Its ignition temperature is 207°C. It is exceptionally strongly endothermic, its heat of formation ($-\Delta H_f$) being -138.8 kcal/mole (Berthelot and Vieille [116]).

In many patents nitrogen sulphide is recommended as a filling for fuses, primers etc. but in spite of this it has not been used in practice.

NITROGEN SELENIDE

Nitrogen selenide, N_4Se_4, was prepared by Espenschied [117] by the action of ammonia on selenium chloride. It is an orange-red, amorphous, explosive powder.

The explosive properties of this substance were studied by Verneuil [118], and Berthelot and Vieille [116]. Its ignition temperature is 230°C. It is very sensitive to friction and impact. Its heat of formation ($-\Delta H_f$) is strongly endothermic: -169.2 kcal/mole.

SALTS OF THIOCYANIC ACID

At the beginning of the twentieth century the thiocyanates (rhodanates) of certain metals (e.g. mercury, copper) were recommended as components of cap compositions with potassium chlorate. The rhodanates were intended as a substitute for mercury fulminate, but only lead rhodanate acquired any practical significance.

Lead rhodanate, $Pb(CNS)_2$ is formed, when a solution of lead nitrate, slightly acidified with nitric acid, is treated with a moderately concentrated solution of the rhodanate of an alkali metal.

When exposed to long day-light or ultraviolet irradiation lead rhodanate becomes yellow. When boiled in water it is converted into a basic salt $Pb(CNS)_2 \cdot Pb(OH)_2$ which behaves as a weak initiator. It is used as a constituent in some cap compositions.

COMPLEX SALTS

The complex salts of precious metals, formed by the action of ammonia either on aqueous solutions of silver, gold and platinum salts or on silver oxide were the first substances to reveal the ability to explode violently on heating, on direct contact with flame or by friction or impact ("fulminating" silver and gold).

Later it was found that a number of other metals which can give typical complex salts (Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni and Zn) can form explosive co-ordination compounds.

These substances have a variable composition depending upon the reaction conditions, chiefly the concentration of the reagents used. Salvadori [119] called attention to the interesting explosive properties of the chlorates and perchlorates of complex "ammines" of the type:

$$[M^{II}(NH_3)_4](ClO_3)_2$$

$$[M^{II}(NH_3)_4](ClO_4)_2$$

$$[M^{III}(NH_3)_6](ClO_3)_2$$

$$[M^{III}(NH_3)_6](ClO_4)_2$$

The explosive properties of these salts were partially studied by Ephraim and Jahnsen [120] and were later investigated in detail by Friedrich and Vervoorst [121]. The latter also investigated the analogous combinations described by Franzen and Mayer [122], in which ammonia was replaced by hydrazine.

Friedrich and Vervoorst found that the substance $[Cu(NH_3)_4](ClO_3)_2$ has initiating properties. It is however of no practical use, losing ammonia fairly rapidly in air. In damp air it is easily hydrolysed. Nickel ammino perchlorate $[Ni(NH_3)_6](ClO_4)_2$ is a fairly strong explosive with the rate of detonation 5300 m/sec at the density 1.39.

Friedrich and Vervoorst also prepared chlorates of hydrazinometals:

$$[Cd(N_2H_4)_2](ClO_3)_2$$

$$[Ni(N_2H_3)_4](ClO_3)_2$$

and similar perchlorates, which proved to be basic salts.

The chlorates are strong initiators with an initiating power exceeding that of mercury fulminate and even that of lead azide. The ignition temperature of the cadmium salt is 125°C, and that of the nickel salt 170°C. Basic perchlorates of cadmium and nickel are also initiators, weaker than the chlorates, but somewhat stronger than mercury fulminate.

The sensitiveness of all these salts to impact is very high, in many cases higher than that of mercury fulminate.

The corresponding nitrates (NO_3 instead of ClO_3 or ClO_4) do not possess initiating properties.

Another interesting group of explosive co-ordination compounds is formed by the azides of "ammines" of general formulae

$$[M^{II}(NH_3)_2](N_3)_2$$

$$[M^{II}(NH_3)_4](N_3)_2$$

$$[M^{III}(NH_3)_6](N_3)_2$$

$$[M^{III}(NH_3)_6](N_3)_3$$

The salts of Cd, Cr, Cu^{II}, Ni were first prepared by Strecker and Schwinn [123]. They do not seem to possess sufficient stability to be of practical use.

Another type of complex cobalt ammine including azide groups in the co-ordination were obtained by Linhard and Flygare [124]:

$[Co(NH_3)_5N_3]X_2$
where $X = Cl, Br, I, NO_3, N_3$

and $[Co(NH_3)_5N_3]Y$
where $Y = CrO_4, S_2O_3, S_2O_6$

Only the perchlorate ($X = ClO_4$) shows marked sensitiveness and possibly initiating properties. The other compounds do not seem to possess properties interesting from the practical point of view.

Another kind of complex salts was obtained by Hodgkinson and Hoare [125] by the action of an ammoniacal solution of cupric, nickelous-nickelic or silver oxide on an alcoholic solution of tetranitromethane. Precipitates are then formed which are insoluble in water, explosive, but unstable, decomposing on boiling in water.

There are many other explosive complex salts but at present they are of no practical use.

An extensive review of various explosive complex compounds has been published by Fedoroff *et al.* [126].

SILVER PERCHLORATE

There are some indications that silver perchlorate has initiating properties since in some unexplained cases, the large crystals detonate on slight friction in a way similar to the detonation of crystals of lead azide or silver azide (Hein [127]).

These properties have not been examined in detail.

INITIATING COMPOSITIONS

Initiators are usually compositions from which the desired results are obtained by the interrelation of the components. This is of particular importance in the manufacture of percussion caps which are fired by striker pins to give a hot flame capable of igniting propellants and should therefore have ability to detonate.

Blasting caps, i.e. detonators, (Fig. 56, p. 218) were originally filled with mercury fulminate alone or with a 80:20 mixture of mercury fulminate and potassium chlorate. The chlorate is added to facilitate pressing since mercury fulminate alone cannot be pressed conveniently. In addition, potassium chlorate increases the ignitability of mercury fulminate, thus permitting a greater pressing pressure to be used which in turn improves coherence.

Mercury fulminate, or its mixture with potassium chlorate, is usually pressed under a pressure of 250–300 kg/cm^2. Pressed at pressures of 600 kg/cm^2 it ignites with difficulty and misfires may occur.

Detonators for mining explosives are manufactured in various sizes and numbered according to the amount of fulminate which they contain. The charges of fulminate for each size are shown in the following table:

TABLE 40

No. of detonator	1	2	3	4	5	6	7	8	9	10
Charge of mercury fulminate, g	0.3	0.4	0.54	0.65	0.8	1.0	1.5	2.0	2.3	3.0

In mining, a No. 8 detonator is used for ammonium nitrate explosives, No. 6 and No. 3 for nitroglycerine explosives.

Modern detonators have a double filling, i.e. a charge of high explosive such as tetryl or penthrite at the bottom, initiated by a layer of mercury fulminate or fulminate–chlorate placed on top (Fig. 56b). In this way more powerful detonators have been produced for mining purposes, containing the following charges:

TABLE 41

No. of detonator	5	6	7	8
Tetryl, g	0.3	0.4	0.75	0.9
Mercury fulminate, g	0.3	0.4	0.5	0.5

Detonators containing lead azide are loaded into aluminium capsules. Lead azide may be used alone or in conjunction with lead styphnate or tetrazene, the use of which facilitates ignition of azide. The layer of azide may also be covered with a layer of lead styphnate. Lead azide or its mixtures may be pressed at a very high pressure (e.g. 1000 kg/cm^2).

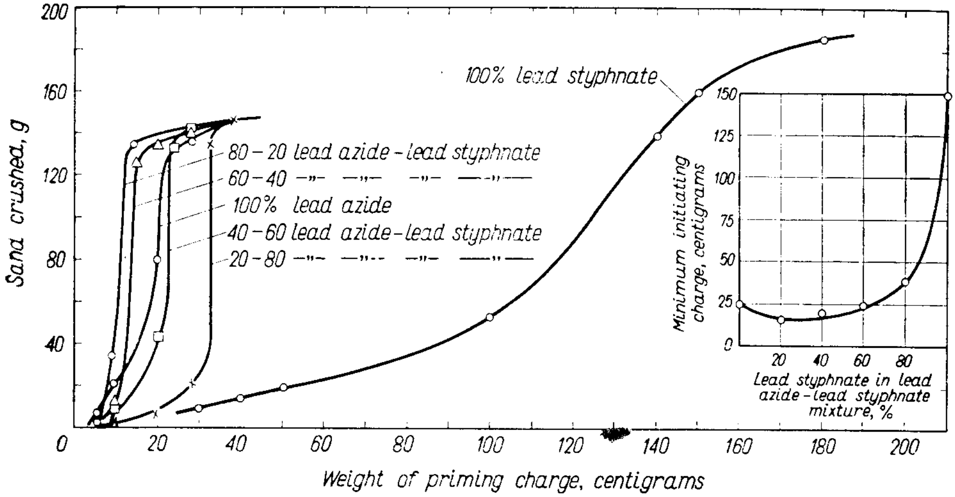


FIG. 58. Minimum initiating charge of lead azide, lead styphnate and their mixtures for 1.25 g of tetryl, according to Grant and Tiffany [40].

A general idea of the change in the minimum initiating charge of lead azide–lead styphnate mixtures with their composition is given in Fig. 58 by Grant and Tiffany [40]. The low priming ability of lead styphnate alone is also indicated.

The minimum charge required to detonate the base explosive in the detonator was determined by the sand test of Snelling [127a].

Aluminium detonators with lead azide and other explosives were used in the mining industry for some time, e.g. a No. 8 detonator, contained 1 g of tetryl and 0.3 g of a mixture of lead azide and lead styphnate. These were more powerful than those with a fulminate–tetryl charge, but the use of detonators with aluminium sheathing was soon forbidden in coal-mines due to the danger created by the burning of the aluminium.

The modern detonator TAT-1, used in U.S.S.R. is filled in three layers (Fig. 56c) as follows:

bottom—tetryl	0.12 g
middle—lead azide	0.21 g
top—lead styphnate	0.06 g

Modern artillery primers also include a charge of penthrite and lead azide sensitized to flame by the addition of lead styphnate or tetrazene.

(1) The bottom layer is loaded with 0.35 g of penthrite (pressed at 1800 kg/cm^2), the middle with 0.35 g of penthrite (not pressed) and the top with 0.30 g of a mixture of 92.5% of lead azide and 7.5% of tetrazene (pressed at 1100–1800 kg/cm^2).

Thus a layer of bursting charge adjacent to the initiator is compressed more weakly and in consequence complete explosion occurs with greater ease.

(2) The bottom layer is loaded with 0.2 g of penthrite (pressed under a pressure of 500 kg/cm^2), the middle with 0.2 g of penthrite (not pressed) and the top with 0.4 g of a mixture of 80% of lead azide and 20% of lead styphnate (pressed under a pressure of 500 kg/cm^2).

Mixtures of mercury fulminate, potassium chlorate (as an oxidizing agent), antimony sulphide and ground glass were widely utilized for many years in percussion caps. The content of mercury fulminate was small so that the mixture had no explosive properties. For the same reasons significant amounts of potassium chlorate were used as an oxidizing agent, thus diluting the fulminate to some extent. Antimony sulphide is a combustible component which gives a hot flame. Ground glass was added in order to increase the internal friction and make it more sensitive to percussion.

Some compositions also contained an adhesive, e.g. shellac, gum etc.

A German composition of 1883 contained, for example:

Mercury fulminate	27%
Potassium chlorate	37%
Antimony sulphide	29%
Ground glass	7%

To 100 parts of this mixture 0.6 part of shellac were added.

The composition of other caps according to Gorst [128] is given in Table 42.

TABLE 42

Cap	Mercury fulminate	Potassium chlorate	Antimony sulphide
Rifle and pistol	16.5	55.5	28.0
Fuse	25	37.5	37.5
Fuse	50	25	25

The English caps contained a little blackpowder which elongates the flame produced by the explosion of

Mercury fulminate	by	15%
Potassium chlorate	by	35%
Antimony sulphide	by	45%
Sulphur	by	2.5%
Blackpowder	by	2.5%

Mixtures containing mercury fulminate, potassium chlorate, and antimony sulphide tend to destroy the inside of firearm barrels, since on decomposition the mercury fulminate evolves free mercury which causes erosion of the barrel at the high temperatures created inside the bore. Decomposition of the potassium chlorate gives potassium chloride which remains in the bore and strongly corrodes the steel. Sulphur dioxide formed by the combustion of antimony sulphide also helps to destroy the barrel. For a long time therefore, the use of compositions not containing mercury fulminate and potassium chlorate were advocated, but a satisfactory formulation for non corrosive mixtures was found ("Sinoxyd") only when lead styphnate was introduced as their chief component. Since styphnate is hard to ignite by impact it was sensitized by an admixture of tetrazene. At the same time potassium chlorate was replaced by barium nitrate.

German compositions for rifle and pistol caps are tabulated below [31, 32].

TABLE 43

Components	Composition No. 30/40 for rifle and pistol caps	Composition for rifle caps manufactured at Stadeln
Lead styphnate	40	30–35
Tetrazene	3	2–3
Barium nitrate	42	40–45
Lead dioxide	5	5–8
Calcium silicide	10	6–12
Antimony sulphide	—	6–9

The Czechoslovak mixture, Oxyd, for pistol cartridges has a similar composition, viz.:

Lead styphnate	45%
Tetrazene	5%
Barium nitrate	33%
Antimony sulphide	20%
Aluminium–magnesium alloy	5%

The German mixture No. 30 for the friction fuses of hand grenades has the following composition:

Lead styphnate	25%
Barium nitrate	25%
Lead dioxide	24%
Silicon	15%
Ground glass	3%

THE PREPARATION OF PRIMER COMPOSITIONS

Formerly cap compositions were prepared by mixing the well-damped components on a glass-topped table, while adding water continuously to the mixture (especially at the edges which are liable to more rapid drying). A wooden spade was used for mixing. The mixture in the form of a paste, was made into pellets which were then dried and pressed either into the sheaths of blasting caps or into the capsules of percussion caps.

This method was widely employed before World War I and for some time afterwards, but it is now discontinued due to the changes which occur during storage to caps so manufactured. These changes reduced the caps efficiency possibly due

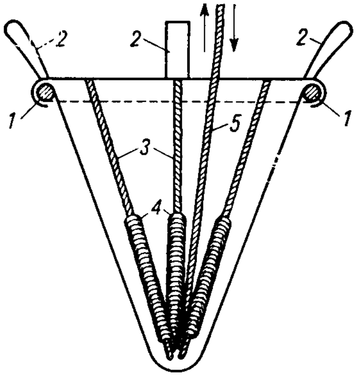


FIG. 59. Silk bag for mixing an initiating composition: *1*—rubber frame, *2*—leather lug for suspending the bag, *3*—strings, *4*—rubber rings, *5*—mixing string, according to Vennin, Burlot and Lécorché [132].

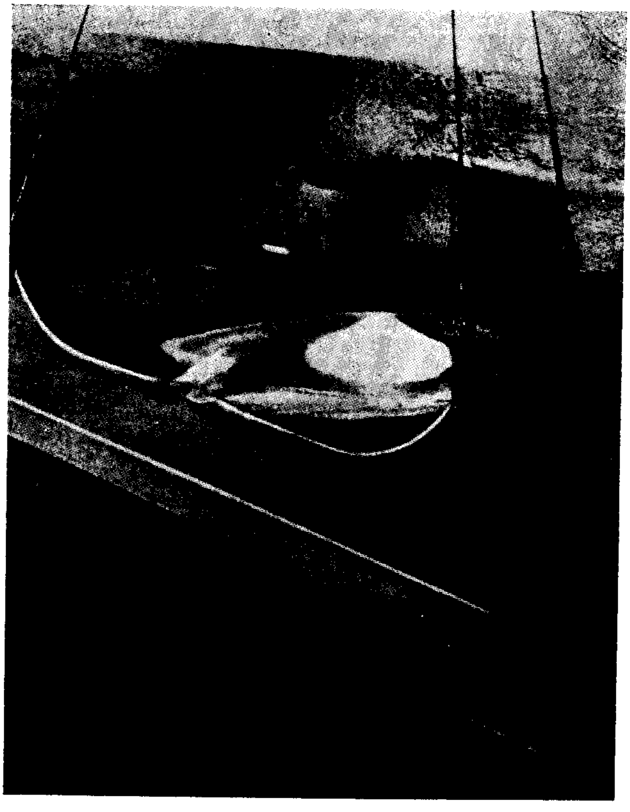


FIG. 60. Mixing of primary explosive charge on a rubber tray at Hercules Powder Company, according to Davis [133].

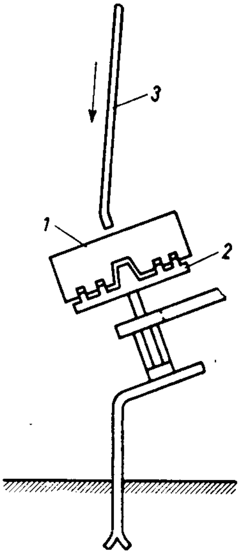


FIG. 61. A device for mixing and simultaneously drying an initiating composition: *1*—ebonite drum, *2*—tilted revolving drum plate, *3*—warm air conduit, according to Vennin, Burlot and Lécorché [132].

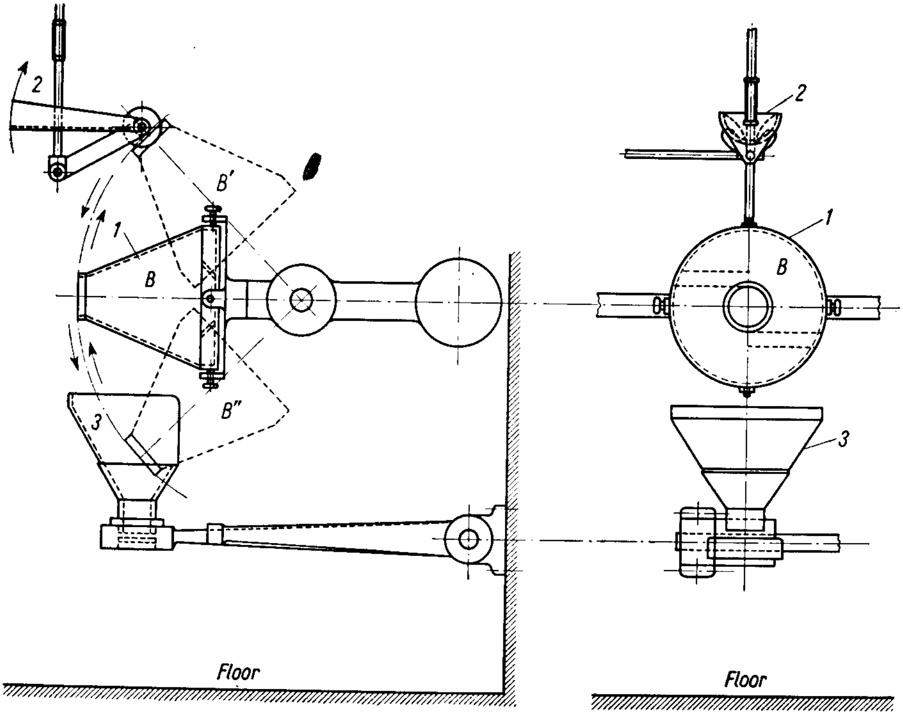


FIG. 62. Automated arrangement for mixing initiating compositions at Stadeln [130]: *1*—papier mâché drum (*B*—in a horizontal position when mixed, *B′*—when loaded, *B″*—when unloaded), *2*—papier mâché spoon, *3*—paper funnel.

to traces of moisture in the cap composition which are particularly persistent if binders such as gum arabic etc. have been incorporated. The presence of moisture also enhances the reaction of mercury fulminate with the metal into which the composition is pressed.

For this reason the components are now not mixed wet. There are several methods of dry mixing. One of them (the earlier "jelly-bag" method) is to place the dried and sieved components of the composition into a conical silk bag (Fig. 59) which is fastened at its base to a rubber frame. There are strings within the bag fitted with rubber rings. Another string fastened to the top of the cone passes over a pulley fixed to the ceiling. This string leads outside the building or protective wall. By manipulating the strings the bag is put into motion and its contents are stirred. The bag is emptied by turning it upside down by a pull on the string.

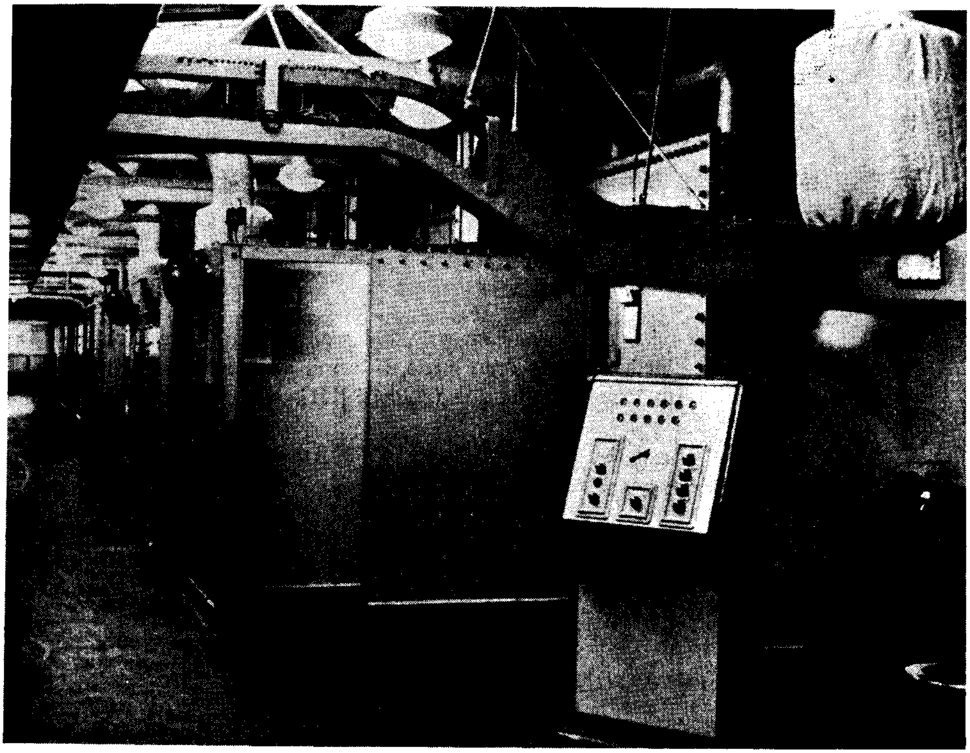


FIG. 63. Detonator manufacture—a line of compartments in which the filling and pressing of detonators is carried out automatically. Courtesy Imperial Chemical Industries Ltd., Nobel Division.

The same type of arrangement for mixing primary explosive charge used by the Hercules Powder Company, according to Davis [129], is shown in Fig. 60. It consists of a triangular rubber tray. The composition is mixed by lifting and lowering the corners of the tray in turn. The lifting and lowering is accomplished behind a concrete safety barriers.

In a more modern method, the mixing may be combined with drying. A diagram illustrating such a device is presented in Fig. 61. Here the composition is placed in an open ebonite drum which is laid on a tilted, revolving plate. The moist components are placed in the drum (weighed and containing a known amount of moisture), and the latter is then aerated with a warm air stream which dries the contents when stirred. This system can also be used for drying initiators, e.g. mercury fulminate, lead azide etc.

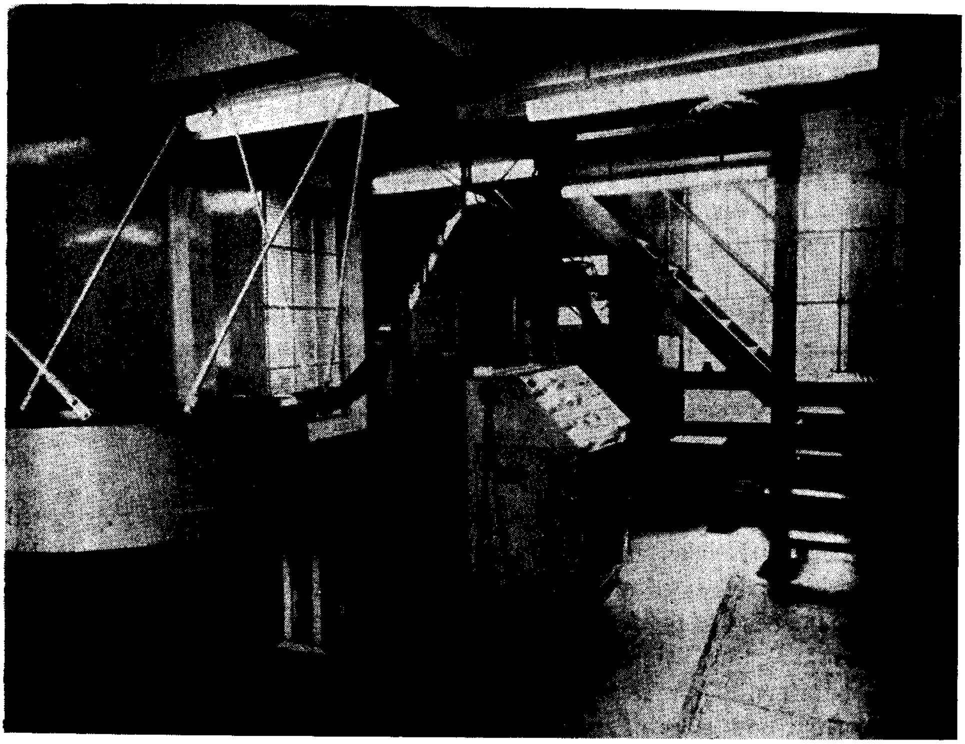


FIG. 64. Detonator manufacture—the plating section of the automatic plain detonator unit. Courtesy Imperial Chemical Industries Ltd., Nobel Division.

In the German plant at Stadeln [130] drums of papier mâché about 20 cm in diameter and 45 cm long are used, mounted on a horizontal, revolving axis, and provided with an aperture on the drums' cylindrical surface. Before being set in motion this opening is closed with a rubber cork. Subsequently it is opened by remote control by means of hooks and strings. After being stirred, the contents of the drum are poured into boxes previously ranged in readiness. Each drum is sited in a chamber, protected by a concrete partition wall. It is desirable to cover the floor with a soft material that conducts electricity. With compositions which are very dangerous to handle, containing lead styphnate, stirring proceeds stepwise so that the preparation of the final, dangerous composition lasts for as short a time as possible. Thus a composition consisting of barium nitrate, calcium silicide, antimony sulphide and lead dioxide is first prepared. This composition is manufactured in large amounts in ordinary, wooden drums. A weighed amount of the composition is then mixed automatically with tetrazene and lead styphnate (Fig. 62). The papier mâché drums are in the shape of a truncated cone with bases of about 8–30 cm in diameter. Such a drum will hold about 400 g of material. Above the drum there is a papier mâché spoon into which a worker pours a batch of the mixture. The worker then leaves the building and sets the driving mechanism in motion from a distance. This engine first rotates the spoon so that its contents run into the drum. Then the drum is moved into a horizontal position, in which it revolves for 7 min with a velocity of 60 r.p.m., from which it is tilted downwards, pouring its contents into a paper funnel. After being emptied the drum is returned to the initial position and the drive is stopped. The whole mechanism is so arranged that all these movements are carried out automatically.

An idea of a modern plant lay-out for the manufacture of priming compositions and detonators is given by Figs. 63 and 64 showing installations at Imperial Chemical Industries, Nobel Division, in Great Britain.

COMPOSITIONS FOR EXPLOSIVE RIVETS

In 1937 rivets containing a small explosive charge in their shanks were constructed (Aircraft Factory Heinkel and Rheinisch-Westphälische Sprengstoff A. G. [131]). The composition of the explosive mixture is so selected that a slight explosion occurs on heating the head of the rivet with a hot iron. The explosion causes an expansion of the shank thus fixing the rivet in place. Explosive rivets have found wide application primarily for riveting aircraft components in which rivets are not accessible from both sides of the riveted surface.

Initially only aluminium alloy rivets (duralumin) were employed. Later, during World War II, steel explosive rivets were also used. The principle is limited to rivets of small size. For filling these rivets, charges of chlorate explosive mixtures with fairly low ignition temperatures (e.g. 180°C) were originally used. Their composition was similar to that of priming caps. During World War II the following mixture was used for aluminium rivets:

Nitromannite	15%
Tetrazene	10%
Aluminium	70%
Adhesive	5%

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Part 3

COMPOSITE EXPLOSIVES

GENERAL INFORMATION

MOST modern explosives used for practical purposes are not single chemical substances, but composite mixtures, their ingredients being selected to obtain the required properties.

Thus, if there is a need to reduce the melting point of a nitro compound, e.g. picric acid, other nitro compounds are added to form an eutectic mixture; to decrease the sensitiveness of picric acid to mechanical impact it is mixed with paraffin.

Smokeless propellants may be taken as another example of composite explosives. These may be either mixtures of nitrocellulose of differing degrees of nitration, partly in a colloidal and partly in a fibrous state with an admixture of the remaining solvent and a stabilizer or a solution of nitrocelluloses in carbamite (centralite) and nitroglycerine with an admixture of components such as aromatic nitro compounds, nitroguanidine, graphite etc.

Blackpowder is yet another type of composite explosive being an intimate mixture of potassium nitrate, charcoal and sulphur. A distinguishing feature of this composition is that none of its components is explosive. Blackpowder and similar compositions are examples of a large group of explosives which contain an oxidizing agent as a chief component. Salts of nitric acid, e.g. ammonium, sodium and potassium nitrates and oxy-salts of chlorine such as ammonium and potassium perchlorates or sodium and potassium chlorates are used as oxidizing agents. Other constituents of such mixtures are combustible substances. These are often explosive substances such as aromatic nitro compounds. Explosive mixtures are frequently formulated so as to fully utilize the oxygen present in the oxidizing agents.

The amount of high melting material present, e.g. ammonium nitrate, regulates the fusibility of these mixtures so that they may be fusible, semi-fusible or infusible, free-pouring. There are also explosives with a plastic consistency. Usually these consist of a plastic substratum containing a polymeric component. Again, there are liquid explosives, containing liquid oxygen or a liquid oxidizing agent, e.g. nitrogen dioxide.

Finally, mention should be made of a group of explosives in which the components are selected on another principle. These mixtures contain combustibles which increase considerably the heat of explosion, for instance aluminium, ferrosilicon etc. They burn by utilizing the oxygen contained in the explosive.

Composite explosives will be considered, according to their uses, in three main categories: the high explosives, the low explosives or propellants and the primary explosives or initiators.

High explosives will be classified primarily according to their consistency, which may be fusible, semi-fusible or infusible, plastic or liquid. They will then be arranged according to their most characteristic component.

Propellants will be grouped on the basis of their composition, into blackpowder and similar mixtures, smokeless powders and rocket liquid propellants.

Because of the importance of rocket liquid propellants a separate chapter will be dedicated to these mixtures. It will also include liquid high explosives.

Initiating compositions were reviewed together with primary explosives.

CHAPTER I

HIGH EXPLOSIVES

FUSIBLE EXPLOSIVES

MIXTURES OF NITRO COMPOUNDS

WHEN picric acid was first used for filling shells by pouring it, in the molten state, difficulties arose due to its high melting point. The necessity of using superheated steam for melting was an added complication introducing the danger associated with the prolonged heating of the explosive to a high temperature.

Data from the Griesheim factory [1] show that this may be avoided by adding other aromatic nitro compounds, e.g. TNT, to the picric acid. The addition of even a small amount (5–10%) of such a substance facilitates melting without seriously decreasing the explosive power of the picric acid.

Easily fusible mixtures containing picric acid as the chief component were very widely employed in Russia and France during World War I and in the period immediately afterwards. A mixture of 51.5 or 80% picric acid with 48.5 or 20% dinitronaphthalene was used in the U.S.S.R. for filling aerial bombs and manufacturing demolition charges.

The composition of mixtures used in France is given in Table 44.

TABLE 44

COMPOSITION OF FUSIBLE EXPLOSIVE MIXTURES EMPLOYED IN FRANCE

Name of mixture	Composition, %					
	Picric acid	Dinitrophenol	TNT	Trinitrocresol	Nitronaphthalene	Dinitronaphthalene
MDN	80	–	–	–	–	20
MNN	70	–	–	–	30	–
MTTC	55	–	35	10	–	–
MDPC	55	35	–	10	–	–
Cresylite No. 2 (60/40)	40	–	–	60	–	–

Attempts were made in Britain to use mixtures of picric acid with dinitrobenzene. Maxim [2] suggested mixing picric acid with dinitronaphthalene or nitronaphthalene.

Kast [3] examined a number of readily fusible mixtures:

(1) 50 parts of picric acid
50 parts of trinitrocresol } m.p. 80–83°C
(2) 55 parts of TNT
45 parts of DNT } m.p. 42–44°C
(3) 10 parts of TNT
90 parts of DNT } begins to melt at 39°C
completely melts at 65°C

The use of a mixture of 35 parts of TNT and 65 parts of hexanitrodiphenylamine (hexyl) for filling torpedoes was introduced by the Germans in 1912. Hexyl, which is only very slightly soluble in molten TNT, on being heated to 80°C forms a suspension in the molten mixture; the resulting semi-fluid mass may be poured into the shells. During World War I this mixture was widely used for filling torpedoes, mines and aerial bombs. During World War II metallic aluminium was added (p. 266). As the raw materials during World War I grew more difficult to obtain, this material, when intended for aerial bombs, was mixed with ammonium nitrate to obtain a semi-fluid mass of the ammonal type. Where there was a lack of hexyl it was sometimes replaced by hexanitrodiphenyl sulphide and trinitroanisole was substituted for TNT. This led to the following mixtures:

(1) 50% of TNT
50% of hexanitrodiphenyl sulphide
(2) 50% of trinitroanisole
50% of hexanitrodiphenylamine
(3) 50% of trinitroanisole
50% of hexanitrodiphenyl sulphide

These mixtures were poured into the shells as a molten mass usually containing a suspension of unmelted hexanitro compounds.

When toluene was in short supply TNT was partly replaced either by dinitrobenzene or by trinitronaphthalene. Thus the following mixtures were derived:

(1) DiFp consisting of TNT and dinitrobenzene in various proportions
(2) 65% of TNT
35% of trinitronaphthalene

During World War I, the Italians employed the following fusible mixtures:

(1) MAT—60% of picric acid
40% of TNT } begins to melt at 55–56°C
completely melts at 85°C
(2) MBT—60% of picric acid
40% of dinitrophenol

A more modern solution of the problem of fusible materials was given by Leitman [4] in the U.S.S.R. who developed "L-alloy", an explosive consisting of 95% TNT and 5% trinitroxylene melting at 74°C. L-Alloy has an explosive power similar to that of TNT although it differs from the latter in detonating more readily due to the fact that during the cooling down process very fine crystals of TNT are formed in L-alloy.

During World War II the Germans partly replaced TNT either by trinitroxylene or by a mixture of trinitroxylene with TNT. The following mixture was the one most frequently used:

$$\left.\begin{array}{l}20\% \text{ of trinitroxylene}\\ 80\% \text{ of TNT}\end{array}\right\}\text{ melts cloudily at } 77°\text{C}$$

This mixture was prepared by the nitration of a mixture of nitrotoluenes with nitroxylenes.

Another mixture used as a substitute for TNT had the following composition:

45% of trinitroxylene
5% of TNT
50% of tetryl.

It was prepared in a similar manner by nitrating a mixture of nitroxylenes with dinitromethylaniline and mixing it with TNT. This mixture melts at 80°C and is a more powerful explosive than TNT, but it requires a stronger detonator.

In the United States a fusible mixture of 70% tetryl and 30% TNT, Tetrytol, was used for demolition charges and land mines, since this mixture has a higher brisance than TNT and detonates more readily. The melting point of the mixture is 68°C. Cast mixture (solidified) has a density of 1.61–1.65, i.e. greater than that of TNT, thus making possible the use of charges stronger than those of TNT. Its rate of detonation is 7350 m/sec and in the ballistic pendulum gives a value of 120 (taking 100 for TNT). Its sensitiveness to impact by rifle bullet is a little higher than that of TNT. Its chemical stability at temperatures of 100–120°C is somewhat lower than that of tetryl, although specimens were successfully stored at 65°C for 2 years.

Mixtures with trinitroanisole have been employed in Japan; e.g. the 98 H_2 explosive, containing 60% of trinitroanisole and 40% of hexyl, which was used for filling bombs, torpedoes and depth charges.

During World War II cyclonite was used by all the combatants to increase the power of composite explosives. Fusible mixtures of TNT with cyclonite were prepared, mainly with an admixture of aluminium, and mixtures of TNT with hexyl and cyclonite also with admixture of aluminium (pp. 271–272).

In the United States a mixture of 60% cyclonite and 40% TNT was used under the name of Cyclitol as a filling for aerial bombs. The density of the cast explosive was 1.65–1.70, its rate of detonation 7800 m/sec, and in the ballistic pendulum it gave a value of 130 (100 for TNT). In the United States this mixture is considered to be only a little more sensitive to impact than TNT with a stability similar to that of cyclonite. This does not agree with T. Urbański's [5] investigations according to which the sensitiveness to impact of such a mixture, in a powdered form, and its ignition temperature (225°C) approximate to the corresponding values for tetryl.

Table 45 and the graphs in Figs. 65 and 66 summarize T. Urbański's findings on the rate of detonation, the lead block expansion, the sensitiveness to impact and the ignition temperatures of powdered mixtures of cyclonite with TNT, of various composition.

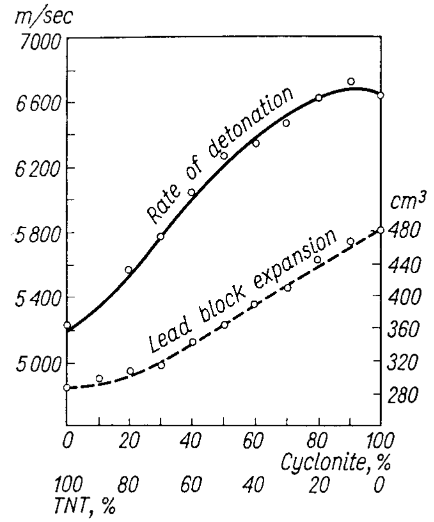

FIG. 65. The relation between the rate of detonation (density 1.04) and lead block expansion of mixtures of cyclonite and TNT, and their composition (according to T. Urbański [6]).

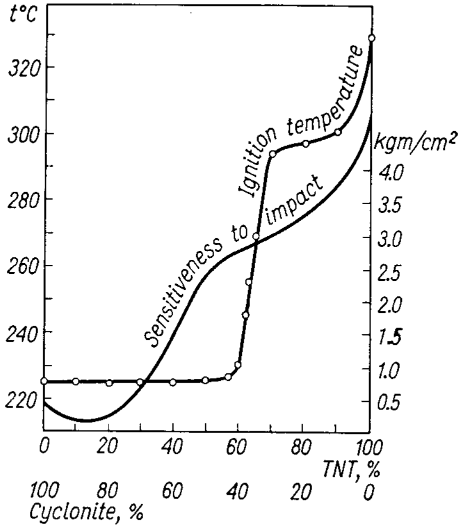

FIG. 66. The relation between the ignition temperature and sensitiveness to impact of mixtures of cyclonite and TNT, and their composition (according to T. Urbański [6]).

TABLE 45

EXPLOSIVE PROPERTIES OF MIXTURES OF CYCLONITE WITH TNT

Content of TNT %	Rate of detonation (at a density of 1.04) m/sec	Lead block expansion cm³	Sensitiveness to impact (50% of explosions) kg/cm²	Ignition temperature (10°/min) °C
0	6590	480	0.22	225
10	6710	465	0.16	225
20	6620	445	0.21	224
30	6460	410	0.42	225
40	6335	390	0.95*	225
50	6260	365	2.40	226
60	6035	345	2.50**	231
70	5770	315	2.60	295
80	5570	310	2.80	298
90	5260	300	3.35	302
100	5230	290	4.10	328

* Equals the sensitiveness of tetryl.

** Equals the sensitiveness of picric acid.

In Japan, the 94 M mixture consisting of 60% trinitroanisole and 40% cyclonite was employed for filling torpedoes and armour-piercing shells with hollow charges. Such a mixture solidifies with a density of 1.64, its rate of detonation being 7700 m/sec. In the United States a mixture of 75% HMX (Octogen) and 25% TNT was in use under the name of Octol.

During World War II PETN was also used, although to a lesser extent than cyclonite, since the former is more sensitive to impact and has a lower chemical stability. Mixtures of various compositions were employed according to their intended use. The most widely used mixture comprised 50% PETN and 50% TNT. This was employed in the molten state for filling hand and anti-tank grenades, and powdered and compressed, for filling detonators.

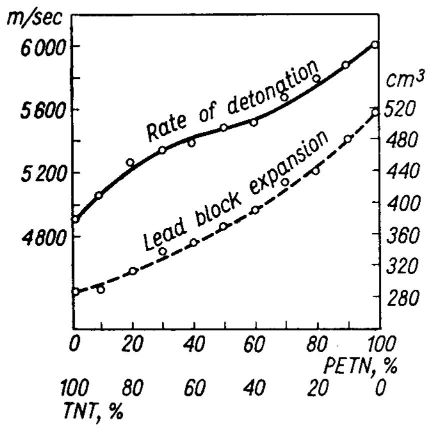

FIG. 67. The relation between the rate of detonation (density 1.04) and lead block expansion of mixtures of PETN and TNT, and their composition (according to T. Urbański [6]).

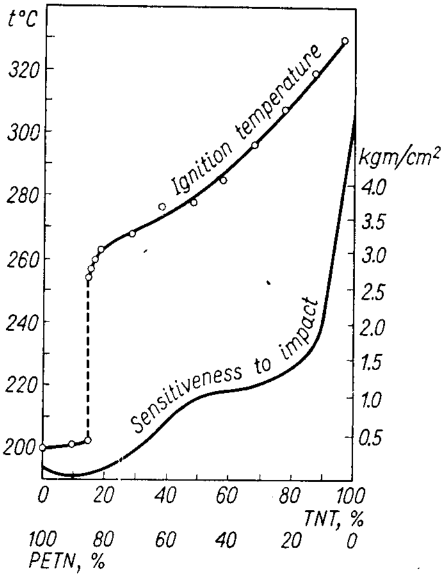

FIG. 68. The relation between the ignition temperature and sensitiveness to impact of mixtures of PETN and TNT, and their composition (according to T. Urbański [6]).

Mixtures of PETN with TNT are known as pentrolit or pentolit. Pentolit 50/50 has a density of 1.63–1.67; its rate of detonation is 7450 m/sec. It is highly sensitive to impact and its stability is lower than that of PETN alone (T. Urbański, Kwiatkowski and Miładowski [7]).

The rate of detonation, the lead block expansion, the sensitiveness to impact and the ignition temperatures of mixtures of PETN and TNT, according to T. Urbański [6, 8] and the rate of detonation according to Laffitte and Parisot [9] are presented in Table 46 and in the graphs shown in Figs. 67 and 68.

Williamson [10] examined the cast structure of various fusible or semi-fusible mixtures containing TNT as one component, the other being chosen from the following substances: ammonium nitrate, PETN, cyclonite and tetryl. The author also prepared casts of TNT alone. When dealing with mixtures of TNT and PETN or cyclonite, the author discovered that PETN and cyclonite recrystallize in suspension in molten TNT. This phenomenon leads to an increase in the size of the crystals of the suspended component (e.g. cyclonite) and, in consequence, reduces the fluidity of the semi-molten mass on heating. Sometimes, however, a TNT mixture containing cyclonite in suspension may become more fluid on heating. This occurs when cyclonite is present in the form of very small irregularly-shaped crystals. This is also caused by recrystallization which in a given case leads to the formation of a small amount of relatively large crystals without lowering the fluidity of the molten mass.

In the solidification of a TNT–tetryl mixture the author did not establish the presence of an addition compound of the two components in the solidified mass.

Viscosity — another important parameter of molten mixtures of TNT with cyclonite containing mainly suspended particles of RDX — was examined by a number of authors [11, 12]. The viscosity increases with increasing RDX content, viz.:

TABLE 46

EXPLOSIVE PROPERTIES OF MIXTURES OF PETN WITH TNT

Content of TNT %	Rate of detonation (at a density of 1.04, and 30 mm dia.) m/sec	Lead block expansion cm³	Sensitiveness to impact (50% of explosions) kg/cm²	Ignition temperature (10°/min) °C	Rate of detonation according to Laffitte and Parisot [9] (at a density of 1.0 and 8 mm dia.) m/sec
0	6005	515	0.20	200	5200
10	5870	480	0.15	201	5000
20	5785	440	0.22	262	4790
30	5675	425	0.42	267	4600
40	5510	390	0.80	275	4550
45	—	—	—	—	4680
50	5490	370	0.99*	277	4650
55	—	—	—	—	4950
60	5385	350	1.25	284	4400
70	5245	340	1.60	295	4100
80	5260	315	1.65	306	3720
85	—	—	—	—	3800
90	5050	295	1.75	317	3650
95	—	—	—	—	2050–3000
100	4865	290	4.10	328	—

* Equals the sensitiveness of tetryl.

RDX, % in 100 cm^3 of molten TNT	Viscosity cP
0	11.526
10	14.42
20	19.16
30	29.07
40	44.02
50	126.70

The rheological properties of the suspensions of RDX in molten TNT were studied by Koch and Freiwald [13].

MIXTURES WITH AMMONIUM NITRATE

There is another type of fusible mixture with ammonium nitrate as the chief constituent. These mixtures include substances which act as ammonium nitrate fluxes, lowering its melting point. Most of them are nitrates of various metals and various organic bases. Thus, Girard [14] by mixing equal amounts of guanidine nitrate and ammonium nitrate obtained a mixture, m.p. 140°C. In numerous later patents the following substances are mentioned as additives to ammonium nitrate: 10–20% of sodium nitrate and approximately 5% of other substances such as inorganic chlorides, urea, acetates or dicyandiamide.

Between 1914 and 1918 the Germans used the following mixtures:

(1) No. 16	(2) No. 20
60–65% of ammonium nitrate	65–67% of ammonium nitrate
10% of sodium nitrate	10–12% of sodium nitrate
5% of dicyandiamide	3% of sodium acetate
25–20% of TNT	20% of TNT

These mixtures melted at 105–110°C.

The Dynamit A.G. factory [15] patented a number of mixtures consisting of ammonium nitrate and nitrates of aliphatic amines, e.g.:

(1) 55% of ammonium nitrate
45% of ethylenediamine nitrate
(2) 60% of ammonium nitrate
40% of methylamine nitrate
(3) 55% of ammonium nitrate
40% of ethylenediamine nitrate
5% of methylamine nitrate

A different method for lowering the melting point of ammonium nitrate was suggested a few years before World War II. It consists of the addition of hydrated magnesium nitrate (i.e. containing water of crystallization) $Mg(NO_3)_2.6H_2O$ to ammonium nitrate. Due to the presence of the water of crystallization such mixtures melt at temperatures below 100°C (Boyd [16]).

Fusible mixtures with ammonium nitrate as the chief constituent were also manufactured and utilized in Germany during World War II under the name of S explosives.

In all explosives of this kind the fusible constituent of the mixture was ammonium nitrate with other nitrates, e.g. of sodium, potassium or calcium (with water of crystallization), of organic bases such as methylamine, ethylenediamine, guanidine etc. and urea. Since on solidification these mixtures become very dense and detonate with great difficulty, PETN, cyclonite or TNT were usually added. The composition of some of these mixtures is given in Table 47.

TABLE 47

COMPOSITION OF AMMONIUM NITRATE MIXTURES

Mixtures / Components	S-19	H-5	–	43C
Ammonium nitrate	73.3	50	50	45
Sodium nitrate	17.4	5	–	–
Potassium nitrate	–	–	–	–
Calcium nitrate $Ca(NO_3)_2 \cdot 4H_2O$	–	15	15	15
Ethylenediamine dinitrate	–	10	–	–
Guanidine nitrate	–	–	10	10
Urea	9.3	–	–	–
Cyclonite	–	20	25	–
TNT	–	–	–	30

The composition of similar mixtures, containing metallic aluminium, is given below in Table 56 (p. 271).

Manueli and Bernardini [17] proposed an easily fusible mixture consisting of ammonium nitrate, guanidine nitrate and nitroguanidine. According to them such mixtures may be melted at a temperature below 130°C. The explosive Albit, based on Manueli and Bernardini's patent, consisting of six parts of ammonium nitrate, two parts of guanidine nitrate and two parts of nitroguanidine, has been used in Italy.

Urbański and Skrzynecki [18] found that a eutectic formed by these three components solidifies at 113.2°C and contains:

60% of ammonium nitrate
22.5% of guanidine nitrate
17.5% of nitroguanidine

Le Roux [19] proposed the use of fusible mixtures of ammonium nitrate with tetramethylammonium nitrate (Vol. II, p. 466).

It was also suggested recently that fusible explosives should be used instead of semi-fusible ones. For this purpose TNT is replaced as a component by relatively low-melting nitric esters.

Médard [20], for instance, recommends a mixture of 62% ammonium nitrate and 38% trimethylolpropane trinitrate. Such a mixture has on oxygen balance corresponding to complete combustion. A charge with a diameter of 30 mm and a density of 1.50 detonates with a rate of 6150 m/sec, and a charge with a density of 1.10 detonates with a rate of 4230 m/sec. Its lead block expansion is 127.5 (taking picric acid as 100).

Its sensitiveness to impact is very low, lower than that of TNT.

A mixture of 40% ammonium nitrate and 60% trimethylolpropane trinitrate may be melted at 60°C and used as a poured filling for shells. The substance solidifies into a mass with a density of 1.36, giving a rate of detonation of 5200 m/sec.

MANUFACTURE AND SELECTION OF FUSIBLE MIXTURES

As a rule fusible mixtures are prepared in metallic kettles heated with steam or water jackets and fitted with stirrers, which are emptied either by tilting or through a valve placed in the bottom of the vessel.

In France mixtures containing picric acid were prepared in wooden tubs to avoid the formation of picrates. They were heated with live steam injected through an ebonite nozzle. After the mass has been mixed the steam supply was turned off and water was decanted from above the layer of nitro compounds by a glass syphon. The mixture was drawn off with wooden buckets in which it was cooled while being stirred continuously. The granular mass was then poured onto wooden trays where it was cooled further. Stirring was still continued during cooling, so as to produce granules approximately 10 mm dia.

It must be borne in mind that generally aromatic nitro compounds are not highly sensitive to impact and friction, but become more sensitive at elevated temperatures as they melt (changes in the sensitiveness of TNT are discussed in Vol. I, p. 319). If, therefore, a mechanical device is used for the preparation of mixtures by melting, its construction should be such as to exclude any possibility of friction or impact. It is probably best to use a converter heated with steam or water jackets and fitted with a stirrer that can be lifted out by a special arrangement. After the stirrer has been removed, the contents are poured out by tilting the vessel.

Fusible mixtures, with a composition having a suitable melting point, are selected by the thermal analysis of the two- and three-component system. Thermal analysis determines either the beginning and end of solidification or the beginning and end of the melting of the mixture.

To examine the possibility of using a given mixture for filling shells the changes in these temperatures are determined with mixtures of varied composition and it is established whether the components are eutectic mixtures or molecular compounds. The analysis also shows whether, in liquid phase, the components form a homogeneous system, solid solutions, etc.

In fact, the presence of solid solutions considerably effects the homogeneity of the mixture, preventing the formation of inner cracks and fissures. If the solidifying point of the eutectic is too low (i.e. below 60°C) the explosive may exude from the shell, whereas too high a solidifying point hinders melting, and in turn complicates the process of filling the shell.

The literature on thermal analysis of mixtures either deals with purely theoretical studies of the formation of molecular compounds, solid solutions, etc., e.g. Kremann's [21, 22] work, or describes the search for materials of immediate practical value.

Research relating to practical matters has two aims:

(1) To determine the contents of various isomers in nitration products. Such studies include the work of Giua [23] on systems consisting of DNT and TNT isomers, those of Pascal [24] on systems consisting of dinitro- and trinitronaphthalene isomers, and those of Andrews [25] and of Wyler [26] on systems consisting of dinitrobenzene isomers. The graphs obtained by these authors may be helpful when studying the composition of nitration products.

(2) To decide whether a given mixture is suitable for filling shells or for producing non-freezing dynamites. Thermal analysis of the components of mixtures in practical use, e.g. nitroglycerine and centralite, fulfils a similar, practical aim by explaining the interaction of these substances, in particular whether they form simple eutectics, molecular compounds or solid solutions.

Studies of this kind which include a number of papers mentioned in corresponding sections of this book, are recommended for reference. They are concerned with the following substances:

(a) Mixtures containing aromatic trinitro compounds:

Yefremov *et al.* [27, 28] (systems containing TNT, picric acid, trinitrocresol, trinitroresorcinol, tetryl, trinitroxylene etc.); Wogrinz and Vári [29] (systems containing TNT and picric acid); C. A. Taylor and Rinkenbach [30] (systems containing TNT, picric acid and tetryl); Jovinet [31] (the system: picric acid–nitronaphthalene); Hrynakowski and Kapuściński [32] (systems containing TNT and picric acid); T. Urbański and Kwiatkowski [33] (systems containing picric acid and dinitronaphthalenes).

(b) Mixtures containing nitroglycerine: Tamburrini [34], Kurita and Hagui [35], Médard [36], and Hackel [37].

(c) Mixtures containing PETN: T. Urbański [38] and Desseigne [39].

(d) Mixtures containing cyclonite: T. Urbański and Rabek-Gawrońska [40].

Khaibashev and Bogush [41] examined ternary systems containing cyclonite. They discovered eutectic mixtures of the followin compositions:

(1)	82%	of *m*-dinitrobenzene	
	9%	of cyclonite	m.p. 80.5°C
	9%	of trinitroxylene	
(2)	74.5%	of *m*-dinitrobenzene	
	7%	of cyclonite	m.p. 74.5°C
	18.5%	of 1,8-dinitronaphthalene	

(e) Mixtures of guanidine nitrate, nitroguanidine and ammonium nitrate: T. Urbański and Skrzynecki [18].

(f) Three-component mixtures of inorganic nitrates: T. Urbański and Kołodziejczyk [42] established the existence of a eutectic of the following composition:

66.5% of NH_4NO_3
21.0% of $NaNO_3$ f.p. 118.5°C
12.5% of KNO_3

THE PHLEGMATIZATION OF FUSIBLE MIXTURES

Even by the end of the nineteenth century it had become clear that some explosives safe to handle in principle (e.g. picric acid), are nevertheless too sensitive to the impact that occurs when the projectile containing them strikes against heavy armour plate. Attempts were made therefore to decrease this sensitiveness by desensitization, or "phlegmatization" of the explosive.

In France, picric acid intended for armour-piercing shells was phlegmatized with paraffin. MP (mélinite paraffiné) mixture, containing 88% of picric acid and 12% of paraffin, was chosen for this purpose. Paraffin desensitizes picric acid, making it less sensitive than TNT. Since paraffin is insoluble in molten picric acid, the mixture is prepared by melting the paraffin in an aluminium kettle, heating it to 100°C and adding powdered picric acid while stirring with a wooden paddle. The granules so formed are transferred to a table, rolled out and mixed by rubbing several times through a sieve.

Paraffin, however, is not a good phlegmatizing agent. It was discovered that higher fractions of crude oil, with a waxy consistency, and composed of more polar molecules, are considerably more effective so that desensitization may be achieved by using a smaller amount of phlegmatizing substance. This is decidedly preferable since too large an admixture of a phlegmatizing substance weakens the explosive.

Montan wax, widely used in Germany, is a better phlegmatizing agent than paraffin. Hence before and during World War I German naval armour-piercing shells were filled with TNT, desensitized by 6% of montan wax.

During World War II PETN, desensitized by 10% (sometimes 5 or 15%) of montan wax was employed for small shells (e.g. 20 mm) in Germany.

The mixing of TNT or PETN with montan wax is usually carried out under water at a temperature above the melting point of wax (70°C). With TNT the temperature should be maintained below 80°C; with PETN the whole is heated to 95°C and vigorously agitated so that the phlegmatizing substance is dispersed. The whole is then cooled to 30–35°C, while still being agitated. The granules and crystals of the explosive, coated with a layer of wax, are filtered off and dried at 60–65°C. A detailed description of PETN phlegmatization is given in Vol. II, p. 189.

The inclusion of wax-type phlegmatizing substances in the mixture facilitates the pressing of the explosive as it decreases the friction between the crystals. Thus a mixture with a higher density can be obtained by applying a lower pressure.

Non-explosive substances which, when molten, act as solvents for explosives, are another type of desensitizing agents. For instance, pentaerythritol tetra-acetate was suggested by Bombrini-Parodi Delfino [43] as a phlegmatizer of PETN.

The phlegmatization of PETN with nitronaphthalene recommended by T. Urbański [6] is based on the same principle of the partial dissolution of PETN. A mixture of PETN plus 20% nitronaphthalene has approximately the same sensitiveness to impact as tetryl, and with 40% nitronaphthalene the same sensitiveness to impact as picric acid.

Chlorofluoropolymers of the Kel and Exon types are now used in the U.S.A. as modern phlegmatizers of cyclonite, e.g.

90/10 RDX/Kel F 3700 in granules 0.8–1.4 mm dia.

94/6 RDX/Exon 461 in granules *ca.* 0.3 mm dia.

Nitrocellulose dissolved ("gelatinized") with phosphoric acid esters can also be used to produce a granulated and partly desensitized nitramine explosives, e.g. a mixture:

94/3/3 HMX/NC/tris(β-chloroethyl)phosphate with 0.1% diphenylamine as stabilizer, in granules 1–7 mm dia. [44].

Phlegmatizing compounds in chlorate, and perchlorate explosive mixtures play a special role since they are essential as a combustible constituent. They are discussed in more detail on pp. 274–280.

SEMI-FUSIBLE AND INFUSIBLE EXPLOSIVES

The molecular composition of picric acid was established in the early ninteenth century when it was the only highly-nitrated aromatic compound then known. It was evident that its oxygen content was insufficient for complete combustion (to CO_2 and H_2O). This was considered to be an adequate foundation for the erroneous theory that, because of its insufficient oxygen content, the substance has no explosive properties. It was believed that explosive properties are achieved only by mixing picric acid with oxidizing agents such as chlorates, or sodium or potassium nitrates.

These mixtures found no practical application since picric acid gradually reacts with salts to form picrates with the evolution of free acid. The picrates so formed are highly sensitive to friction and impact, and the free acid acts corrosively. Mixtures with chlorates showed a particular sensitiveness to friction and impact, hence doubt was expressed as to their practical value. Nevertheless, the idea of completing the defective oxygen balance in aromatic nitro compounds by the addition of such oxidizing agents as nitrates was carried out in such a way as to produce mixtures useful for various practical purposes.

Cheltsov [45] obtained (1886) a stable explosive, suitable for storage, called Gromoboi or Maïzit, by mixing ammonium picrate with ammonium nitrate in the ratio of 72.5 : 27.5.

To achieve the necessary stability he used its ammonium salt, which has no acidic properties instead of picric acid.

The same principle has been employed in some countries (e.g. U.S.A.) to produce the explosives in which the chief component was ammonium picrate together with ammonium nitrate.

There have also been interesting and promising attempts to use ammonium nitrate as a component of high explosives. Particularly noteworthy are the experiments in which potassium nitrate in blackpowder is completely or partially replaced by ammonium nitrate to improve brisance. This led to the ammonium nitrate mixtures, Ammonpulver M90 and M96, 15/85 mm. They were employed in Austria for filling shells at the end of the nineteenth century but were not used for long, due to the difficulty of detonating them.

Ohlsson and Norrbin [46] suggested another type of ammonium nitrate explosive for mining purposes (see p. 395).

With the development of the organic chemical industry, aromatic nitro compounds of the TNT type were introduced as ingredients of composite explosives. TNT is preferable to picric acid since it has no acidic properties and hence is much less reactive. Mixtures with TNT and similar nitro compounds showed an excellent chemical stability.

High explosive mixtures with potassium and sodium chlorates or potassium and ammonium perchlorate belong to a separate group; a mixture of these salts with any combustible used in a suitable quantity will act as an explosive.

MIXTURES WITH NITRATES—MAINLY WITH AMMONIUM NITRATE

Mixtures of aromatic nitro compounds with ammonium nitrate were widely used during World War I, when the enormous demand for high explosives could not be met by the output of TNT, trinitronaphthalene, picric acid, trinitroanisole, trinitrophenetole, dinitrobenzene, hexyl etc.

Ammonium nitrate, which was then being manufactured from atmospheric nitrogen for the first time, is the most readily available explosive ingredient, and all the more valuable since on decomposition it leaves no solid residue and ensures a great volume of gaseous explosion products. Its great disadvantage lies in its high hygroscopicity but this is unimportant if the explosive charge is tightly packaged.

The explosive properties of mixtures with ammonium nitrate depend on the quantitative relationship between the oxidizing agent and the explosive or combustible substance. According to Parisot and Laffitte's [9, 47] investigations the explosive properties of mixtures of aromatic nitro compounds with ammonium nitrate vary with the change in composition of the system in an almost rectilinear manner. The graph in Fig. 69 shows how the rate of detonation depends on the composition of mixtures of tetryl or picric acid with ammonium nitrate. T. Urbański *et al.* [48] also obtained a rectilinear relationship for nitrostarch mixtures with ammonium or sodium nitrate (Fig. 71, p. 265).

The sensitiveness to impact of mixtures of nitro compounds with ammonium nitrate is higher than that of pure nitro compounds due to the friction produced by the hard crystals of the ammonium nitrate. This was established for TNT mixtures with ammonium nitrate by Hackel [49] (c.f. pp. 262–263).

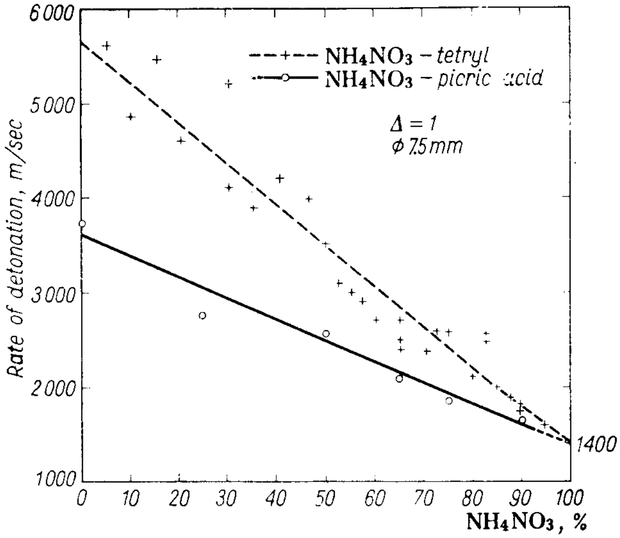

FIG. 69. The relation between the rate of detonation and the composition of tetryl or picric acid mixtures with ammonium nitrate (Parisot and Laffitte [9]).

One of the most widely used mixtures comprised ammonium nitrate with dinitronaphthalene in a ratio giving complete decomposition with a zero oxygen balance:

87.5% of ammonium nitrate
12.5% of dinitronaphthalene

This mixture was used extensively during World War I for filling artillery shells in France (under the name of Schnéiderite), Italy and Russia. The spelling "sznajderyt" was adopted in Poland and "shnaiderit" in the U.S.S.R.

Schnéiderite may detonate at a density of 1.30 with a rate ranging from 3815–5840 m/sec, depending on the way the ingredients are mixed. It is used either as a powder pressed into shells with an initiating charge of TNT (called SCPT-explosive in France) or as granules obtained by breaking up the pressed cake. The granules are poured into the shells and the spaces between filled with molten TNT. In France this kind of explosive bore the symbol STF.

This explosive used in France and Russia had the composition

78% of ammonium nitrate
22% of dinitronaphthalene

During World War II these substance were not widely employed, being relatively weak explosives; they are not so valuable in this respect as similar TNT mixtures.

TNT mixtures with ammonium nitrate were in common use during the World Wars I and II in Germany and Great Britain. The mixture consisting of:

40% of ammonium nitrate
60% of TNT

acquired considerable importance. It was known in Germany as Fp 60/40 (Füllpulver 60/40) and in Britain as Amatol 40/60. It was heated to a temperature above the melting point of TNT and then poured into shells as a semi-molten mass. Due to the shortage of TNT in Germany during World War I originally a part, and then the whole of the TNT in this mixture was replaced by dinitrobenzene. This resulted in the mixture DiFp 60/40 with the following compositions:

40% of ammonium nitrate
60% of dinitrobenzene or a TNT mixture
with dinitrobenzene

The Germans also used a similar mixture containing trinitroanisole instead of TNT for filling aerial bombs. In Britain other Amatols were also employed, i.e. ammonium nitrate mixtures with TNT in various ratios (Table 48).

TABLE 48

COMPOSITION AND PROPERTIES OF AMATOLS

Name	Composition		Consistency	Properties		
	NH_4NO_3	TNT		Density	Rate of detonation m/sec	Lead block expansion cm^3 (TNT =290 cm^3)
Amatol 40/60	40	60	Semi-molten when hot Can be cast	1.54–1.59	6470–7440	320–350
Amatol 45/55	45	55				
Amatol 50/50	50	50		1.56 1.60	7020 5850*	340–360
Amatol 60/40	60	40		1.50 1.60	6060** 5600*	350–370
Amatol 80/20	80	20	Loose powder, plastic when hot	1.46–1.50 1.60	5080–5920* 5200*	370–400

* According to Evans [50].
** In a steel tube 17 mm dia. according to Copp and Ubbelohde [51].

Amatol 80/20 is a mixture approaching the proportion in which all the oxygen contained in ammonium nitrate is used (the oxygen balance is +1.2% in Amatol

80/20). This is a free-flowing mixture when cold. It is usually stemmed or extruded into the shells by means of a screw wheel (worm wheel).

Amatols 50/50 and 60/40 were loaded into shells as substitutes for Amatol 40/60, in a semi-molten state obtained by heating to above the melting point of TNT.

Semi-fusible mixtures which contain 40–60% of nitro compounds tend to separate out after the nitro compound has been melted. During World War II these mixtures were used for filling large aerial bombs. To prevent stratification of the ingredients (the separation of crystals of ammonium nitrate) emulsifying substances were added to the mixtures.

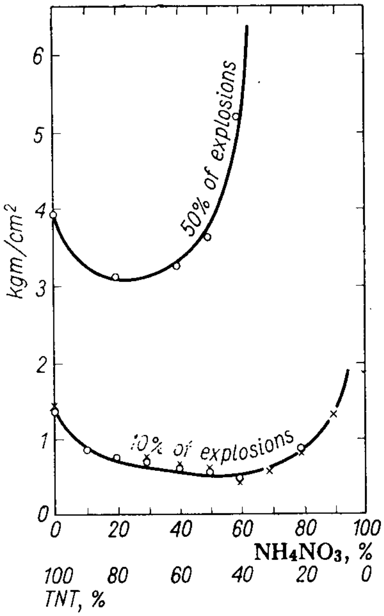

FIG. 70. The sensitiveness to impact of TNT mixtures with ammonium nitrate. Curves of probability of 10 and 50% explosions (Hackel [49]).

TNT mixtures with ammonium nitrate are more sensitive to impact than TNT itself. As shown by Hackel [49] (Table 49 and Fig. 70) mixtures containing 30–60% of ammonium nitrate are equally as sensitive as picric acid. Mixtures of this kind should not, therefore, be used for filling high initial velocity heavy calibre shells, e.g. armour-piercing shells.

Amatols in the form of cast charges detonate more readily than TNT in the same form. Initially, it was believed that the size of the ammonium nitrate crystals influences the ease of detonation, viz. that finely ground ammonium nitrate facilitates detonation.

Hackel [52], however, made it clear that in Amatols the ease of detonation also depends on the size of the crystals of the solidified TNT and increases in proportion

TABLE 49

SENSITIVENESS TO IMPACT OF TNT MIXTURES WITH AMMONIUM NITRATE (ACCORDING TO HACKEL)

Composition of mixture		Sensitiveness to impact. Impact of a 5 kg weight causing 10% of explosions, kgm/cm^2
TNT %	Ammonium nitrate %	
100	0	1.37
90	10	0.85
80	20	0.74
70	30	0.71
60	40	0.64
50	50	0.57
40	60	0.48
30	70	0.53
20	80	0.81
10	90	1.27

to the decrease of size of the crystals (i.e. in proportion to the rate of the cooling of the explosive).

During World War II Amatols of increased explosive power, in which a part of the ammonium nitrate was replaced by cyclonite, were also used. Thus German Ammonals were evolved from Amatol 50/50. Dinitrobenzene was used in Amatols 39a and 40 (Table 50) as a substitute for TNT.

TABLE 50

COMPOSITION OF AMATOLS WITH CYCLONITE

Ingredients	Amatol 39	Amatol 39a	Amatol 40
TNT	50	–	–
Dinitrobenzene	–	50	50
Cyclonite	5–10	15	10
Ammonium nitrate	40–45	35	40

The mining explosive Donarit was first used for filling hand grenades and manufacturing demolition charges during World War I. It consisted of

80% of ammonium nitrate
12% of TNT
4% of nitroglycerine (gelatinized with collodion cotton)
4% of wood flour

Due to the presence of nitroglycerine, this material was found to be too sensitive to mechanical impulses (it exploded when struck by a 2 kg weight falling 30 cm).

Kast [3] therefore proposed, as an alternative, an explosive called Perdit which consisted of:

72%	of ammonium nitrate
10%	of potassium perchlorate
15%	of liquid DNT
3%	of wood flour

This material gives a lead block expansion of 380 cm^3. It was employed widely up to the end of the World War I not only for hand grenades and demolition charges, but also for filling shells with a low muzzle velocity.

Apart from composite explosives with ammonium nitrate, mixtures with other nitrates also acquired temporary significance, e.g. a mixture used in Russia during World War I for filling hand grenades had the following composition:

60%	of TNT
35%	of potassium nitrate
4%	of ammonium nitrate

and Baratol, employed in Britain during both World Wars, consisting of TNT and barium nitrate in the ratio of 40 : 60.

An explosive called Macarit with a composition recommended by Macar [53]:

28%	of TNT
72%	of lead nitrate

also achieved some importance before World War I.

A similar substance under the name of Piombitto was used in Italy at the same time for filling artillery shells.

During World War I, in the United States Trojan Explosive was widely employed for filling hand grenades and mortar bombs. Its explosive constituent was nitrostarch:

23–27%	of nitrostarch
31–25%	of ammonium nitrate
36–40%	of sodium nitrate
1.5–2.5%	of charcoal
0.5–1.5%	of lubricating oil
0.5–1.5%	of calcium carbonate or magnesium oxide
0.2–0.4%	of diphenylamine
0–1.2%	of water

Since this explosive is infusible it was loaded by ramming down with a wooden plug. Grenite was another granulated nitrostarch material for filling hand grenades, consisting of 97% nitrostarch with lubricating oil (1.5%) and gum arabic (1.5%) as granulating materials.

The explosive properties of nitrostarch mixtures (containing 12.7% of nitrogen) with ammonium or sodium nitrates have been studied by T. Urbański *et al.* [48]. Values for rate of detonation of mixtures with a density of 1.0 are given in Fig. 71. They conform to Laffitte's rule that the variation in rate of detonation with the composition of mixtures with ammonium nitrate is almost rectilinear.

Other examples of infusible explosives are the Ammonites with the composition shown in Table 51.

A shortage of ammonium nitrate in Germany (from 1944) led to the use of a TNT mixture with 40% of sodium nitrate and later even with 50–60% of sodium chloride for shell filling as cast charges. Sodium chloride was used merely to keep the right charge weight.

Sometimes sodium and potassium silicates were used instead of sodium chloride. Thus the consumption of TNT did not need to be increased while the consistency and density of Amatols were maintained in mixtures which in turn averted the necessity for the alteration of the design of shells and the method of filling. Such mixtures were used to the same extent as Amatols for filling shells, bombs and hand grenades. It is obvious that they were of little value.

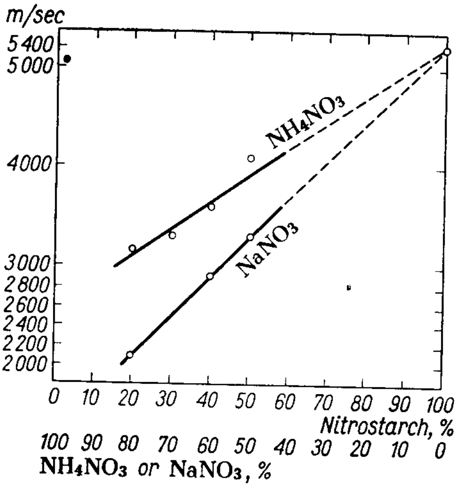

FIG. 71. The rate of detonation of nitrostarch mixtures with ammonium or sodium nitrates (according to T. Urbański *et al.* [48]).

TABLE 51

THE COMPOSITION OF AMMONITES

Ingredients	H−1	H−8
Ammonium nitrate	50	50
Potassium nitrate	—	25
Calcium nitrate ($4H_2O$)	15	—
Cyclonite	25	15
PETN	10	10

In Japan explosive consisting of 60% of trinitroanisole and 40% of ammonium nitrate was manufactured and used for filling bombs.

During World War II a mixture of TNT (48%) with ammonium picrate (52%) known as Picratol was employed to replace pure ammonium picrate (Explosive D) in the United States. This was a semi-fusible mixture cast into shells at a temperature above the melting point of TNT. After solidification the density of the mixture was 1.62. In accordance with the opinion prevailing in that country that ammonium picrate is an explosive with a low sensitiveness to impact, it was used for filling armour-piercing shells.

Various loose powder mixtures of ammonium picrate and aluminium were also used by the Japanese during World War II. They will be dealt below, as mixtures with aluminium.

The preparation of infusible (loose powder) ammonium nitrate mixtures is usually carried out in the same way as the manufacture of composite mining explosives. Since the military explosives are not very sensitive to mechanical stimulants, and it is important to obtain a high density, mixing is usually performed by edge runner mills.

The mixing of semi-fusible explosives is commonly carried out in kneaders, first heating the ammonium nitrate to a temperature of 85–90°C and then pouring in the molten TNT. After stirring, the material is cooled down in the kneader to produce a mixed crystalline mass.

MIXTURES WITH ALUMINIUM AND OTHER METALS

The addition to an explosive of combustibles which burn with very great evolution of heat is advantageous in spite of the fact that the oxygen balance is impaired. The heat of explosion so obtained is very great and the temperature of the explosion products is very high.

The following metals have been suggested for this purpose: magnesium, aluminium, zinc and also silicon; sometimes ferro-silicon, alumino-silicon and calcium silicide are also employed. Deissler [54] was the first (1897) to recommend aluminium as a component of explosives. He was followed by Goldschmidt [55], Escales [56], von Dahmen [57] and Roth [58]. In later years Kast [59] investigated military explosives which contained aluminium.

Magnesium and zinc are readily oxidized, and are liable to undergo oxidation during the storage of mixtures containing them, hence they have not been utilized for military purposes. Apart from this, magnesium is a valuable component of various pyrotechnic mixtures such as those used in signals or for illumination, for which it is hard to find a substitute. With the exception of calcium silicide the silicon alloys burn with more difficulty and are less efficient. For this reason aluminium and calcium silicides are the most widely used.

Originally aluminium was employed in the form of fine powder ("aluminium bronze"). It appeared later that such a high degree of sub-division is unnecessary and good results may also be achieved with aluminium filings, shavings and especially flakes. The latter form is particularly advantageous as the smaller total surface of aluminium present with mixture slows down the rate of oxidation during storage.

In explosives in which there is no surplus of oxygen, aluminium reacts initially with carbon dioxide formed as an explosion product, according to the equation:

$$3CO_2 + 2Al = 3CO + Al_2O_3 + 180.7\ \text{kcal} \qquad (1)$$

The heat effect of this reaction is very great and it makes a big contribution to the general heat balance.

Originally the addition of aluminium was limited to explosives with a positive oxygen balance, i.e. mixtures containing a considerable amount of an oxygen carrier. However, during World War II, the Germans extended the use of aluminium by adding it to nitro compounds, for example to a mixture of TNT with hexyl.

It might seem paradoxical to add aluminium to such explosives, as it would result in a large reduction of volume of the gases:

$$3CO + Al \rightarrow 3C + Al_2O_3 \qquad (2)$$

However, under the very high pressures prevailing during detonation, the carbon monoxide decomposes in part into carbon dioxide and carbon. Aluminium reacts with carbon dioxide according to eqn. (1) and with water according to eqn. (3):

$$3H_2O + 2Al \rightarrow 3H_2 + Al_2O_3 \qquad (3)$$

This would develop a considerable heat. Thus, replacing 15% of TNT–hexyl with aluminium would increase the heat of detonation from *ca.* 1000 kcal/kg to *ca.* 1400 kcal/kg [60].

In military ammonium nitrate explosives containing aluminium even those in which the oxygen balance is negative, the main reaction is assumed to be that of oxidation of the aluminium by reaction with ammonium nitrate:

$$2Al + NH_4NO_3 \rightarrow Al_2O_3 + 2H_2 + 2350\ \text{kcal/kg}$$

The gas volume is 502 l./kg and calculated explosion temperature 5400°C. It is also possible that aluminium reacts with nitrogen to form aluminium nitride (Al_2N_2). The reaction is also exothermic ($-\Delta H = 80$ kcal). (The work was done at the Chemisch-Technische Reichsanstalt in Germany in the period between the two World Wars [61].)

The mixtures containing the oxidizing agent, e.g. ammonium nitrate and aluminium were termed Ammonals.

The system: ammonium nitrate, aluminium, nitro compound (e.g. TNT) would be expected to undergo gradual decomposition, e.g. that in stored shells and bombs filled with such mixtures changes would occur, leading to the oxidation of the aluminium. Obviously, a mixture containing oxidized aluminium has lower explosive power than the same mixture containing metallic aluminium. It was therefore very important to determine the mechanism of the oxidation of aluminium. It became apparent that this is caused by impurities in the ammonium nitrate, not by the ammonium nitrate itself. Chaylan's [62] experiments showed that mixtures of pure ammonium nitrate, TNT and aluminium are stable within the temperature range of 60–95°C, and at 100°C, after 1000 hr of heating, only a few cm^3 of gas are evolved. Experience has shown that traces of chlorides in ammonium nitrate should be avoided as they can induce aluminium to react even at room temperature. Aluminium also undergoes a corrosion reaction which is caused by the metallic walls of the shell, and which has not yet been fully explained. In all probability its origin is electrochemical. Other data show that aluminium reacts with copper alloys.

It is well known that ammonium nitrate evolves ammonia on storage, particularly in the presence of moisture. It was found that the amount of ammonia evolved in the presence of aluminium is much greater [63]. The evolution of ammonia is particularly undesirable in the mixtures containing TNT, as TNT reacts with ammonia to yield readily ignitable compounds (Vol. I, p. 304; see also [64]).

According to Aubertein [65] aluminium particles used as a component in explosives may be coated with 2–8% of paraffin, mineral oil or resin to prevent premature reaction with other ingredients.

Ammonals were originally intended for use in mines. In Austria [66] for instance, ammonals with the following composition were used in gas-free mines:

80–90% of ammonium nitrate
4–6 % of charcoal
4–18% of aluminium

Soon afterwards, however, the use of ammonals in collieries was forbidden and their utilization restricted to above ground operations, e.g. quarrying. During World War I ammonals were extensively used for this purpose.

Ammonal was used to a certain extent in Russia and Great Britain. Its composition was as follows:

65% of ammonium nitrate
15% of TNT
17% of aluminium
3% of charcoal

The presence of charcoal, however, proved to be unnecessary; during World War I Russian mines were loaded with ammonal made without it:

7.65% and 68% of ammonium nitrate
16.0% and 15% of TNT
7.5% and 17% of aluminium

Detonators for initiating a Schnéiderite charge in Russian shells were also filled with an aluminium mixture:

65% of ammonium nitrate
15% of TNT
20% of aluminium

According to Förg [66] even before 1914 T-Ammonal manufactured by the G. Roth factory at Felixdorf was employed for filling artillery shells in Austria. The composition of this explosive was as follows:

45% of ammonium nitrate
30% of TNT
23% of aluminium
2% of "red" charcoal (p. 345)

Kast [3] gives for this substance the following figures as characteristic of its explosive power:

Heat of explosion 1465 kcal/kg
Gas volume (V_0) 605 l./kg
Temperature of explosion 4050°C
Specific pressure (f) 9900 m
Rate of detonation in an iron pipe at a density of 1.62 5650 m/sec
Lead block expansion 470 cm^3

In Germany "Deutsche Ammonal" was used for filling large calibre shells. Various ammonals were employed to an appreciable extent for filling bombs, land mines in Italy and to a lesser extent in France. The composition of these explosives is represented in Table 52.

TABLE 52

COMPOSITION OF AMMONALS

Ingredients	Italian ammonals		Belgian Sabulite	French	British	German
	Nitramit	Echo				
Ammonium nitrate	72	62	78	65	64	54
TNT	–	–	8	15	15	30
Nitrocellulose	–	5.5	–	–	–	–
Paraffin	6	–	–	–	–	–
Animal grease	–	7.5	–	–	–	–
Charcoal	–	–	–	10	3	–
Aluminium	22	25	–	–	18	16
Calcium silicide	–	–	14	10	–	–

Ammonals containing a little or no TNT detonated with difficulty and were therefore not pressed but rammed down to a relatively low density. For the same reasons their use was restricted to the shells with a low muzzle velocity. Shells with a high muzzle velocity were loaded by pressing with ammonals rich in TNT (T- or German ammonals). Ammonals were also used when a high brisance was required, e.g. for filling torpedoes.

A few other simple German ammonals containing ammonium nitrate were used for shell filling during World War II. Their composition is given in Table 53.

TABLE 53

COMPOSITION OF GERMAN AMMONALS

Ingredients	Fp* 19	Fp* 13-113	Fp* 110
Ammonium nitrate	35	70	90
TNT	55	20	—
Naphthalene	—	—	5
Wood meal	—	—	2.5
Aluminium	10	10	7.5

* Fp stands for Füllpulver.

The compositions of American ammonals are collected in Table 54.

TABLE 54

COMPOSITION OF U.S. AMMONALS

Ingredients	1	2	3
Ammonium nitrate	22.0	72.0	65.0
TNT	67.0	12.0	added 15.0
Aluminium (fine powder)	11.0	16.0	16.0
Aluminium (coarse grain)	—	—	16.0
Charcoal			3.0

During World War I another type of explosive —"Mischpulver"—was used by the Germans for filling hand grenades. This was blackpowder mixed with potassium perchlorate and aluminium. The mixture consisted of:

83% of blackpowder
12% of potassium perchlorate
5% of aluminium

The presence of perchlorate and aluminium conferred high explosive properties on the mixture.

Perchlorate ammonal was also used in Britain for filling land mines. It consisted of:

78% of ammonium perchlorate
16% of paraffin
6% of aluminium

After World War I the use of ammonals was restricted to quarrying: in coal mines they were banned since their high flame temperature (due to presence of metallic aluminium) makes them inherently dangerous there.

In Spain during the Spanish Civil War, General Franco's forces used Ammonal I composed of [63]:

92.4% of ammonium nitrate
6.6% of charcoal
1.0% of aluminium

During World War II the use of aluminium in military explosives was resumed on a wide scale. Thus sea mines and German torpedoes were loaded with a fusible mixture of hexyl and TNT supplemented by 10–25% of metallic aluminium (Trial).

TNT was partly replaced by dinitronaphthalene in the KMA mixture. Alternatively, hexyl was replaced by dinitrophenylamine to form fusible S-6 mixtures.

TABLE 55

COMPOSITION OF KMA AND S-6 MIXTURES

Ingredients	KMA	S-6	S-6 modified
TNT	40	40	30
Dinitronaphthalene	20	–	–
Hexyl	30	30	30–35
Dinitrodiphenylamine	–	20	15–20
Aluminium	10	10	15–25

Haid in the Chemisch-Technische Reichsanstalt in Berlin suggested [67] substitute fusible mixtures of the S-type which were introduced towards the end of World War II owing to the shortage of nitro compounds. Their composition is given in Table 56.

TABLE 56

COMPOSITION OF S-TYPE SUBSTITUTE MIXTURES

Ingredients	S-16	S-19 (modified)	S-22 (with cyclonite)	S-22	S-26
				(with hexyl)	
Ammonium nitrate	32	55	44	44	55
Sodium nitrate	6–8	9	9	9	9
Potassium nitrate	0–2	4.2	3	3	4.2
Ethylenediamine dinitrate (PH-Salz)	10	–	14	14	–
Urea	–	1.8	–	–	1.8
Hexyl	–	–	–	15	15
Cyclonite	10	15	15	–	–
Aluminium	40	15	15	15	15

For filling V2 missiles Trialen, a mixture of TNT, cyclonite and aluminium, was used in Germany.

Another German explosive, Hexal, consisted of:

71% of cyclonite
4% of montan wax
25% of aluminium

The moulded slabs of this explosive were cast into the shell and the spaces between them was filled with a fusible mixture, e.g. KMA.

In Great Britain a cast explosive Torpex was developed during World War II. It was composed of 41% of RDX, 41% of TNT and 18% of aluminium. It was used for filling torpedoes and bombs.

Due to the sensitiveness of Torpex a few modifications were developed, as for instance the cast explosives DBX and HBX [68] (Table 57).

TABLE 57

Ingredients	DBX	HBX
RDX	21	39.6
TNT	40	37.8
Ammonium nitrate	21	—
Aluminium	18	17.1
Desensitizer	—	5.0
Calcium chlorate	—	0.5
Density	1.68	—

In the U.S.A. Tritonal, a cast mixture of 80% TNT and 20% aluminium was used. It gave a density of 1.73 [68].

In Japan a cast mixture composed of 60% of trinitroanisole and 40% of aluminium was used for filling high explosive incendiary shells. On solidification this mixture has a density of 1.90.

E-4, an infusible ammonium nitrate explosive was composed of:

44%	of ammonium nitrate
10%	of sodium nitrate
2%	of urea
14%	of hexyl
30%	of aluminium

During World War II the Japanese employed mixtures with aluminium or ferro-silicon. Some examples of these are tabulated below (Table 58).

Recently The Dow Chemical Company (Midland, Michigan) developed a powerful new plastic explosive MS-80 containing 20% aluminium. No details on the composition are available [69].

TABLE 58

MIXTURES WITH ALUMINIUM AND FERRO-SILICON

Ingredients	Type 88 Ko	Type 4, Mk 5, K5	Type 1, Mk 1, P1	Type 1, Mk 6, P6
Ammonium nitrate	—	75	—	—
Ammonium perchiorate	75	55	—	—
Ammonium picrate	—	—	81	86
Aluminium	—	—	16	—
Ferro-silicon	16	10	—	11
Wood meal	6	5	2	2
Lubricating oil	3	1	1	1
Density	1.05	1.05	1.16	1.13
Rate of detonation (m/sec)	3800	—	4280	4620

In addition to aluminium, calcium silicide or ferro-silicon, the use of silicon was also recommended. The comparative figures illustrating the effect of the addition of these compounds on the strength of the explosive have been given by Sartorius [70] (Table 59). The power is expressed in terms of expansion in the lead block (taking picric acid as 100).

TABLE 59

INFLUENCE OF THE INGREDIENTS ON THE EXPLOSIVE POWER OF MIXTURES

Ingredients	Single explosive	Mixtures with addition of		
		10% of silicon	10% of ferro-silicon	10% of calcium silicide
PTN	146	152	148	146
Cyclonite	135	143	141	140
Picric acid	100	108	102	106
TNT	94	93	94.5	96

It was also observed that the increase in lead block expansion caused by the addition of silicon is a half or two thirds smaller than that caused by the addition of aluminium.

Zinc appeared to be too reactive and has not found any practical application.

The preparation of S-type mixtures. The following description of the preparation of S-16 mixture is provided as an example. In a stainless steel kettle of 500 kg capacity equipped with a stirrer and steam-heated to 118°C, 250 kg of the mixture is prepared by pouring in the ingredients, in the following sequence:

50 kg of ethylenediamine dinitrate
30 kg of sodium nitrate
10 kg of potassium nitrate
160 kg of ammonium nitrate

The ingredients are added slowly, in batches, so that the mixture heats up before the next batch is added. It is necessary to prevent the temperature from dropping below 90°C otherwise melting is prolonged.

After all the ingredients have been introduced into the kettle the temperature rises to 113–115°C. At this temperature the mixture forms a clear melt in 20 min. If the mixture remains turbid, further heating and stirring is necessary.

When melting is complete the mixture is allowed to stand without stirring for 5 min, after which the contents are emptied through the bottom valve into another kettle situated below. 200 kg of aluminium powder and 50 kg of cyclonite are added. The temperature falls but must not be allowed to drop below 100°C. The contents of the kettle are then heated to 113°C while stirring for 10 min.

After stirring the mass is cast straight into the shells or onto trays where it solidifies, forming a layer 2 cm thick. The mass is then broken into pieces which are loaded into the shells and the spaces between filled either with fresh material or TNT or an alloy of TNT with cyclonite.

Since the mixture is highly hygroscopic it should be protected against atmospheric moisture. During melting it is also necessary to avoid contact between the mixture and brass or other copper alloys since the latter are liable to react with metallic aluminium. Kettles should be washed with water every 24 hr to remove all residues of the mixture.

MIXTURES WITH CHLORATES AND PERCHLORATES

Mixtures with potassium and sodium chlorates

As early as 1818 Berthollet [71] suggested the replacement of potassium nitrate in blackpowder by potassium chlorate, which he had prepared for the first time in 1786. Thus, "white powder", which is a mixture of potassium chlorate with sugar, was evolved. However, this mixture proved to be particularly sensitive to friction and impact, hence its preparation and use was extremely dangerous. Further experiments showed that pure potassium chlorate has no explosive properties but when used in admixture with combustibles such as sugar, starch or aluminium it gives rise to an explosive highly sensitive to mechanical action, especially to friction. A disastrous explosion occurred in the potassium chlorate factory at St. Helens, near Liverpool, in 1899. The storehouse in which barrels containing 150 tons of potassium chlorate were kept was enveloped in flames. At first the contents of the storehouse burned, but after a time an explosion took place. In all probability, the explosion was caused by the fact that some of the potassium chlorate was melted in the fire and the molten salt, together with the wood of the barrels, formed a mixture which exploded under the influence of high temperature.

The manufacture and use of some mixtures containing potassium and sodium chlorate were forbidden in several countries on account of their high sensitiveness to friction. In Great Britain, for instance, the production of a mixture of potassium chlorate and sulphur was prohibited by law in 1894. Mixtures of potassium chlorate with phosphorus should also be avoided owing to the great dangers involved with their preparation and handling. This is why the heads of safety matches are made from mixtures of potassium chlorate with sulphur and with manganese dioxide and potassium dichromate bound with glue.

The addition to potassium chlorate of vegetable oils, fats or mineral oils in which aromatic nitro compounds are dissolved, as recommended by Street [72], proved to be a milestone in the development of chlorate explosives. The application of an admixture of castor oil was particularly useful. The presence of oils and fats in the explosives reduced their sensitiveness to friction and impact, and the oily ingredient conferred a slightly plastic consistency.

The effect of adding various organic substances to potassium chlorate on the detonating capacity of the resultant mixtures, and on their power was studied system

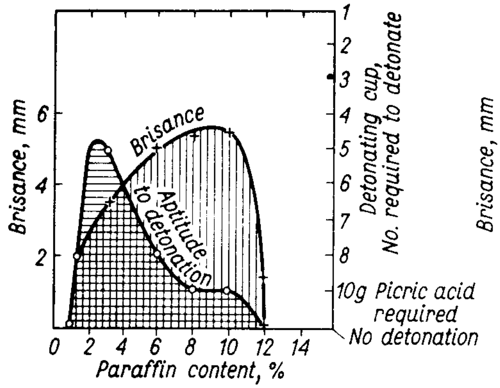

FIG. 72. Explosive properties of the mixtures of potassium chlorate with kerosene (according to Chemisch-Technische Reichsanstalt [73]).

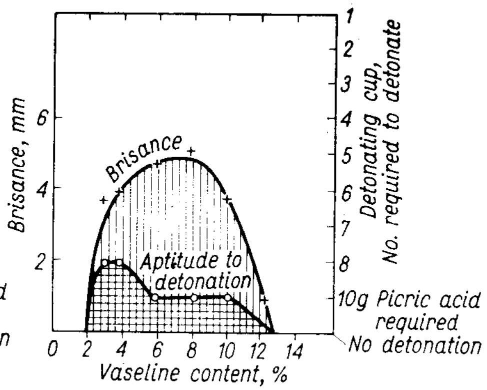

FIG. 73. Explosive properties of the mixtures of potassium chlorate with vaseline (according to Chemisch-Technische Reichsanstalt [73]).

atically at the Chemisch-Technische Reichsanstalt [73]. The results that refer to mixtures of potassium chlorate with kerosene, vaseline and nitrobenzene are shown in Figs. 72, 73 and 74.

As was to be expected, mixtures with nitrobenzene are the most powerful and the most readily detonated. Mixtures with kerosene or vaseline are of equal strength, those with a small kerosene content (e.g. 2–4%) detonate more easily than those containing the same amount of vaseline while the mixtures which contain a larger amount of kerosene or vaseline (e.g. 8–10%) detonate with more or less equal ease.

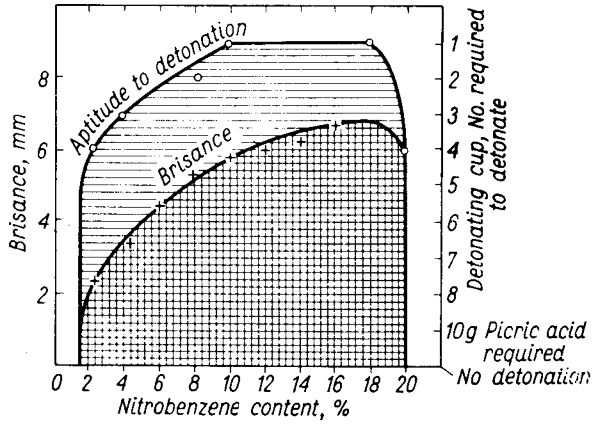

FIG. 74. Explosive properties of the mixtures of potassium chlorate with nitrobenzene (according to Chemisch-Technische Reichsanstalt [74]).

The graphs for mixtures with paraffin oil lie close to those with kerosene while mixtures with paraffin (m.p. 52°C) are similar to those with vaseline.

Other studies of the effect of the structure of phlegmatizing substances on the sensitiveness to impact of potassium chlorate mixtures were carried out by Blinov [74]. He investigated mixtures consisting of 92% potassium chlorate and 8% liquid phlegmatizing compound or of 85% potassium chlorate and 15% solid phlegmatizing compound. As far as phlegmatizing liquids are concerned it turned out that the impact sensitiveness of the resultant mixtures is independent of the viscosity of the liquid. Blinov proved that the phlegmatizing effect of such compounds increases in proportion to the shortness of the carbon chain. This can be seen from the examples given in Table 60. Moreover, increase in the plasticity of a solid substance brings about a decrease in its sensitiveness; this is shown by comparing the phlegmatizing effects of vaseline and paraffin.

TABLE 60

THE PHLEGMATIZING EFFECT OF VARIOUS COMPOUNDS

Phlegmatizing compound	Sensitiveness to impact, cm
Butyric acid	50
Valeric acid	45
Stearic acid	20
Oleic acid	12
Vaseline	55
Paraffin	26

Potassium chlorate can be replaced by sodium chlorate which is cheaper and more widely available although being somewhat hygroscopic it is much less frequently used as a constituent of explosives.

Chlorate explosive mixtures have the disadvantage that they cake and set solid during storage. Some ingredients such as vaseline or paraffin tend to aggravate this trouble. To counteract this tendency ingredients are added which have a loosening effect on the explosive composition, giving a relatively low density (e.g. wood meal or cork dust). In the U.S.S.R. extensive work on this subject was carried out by Shpitalskii and Krause [75].

The most effective method of preventing caking in chlorate explosives is to manufacture them in granular form. For this purpose various resins (e.g. colophony) or waxes (e.g. Carnauba) are added to the mixture. The moist mass is then rubbed through a sieve and dried. The grains so formed are sifted through screens to separate out the dust.

Explosives of this type were manufactured at Chedde in France, whence they derived their name of Cheddite. They were recommended originally for use in mines, but were gradually withdrawn as unsafe to use in the presence of methane and coal-dust.

For military purposes Cheddites were usually produced with the following composition given in Table 61.

TABLE 61

THE COMPOSITION OF CHEDDITES

Constituents	Name				
	Explosif O No. 1 Type 41	Explosif O No. 1 Type 60 bis	Explosif O No. 2 modifié	Type O No. 6B	Explosif S
Potassium chlorate	80	80	79	90	–
Sodium chlorate	–	–	–	–	90
Dinitrotoluene	–	2	15	–	–
Nitronaphthalene	12	13	1	–	–
Castor oil	8	5	5	–	–
Vaseline	–	–	–	3	3
Paraffin	–	–	–	7	7

The first three types of Cheddites were used in France for filling hand grenades and shells with a low muzzle velocity and for manufacturing demolition charges during World War I. When there was a shortage of nitro compounds in France, Cheddite type O No. 6B was employed as a substitute for the first two. This was also manufactured with sodium chlorate instead of potassium chlorate (Explosif S).

Kast [3] gives the following figures as characteristic of Cheddite type O No. 2, modifié:

Apparent density	1.15
Heat of explosion	1185 kcal/kg
Gas volume (V_0)	337 l./kg
Temperature of explosion	*ca.* 4500°C
Specific pressure (f)	6090 m
Rate of detonation (at a density of 1.3)	3000 m/sec
(at a density of 1.5)	4000 m/sec
Lead block expansion	255 cm^3
Sensitiveness to impact (2 kg)	30 cm

The rate of detonation of Cheddite type O No. 6B appears to differ slightly from that of the above composition although it contains no TNT; at a density of 1.4 it is 3500 m/sec.

The chlorate explosives can be easily compressed to a density of 1.9 although at such a high density they are more difficult to detonate (see also Fig. 75, p. 279).

Chlorate explosives yield only a small amount of gaseous products since the major product of explosion is potassium chloride. The specific pressure f is therefore relatively low (the high temperatures do not compensate for the small volume of gases), hence the lead block expansion is low, but Cheddites without nitro compounds—type O No. 6 and S—give an even smaller lead block expansion: 180–200 cm^3. Some chlorate explosives, when detonated in the open, do not transmit detonation from cartridge to cartridge, differing in this respect from dynamites and ammonium nitrate explosives. In a confined space, however, they behave differently. Here the transmission of detonation over a distance is superior to that of ammonium nitrate explosives. T. Urbański [76] has reported that cartridges of Miedziankit (100 g, 30 mm dia.) can transmit detonation in the bore hole of the mortar of an experimental gallery for a distance of over 40 cm.

The main disadvantages of chlorate explosives such as sensitiveness to friction and impact and caking in storage, were overcome by Sprengel [77], who introduced the technique of mixing the ingredients immediately before use. To facilitate mixing, the combustible component of the explosive had a liquid consistency. This led to the development of the explosive "Rack-à-rock", consisting of potassium chlorate and nitrobenzene. It played an important part in many engineering achievements at the turn of the nineteenth century especially, in Russia and in the U.S.A.

A considerable advance was made by Łaszczyński [78], when he worked out the composition and method of preparation of the explosive Miedziankit consisting of:

90% of potassium chlorate
10% of kerosene

Cartridges containing only potassium chlorate were transported in safety to the site, where they were dipped for a definite time into kerosene just before use. Miedziankit was also manufactured by soaking potassium chlorate cartridges with kerosene in the explosive factory. Kerosene with an ignition temperature above 30°C was employed, to render the product safe for rail transport. According to T. Urbański [76] the rate of detonation of Miedziankit is 3000 m/sec in an iron pipe at a density of 1.7.

Miedziankit was one of the most widely used non-military explosives in Germany, Russia and Poland before, during and immediately after World War I, when there was a need to economize in the nitrates, including ammonium nitrate, used for military purposes.

It is a feature of chlorate explosives that ammonium salts (e.g. ammonium nitrate) must not be added to chlorate compositions (Vol. II).

The converse obviously applies to ammonium nitrate explosives, which must not contain any chlorates, since during storage a double exchange reaction may occur resulting in the formation of ammonium chlorate (p. 476, Vol. II), an unstable substance which decomposes spontaneously. A number of patents were taken out between 1880 and 1895, for explosives based on the use of ammonium chlorate or mixtures of ammonium nitrate with potassium or sodium chlorate. Many accidents which occurred through the spontaneous decomposition of these explosives proved the impossibility of using mixtures containing both chlorates and ammonium salts (Hantke [79]).

MIXTURES WITH POTASSIUM AND AMMONIUM PERCHLORATES

Potassium perchlorate in the pure state, like potassium chlorate, is not an explosive, indeed the decomposition of the former is endothermic:

$$KClO_4 = KCl + 2O_2 - 7.8 \text{ kcal}$$

When mixed with non-explosive combustibles, potassium perchlorate produces compositions relatively difficult to detonate; e.g. the mixture of potassium perchlorate with paraffin in a ratio of 85 : 15 gives a lead block expansion of only 60 cm³, whereas a similar mixture with potassium chlorate gives approximately 200 cm³. On the other hand, the higher content of oxygen in potassium perchlorate and the smaller amount of potassium chloride produced during decomposition makes it possible to form mixtures which are 10–15% stronger than chlorate mixtures. The sensitiveness of perchlorate mixtures to friction and impact is lower than that of chlorate mixtures, and their ignition temperature is higher.

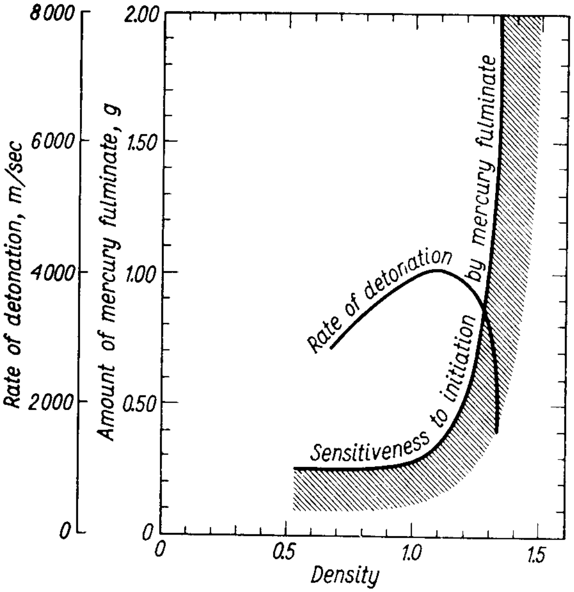

FIG. 75. The relation between the density and the rate of detonation, and sensitiveness to initiation by mercury fulminate of chlorate explosive [80].

In spite of their advantages, mixtures with potassium perchlorate as the chief constituent are not very often used since the latter is too expensive. Other disadvantages of such mixtures lie in their rather high sensitiveness to mechanical impulses, the relatively great difficulty of detonating them, and their fairly high ability for deflagration. Potassium perchlorate is therefore often employed simply as an additive to ammonium nitrate explosives (p. 264).

Another constituent of perchlorate explosives, ammonium perchlorate, unlike ammonium chlorate, is stable. It is also dissimilar to potassium perchlorate in being an explosive in the pure state, like ammonium nitrate. The greater specific gravity of ammonium perchlorate gives to explosives with which it is mixed a greater power than that of similar ammonium nitrate explosives. The former are also more sensitive than chlorate explosives to friction and impact and to thermal ignition.

On explosive decomposition they may produce a certain amount of hydrogen chloride which is highly undesirable in mining explosives.

Perchlorate explosives, like chlorate explosives, can be compressed to a high density, but the detonation at a high density is difficult. This is illustrated by a graph published by the French Commission on Explosives (Commission des Substances Explosives) (Fig. 75) [80] which shows how the rate of detonation and the amount of mercury fulminate required for detonation varies with density.

As early as 1865 Nisser [81] recommended the use of potassium perchlorate instead of potassium chlorate. Ammonium perchlorate as a constituent of explosives was proposed by Nobel [82] in 1888, and explosives with ammonium perchlorate as a chief component were proposed by Alvisi [83] in 1895 and Carlson [84] in 1897. Explosives containing ammonium perchlorate are used in Japan in the mining industry (p. 474). Yonckites, developed by Yonck [85] (p. 447) were extensively used in the Belgian mining industry. Cheddites with ammonium perchlorate instead of potassium chlorate were manufactured in France.

Perchlorate Cheddites were employed in France and Italy for filling shells with a low muzzle velocity during World War I (trench mortar shells, aerial bombs etc.). Originally these were the explosives which imitated Cheddites containing DNT (types B and C). Later, chiefly owing to a shortage of nitro compounds, paraffin was utilized as a combustible ingredient. Thus emerged the explosives 86/14, 90/10 and E (Table 62).

TABLE 62

COMPOSITION OF CHEDDITES

Constituents	Type B	Type C	Type P	Ch or 86/14	90/10	E
Ammonium perchlorate	82	50	61.5	86	90	92
Sodium nitrate	–	30	30	–	–	–
DNT	13	15	–	–	–	–
Castor oil	5	5	–	–	–	–
Paraffin	–	–	8.5	14	10	8

Perchlorate explosives for mining, and technical methods of manufacturing chlorate explosives, will be discussed later (pp. 520–521). Mixtures of potassium perchlorate or ammonium perchlorate with plastics or elastomers have recently come into extensive use for jet propulsion (e.g. methyl polymethacrylate, ester resins, and thiokol-rubber).

In this connexion a number of investigations have been undertaken to examine the physico-chemical and explosive properties of these mixtures.

Gordon and Campbell [86], for instance, examined the exothermic decomposition of potassium perchlorate mixtures with carbon within the temperature range 300–360°C, while Grodzinski [87] studied the thermal decomposition of mixtures of various combustibles with potassium perchlorate.

PLASTIC EXPLOSIVES

Plastic explosives, such as dynamites, are explosives rich in a liquid constituent, e.g. nitroglycerine, usually with dissolved high viscosity polymers. Guhr dynamite (no more in use) composed of 75% nitroglycerine and 25% kieselguhr, the first explosive to have a plastic consistency, owed this property to the high proportion of liquid it contained.

Blasting gelatine is a plastic explosive consisting of 92–94% nitroglycerine and 6–8% collodion cotton (of high viscosity). Blasting gelatine is markedly elastic. It loses its elasticity, becoming plastic, only on heating to a temperature of 40°C or higher, depending on the type and amount of collodion cotton present. Recently a new kind of dynamite was developed in the U.S.S.R. Its plasticity was achieved by dissolving methyl polymethacrylate in nitroglycerine, in the proportions of twenty to forty parts of nitroglycerine to one part of the polymer.

Blasting gelatine and dynamites are now used only for civil purposes. Originally, they were suggested as military explosives, particularly for filling shells with a low muzzle velocity, until it was shown that fillings made with nitroglycerine explosives may cause premature explosions inside the barrel.

The Russian air force used bombs filled with a material resembling blasting gelatine during World War I.

Dynamites were retained for military purposes for some time for use in demolition charges. The disadvantage of these explosives lies in their limited chemical stability. Ultimately, therefore they were replaced by explosives that remain unchanged during storage (aromatic nitro compounds such as TNT, picric acid, and more recently TNT with cyclonite or PETN).

The plasticity in an explosive can be put to practical use, e.g. for demolition purposes. Thus, to sever an iron bar or to blow up a wall or a rock the easiest way is to use a plastic explosive, moulded to fit the shape of the object to be destroyed. Since blasting gelatine is not entirely safe to handle, being elastic, i.e. difficult to shape as required, attention was directed to the development of plastic materials based on other constituents. Thus, mixtures comprising a solution of collodion cotton in liquid aromatic compounds as plasticizers were suggested. Such were Plastrotyl, recommended by Bichel [88] with a composition:

86% of TNT
10% of liquid DNT (m.p. 20–25°C)
0.3% of collodion cotton
3.7% of turpentine

and the Swedish perchlorate plastic explosive Territ suggested by Nauckhoff [89]:

43% of ammonium perchlorate
28% of sodium nitrate
27.8% of TNT and DNT
1.2% of collodion cotton

According to Kast [3] the explosive properties of Territ are:

Density 1.67 (max. 2.15)
Rate of detonation 4700 m/sec
Lead block expansion 340 cm^3
Sensitiveness to impact (2 kg) 20 cm

Plastrotyl and Territ were rather difficult to detonate chiefly due to their great density. To make these mixtures detonate more readily, nitroglycerine was added but this increased their sensitiveness to impact.

In 1929, Stettbacher [90] suggested the use of a mixture of PETN with nitroglycerine, under the name of Penthrinite. Such a mixture may be plastic provided suitable amounts of nitroglycerine and PETN with crystals of a proper size are used and both constituents are thoroughly mixed. Stettbacher recommended a composition ranging with the limits:

10–70% of PETN
90–30% of nitroglycerine

If a mixture rich in nitroglycerine is employed it may be converted into a plastic one by the addition of collodion cotton.

In his later work Stettbacher developed the idea of using penthrinites as substitutes for dynamite, with the following composition:

50% of PETN
46% of nitroglycerine
4% of collodion cotton

Stettbacher's proposals were subjected to sharp criticism by Naoúm [91] who considered the substitution of such mixtures for dynamite to be inexpedient, since:

(a) they are considerably more expensive than nitroglycerine and,

(b) they cannot replace dynamite as mining explosives.

The Chemisch-Technische Reichsanstalt [73] examined the properties of PETN mixtures with nitroglycerine and found that the latter easily exudes from mixtures in which more than 20% is present, especially at an elevated temperature, e.g. 50°C. However, Stettbacher's observation that penthrinite can be compressed to high density more easily than PETN itself was confirmed. Hand tamping of PETN gives a density of 0.9, whereas a mixture of 80% PETN with 20% nitroglycerine gives 1.3. The following densities of these mixtures were obtained under higher pressures:

Pressure, kg/cm^2	Density
250	1.60
1000	1.62
2000	1.66
3000	1.67

The rate of detonation of a mixture compressed to a density of 1.67 is 7600 m/sec whereas PETN of equal density detonates with a rate of 8400 m/sec.

Plastic explosives with cyclonite as the chief constituent were used extensively during World War II. Cyclonite is preferable as it detonates easily even when strongly phlegmatized (desensitized to impact) and as its rate of detonation is very high.

Originally a mixture of 88% cyclonite with 12% lubricating oil was employed. This mass however was not sufficiently plastic and lost its plasticity readily by exuding the oil at a high temperature. It was therefore replaced by a mixture named Composition C-3 of 77% cyclonite and 23% gel made out of liquid nitro compounds (e.g. liquid DNT) and nitrocellulose or of butyl phthalate and nitrocellulose.

The composition C-3 was later improved and designated Composition C-4. It contains:

91.0% of cyclonite
2.1% of polyisobutylene
1.6% of motor oil
5.3% of di-(2-ethylhexyl)sebacate

It is less volatile than C-3 and has less tendency to harden at low temperature. It has a density of 1.59, does not become hard even at −55°C (−70°F), and does not exude at +77°C (170°F).

For some types of explosive working of metals, plastic sheet explosives EL-506 were developed by E. I. du Pont de Nemours and Co., Inc.

One of the representatives of this group of explosives, EL-506 A, consists of PETN combined with plasticizers to form flexible sheets of 10×20 in., fabricated in a number of thicknesses [68].

The German plastic material Hexoplast 75 was composed of:

75% of cyclonite
3.6–3.8% of TNT
20% of DNT (liquid)
1.2–1.4% of nitrocellulose

The freezing point of a TNT and DNT mixture was −20°C. The ingredients were mixed in a Werner-Pfleiderer kneader at 90°C, the cyclonite with the nitrocellulose being added first and nitro compounds added after thorough mixing. This prevented the formation of lumps of swollen nitrocellulose.

INCOMPATIBILITY IN EXPLOSIVE MIXTURES

It is well known that some ingredients of explosive mixtures should not be brought together, as their mutual reaction produces undesirable changes of the properties of the explosive mixture.

Although a considerable amount of work was done on the compatibility of various components of explosive mixtures no systematic study of this particular problem was made until in 1938 T. Urbański [6] began a series of investigations which comprised examination of mixtures:

(1) By thermal analysis [38, 40].

(2) By determining their chemical stability and ignition temperature, e.g. the stability of nitroglycerine- or PETN-, or nitrocellulose-nitro compound mixtures (Vol. II, pp. 49, 181 and Vol. III, p. 566, respectively) [7].

The influence of various non-explosive substances, such as sulphur, was also examined. It was found that the latter considerably reduces the temperature of ignition of TNT and other high-nitrated aromatic compounds (Vol. I, p. 305)—Fig. 76 [92].

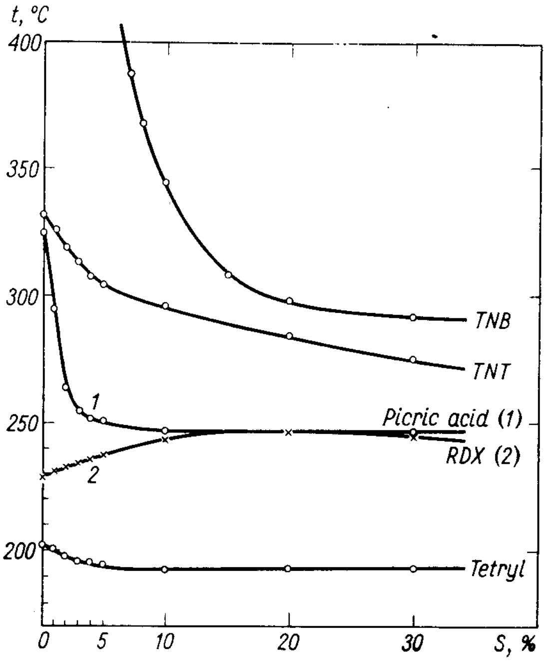

FIG. 76. The influence of sulphur on ignition temperature of nitro compounds and cyclonite (according to T. Urbański and Pillich [92]).

(3) By determining the sensitiveness of mixtures to impact and friction. Foreign crystals were found to increase the sensitiveness of nitro compounds when present in relatively small quantities (e.g. a few percent) [5, 92] — Figs. 66, 68 and 70 (pp. 250, 251 and 262, respectively). On the contrary an addition of soft crystals of wax-like substances is well known to desensitize explosives.

(4) By determining the explosive properties in mixtures [6]; this is discussed on pp. 250–252.

The problem of incompatibility is discussed in various places in this book (e.g. incompatibility of chlorates with ammonium salts, p. 476, Vol. II and p. 278, Vol. III).

The action on TNT of various substances, which may occur in the explosive (e.g. ferric oxide) is described on pp. 304–305, Vol. I.

The action of some inorganic substances on unsymmetrical isomers of trinitrotoluene is mentioned on p. 331, Vol. I.

Another important practical problem is the action of tetranitromethane on TNT (p. 339, Vol. I).

One of the important problems of compatibility in explosive mixtures is whether ammonium nitrate can react with nitro compounds, such as TNT. This was discussed by Lang and Boileau [64]. These authors concluded that no reaction can occur between TNT and ammonium nitrate when they are pure. The evolution of ammonia from ammonium nitrate on storage at room temperature does not suffice to produce any reaction with TNT.

However any alkaline reaction which can be developed by some impurities may produce an evolution of ammonia sufficient to form dark-coloured, readily ignitable products.

Recently Rogers [93] pointed out that two types of incompatibility should be distinguished, otherwise confusion may result. Incompatibility of the first type may be caused by secondary chemical reactions or mobility of residual solvents, gases, or plasticizers, leading to unexpected modifications of mechanical, physical, or electrical properties.

Incompatibility of the second type appears as an unexpected increase in sensitivenes or decrease in thermal stability, and may be caused by any of the foregoing phenomena. Rogers found that zinc reacts readily with ammonium nitrate. He also found that adding 20% urea to RDX reduces the thermal stability of the latter.

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CHAPTER II

LIQUID EXPLOSIVES

HISTORICAL

THE use of explosives obtained from two non-explosive constituents, at least one of which is in the liquid phase, was suggested by Sprengel [1] in 1871. The constituents were mixed just before the explosive was used to avoid the dangers of transport and handling. Nitric acid was one of the liquid constituents, together with liquid or solid aromatic nitro compounds. Such explosives were not, however, successful apart from the Sprengel mixtures in which the oxidizing agent, e.g. potassium chlorate, is a solid constituent; these substances are reviewed on p. 278.

The explosives proposed by Turpin [2], under the name of Panclastites, in which nitrogen dioxide was the oxidizing agent, were more successful.

After the liquefaction of air had been achieved by Olszewski and Wróblewski [3] and on a large scale by Linde [4] the use of liquid oxygen as an oxidizing agent became possible in composite explosives called Oxyliquits (Linde [5]).

Liquid explosives came into extensive use during World War I when nitro compounds and ammonium nitrate became scarce: panclastites were most commonly used for military purposes and oxyliquits in the mining industry. During the World War II the Germans employed liquid mixtures for jet propulsion including a newcomer in this field—a mixture of concentrated (80–85%) hydrogen peroxide with hydrazine for the propulsion of V2 rockets.

MIXTURES WITH NITROGEN DIOXIDE, NITRIC ACID AND TETRANITROMETHANE

Nitrogen dioxide was used in mixtures with such combustibles as paraffin (without aromatic compounds), carbon disulphide or nitrobenzene. These substances were used in the proportions necessary to give complete decomposition into CO_2, H_2O and N_2, thus permitting full utilization of the oxygen present in the nitrogen dioxide. To prevent the solidification of nitrobenzene at low temperatures a binary combustible constituent, e.g. a mixture of nitrobenzene with carbon disulphide, was used.

Kast and Günther [6] examined the explosive properties of these mixtures and found them to be similar to nitroglycerine. They also had its advantages (great power) and disadvantages (high sensitiveness to mechanical stimulants). They differ from nitroglycerine in their lower specific gravity, which obviously contributes to a somewhat lower brisance. A mixture of nitrogen dioxide with 21% by weight of petrol (35% by volume) gives a rate of detonation of 7100 m/sec. A mixture with 35.5% by weight of nitrobenzene (40% by volume) detonates with a rate of 7650 m/sec.

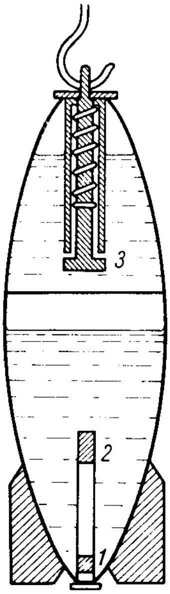


FIG. 77. Aerial bomb filled with liquid nitrogen dioxide (lower compartment) and combustible liquid, e.g. petrol (according to Pascal [7]).

During World War I the French used aerial bombs constructed in such a fashion that the two constituents of the explosive filling were mixed after the bomb had been released. The risk of handling and transporting such a dangerous explosive was thus avoided (Fig. 77). The shell of this bomb was divided into two compartments by a thin partition wall. The lower compartment, fitted with a percussion fuse (*1*) and detonator (*2*) was filled with liquid nitrogen dioxide. A spring hammer (*3*) held back by a hook was located in the upper compartment of the bomb which was filled with petrol immediately before the aircraft had started. On release of the bomb the hammer was unhooked and pierced the partition wall, and at the same time the bomb turned upside down so that the compartment fixed with vanes was uppermost and its contents—nitrogen dioxide (m.p. −10.2°C; b.p. +22°C; density at 0°C 1.4903)—the heavier constituent easily flowed down to mix with the other constituent, i.e. petrol.

The explosives recommended by Hellhoff [8] are also noteworthy. They consist of concentrated nitric acid and dinitrobenzene or a mixture of nitrobenzene with dinitrobenzene. They have not been used very extensively for practical purposes, because their nitric acid content makes them extremely corrosive, but under war-time conditions they were considered to be the cheapest explosives and the simplest to prepare. During World War II they were suggested in Great Britain under the name of Dithekite. According to Cook, Pack and Gay [9] Dithekite-13 or D-13 has the following composition:

24.4% of nitrobenzene
62.6% of nitric acid
13% of water

In liquid mixtures tetranitromethane may be used as an oxidizing agent. A fully oxygen-balanced mixture consisting of 86.5% tetranitromethane and 13.5% toluene has a density of 1.45. It is a powerful explosive (p. 591, Vol. I).

According to Médard and Sartorius [10] the solution of 33.5% dinitrotoluene, 50.0% nitric acid and 16.5% water in a glass tube 30 mm dia. can detonate at the rate of 6700 m/sec. The solution of 47.0% TNT, 50% nitric acid and 3.0% water in an aluminium tube 40/50 mm dia. detonated at the rate of 7500 m/sec.

Andrussow [11] described Nisalit, a mixture of 79.5% nitric acid (99%) with 20.5% acetonitrile. It develops the heat of detonation of 1670 kcal/l., gas volume $V_0 = 708.0$ l./kg and calculated explosion temperature is 4200°K. Its rate of detonation (density 1.27 at 15°C) is 6250 m/sec and its lead block expansion 450 cm^3.

The author suggested another mixture—Disalit:

22% of dimethyl ether
77% of HNO_3
1% of water

He also suggested similar mixtures containing perchloric instead of nitric acid: Niperchlorit and Diperchlorit, respectively.

MIXTURES WITH HYDROGEN PEROXIDE

The Germans used hydrogen peroxide of 80–85% concentration, alone or in mixtures with combustibles, as a fuel for the big V2 rockets during World War II. The utilization of hydrogen peroxide for rocket propulsion and the explosive properties of hydrogen peroxide and its mixtures will be discussed in later sections (pp. 299, 307).

MIXTURES WITH LIQUID OXYGEN (OXYLIQUITS)

These substances are reviewed together with mining explosives. Their use for rocket propulsion will be considered in the section on p. 309.

LIQUID ROCKET PROPELLANTS—PROPERGOLS

The liquid explosives of the type outlined above may serve not only as high explosives but also as propellants for rocket propulsion. Liquids which are not explosives in the strict sense, but which undergo violent decomposition under certain conditions, with heat emission and gas evolution, may also be used for this purpose. The liquids employed for rocket propulsion are called propergols.

The Germans were the first to use them during World War II. The use of concentrated (80–85%) hydrogen peroxide alone, or to a lesser extent, in a mixture with such oxidizing agents as nitric acid, nitrogen dioxide, tetranitromethane, or liquid oxygen, was an innovation.

According to the classification suggested by R. Levy [12] the following types of propergols may be distinguished:

(1) Catergols, i.e. liquids which are decomposable by the action of catalysts, e.g. hydrogen peroxide, decomposed by permanganates.

(2) Hypergols, i.e. systems composed of several (two, at least) liquids which when mixed react spontaneously, usually after a certain induction period (e.g. a mixture of petrol with an admixture of aromatic amines which reacts spontaneously with nitric acid). For practical purposes the induction period of hypergols should be as short as possible—at any rate shorter than 0.1 sec.

Propergols may also be classified according to their homogeneity:

(1) Monergols, i.e. monophase systems composed of at least two components, one of which is an oxidant, the other a fuel, e.g. a solution of methyl nitrate (oxidant) with methyl alcohol (combustible).

(2) Lithergols, i.e. polyphase, at least biphase systems, one of the phases being liquid, another solid, e.g. carbon and liquid oxygen.

MIXTURES WITH NITROGEN DIOXIDE

Nitrogen dioxide can be used together with a combustible substance as a liquid propellant (propergol) for rockets. A mixture of hydrocarbons e.g. petrol or paraffin, may serve as the fuel.

On explosive decomposition the stoichiometric mixture of N_2O_4 with paraffin gives a considerable amount of heat: approximately 1560 kcal/kg.

Since the course of interaction of nitrogen dioxide and paraffin may often be too slow, to facilitate and speed it up a substance that readily reacts with nitrogen dioxide, e.g. aniline, should be added to the paraffin.

Nitrogen dioxide is noteworthy as an oxidant rich in oxygen (it contains 69.5% by weight of oxygen and 1.01 kg of oxygen per 1 l. of substance). However, the physico-chemical properties of nitrogen dioxide, such as its relatively high freezing point (−10.2°C) and a low boiling point (+22°C) limit its direct use as an oxidant.

On the other hand, nitrogen dioxide has proved to be a valuable component of propergolic mixtures in which nitric acid is an essential oxidant. Nitric acid containing approximately 20% N_2O_4 is a particularly valuable oxidant as explained below.

MIXTURES WITH NITRIC ACID

Mixtures of concentrated nitric acid with combustible substances have recently found wide application as liquid propellants for rockets (propergols).

The first attempts to use them were made by the Germans during World War II.

Nitric acid has many advantages as a component of these mixtures, being readily available from large-scale manufacture.

The physico-chemical properties of the chemically pure substance are described in Vol. I, p. 6.

The high specific gravity of nitric acid, its high oxygen content (76% by weight), low freezing and negative heat of formation all are very advantageous for its use as an oxidant in propergols. Its disadvantage lies in its corrosive action.

For practical purposes commercial nitric acid, containing 2–4% of water, is employed. Its freezing point is lower than that of the pure form (a 10% content of water in HNO_3 lowers the freezing point to $-68.5°C$; a higher content of water lowers this temperature to a lesser extent). Propergols containing nitric acid belong to the hypergol group, i.e. the mixtures which react spontaneously.

Since the reaction of nitric acid alone with a fuel such as petrol or paraffin occurs fairly slowly with a long induction period (longer than 0.1 sec) various substances are added to the nitric acid or the hydrocarbon component to speed up the reaction or induce its spontaneous initiation.

Since nitric acid, especially "red" fuming nitric acid "RFNA" which contains a small amount of nitrogen oxides, reacts vigorously with aromatic amines, during World War II the Germans employed solutions of these amines (e.g. aniline or phenylenediamine) in benzene or xylene as the combustible component. They added a small amount of ferric chloride as a reaction catalyst to the nitric acid. It was also shown that the addition of vinyl ethers to amine solutions reduces the induction period.

To improve the properties of nitric acid as a component of propergols the following admixtures were used, or recommended:

(1) Nitrogen dioxide. This substance alone may be used as an oxidant, though it has some disadvantages, as outlined above. The addition of nitrogen dioxide to nitric acid facilitates enormously the reaction of the latter with many organic compounds, including amines. Moreover it also lowers the freezing point of the nitric acid. The lowest freezing point ($-73°C$) is attained by a solution composed of 82% HNO_3 and 18% N_2O_4. Nitric acid containing 20% N_2O_4 is employed most frequently.

According to Canright [13] nitric acid becomes "stabilized" by the presence of nitrogen dioxide and water. Such nitric acid remains unchanged during prolonged storage at an elevated temperature.

(2) Mineral acids. Corrosion by nitric acid can be reduced by the addition of sulphuric acid (up to 10%).

It was found (according to Canright [13]) that the addition of small amounts of hydrogen fluoride to nitric acid considerably reduces its corrosive action on aluminium and stainless steel since these metals become coated with a layer of fluorides.

(3) Mineral salts accelerating the combustion reactions. Apart from ferric chloride, which was discussed above, the use of other salts has also been suggested. Grollier-Baron and Wessels [14], for instance, suggest the addition of 4% potassium dichromate to nitric acid in non-hypergolic propergols formed from nitric acid and petrol. According to these authors, at a temperature of 670°C and when the reagents are injected into the combustion chamber at a rate of 10.3 m/sec, a mixture of nitric acid with petrol is ignited after 23 millisec; at an injection rate of 6.6 m/sec ignition occurs after 33 millisec. At 920°C and an injection rate of 6.6 m/sec the induction period is 31–35 millisec.

If nitric acid with 4% potassium dichromate is used at 650°C and the injection rate is 10.3 m/sec, the induction period is 5.5 millisec and at an injection rate of 5.3 m/sec it is 3.6 millisec. At 850°C and a rate of 6.6 m/sec the induction period is shorter than 1 millisec.

In mixtures containing nitric acid various fuels may be employed. Fuels used for hypergolic ones, i.e. those which autoignite on mixing, differ essentially from those used in other mixtures. In hypergolic mixtures, fuels are used which reac. violently with nitric acid, e.g. aliphatic or aromatic amines, furfuryl alcohol, mercapttans, hydrazine etc. It is also advisable to add surface-active substances to the mixture-

Fuels for mixtures with nitric acid

The following fuels are already in use or recommended for employment in mixtures with nitric acid.

Aliphatic hydrocarbons: petrol, paraffin. In the U.S.A. several types of combustibles for liquid propellant jet aircraft are used. One of them, i.e. JP-4, is employed for rocket propulsion, with nitric acid as an oxidizing agent (it can also be used with hydrogen peroxide or liquid oxygen). The specification of JP-4, is as follows:

Specific gravity at 15.5°C	0.764
Vapour pressure at 38°C	134–160 mm Hg
Fractionation:	
10% distills up to	84–102°C
50% distills up to	142–147°C
90% distills up to	209–227°C

Content of aromatic hydrocarbons	10–12%
Bromine number	1.4
Aniline point	58°C
Ignition point	−13.8°C
Freezing point	−60°C
Heat of combustion	10,400 kcal/kg

Aliphatic hydrocarbons are seldom used separately due to their relatively sluggish reaction with nitric acid. The ignition capacity of hydrocarbons may be increased by dissolving in them aromatic amines or, as the Germans did in earlier experiments, vinyl ethers.

The effect of aromatic amines, however, has been the subject of much controversy. Thus, according to Crollier-Baron and Wessels [14] the addition of 10% aniline to petrol has no obvious influence on the length of the induction period. E.g. if nitric acid containing 4% potassium dichromate is used with petrol containing 10% aniline at 620°C, and a rate of injection is 10.3 m/sec, the induction period is 3.3 millisec; at a rate of injection of 5.3 m/sec it is 24 millisec.

Amines. Amines were the first ingredients to be used in hypergols. A mixture of 50% xylidine with 50% triethylamine is the most widely used.

According to Fedosyev and Sinyaryev [15] this mixture, with 98% nitric acid in stoichiometric proportions has the following physico-chemical constants:

Specific gravity	1.32
Heat of reaction	1500 kcal/kg or 1800 kcal/kg
Gas volume	784 l./kg
Explosion temperature approximately	2710°C

Amines with furfuryl alcohol. The commonest of these mixtures is that with 80% aniline and 20% furfuryl alcohol. Fedosyev and Sinyaryev quote the following values characteristic of this mixture with nitric acid:

Specific gravity	1.39
Heat of reaction	1520 kcal/kg or 1900 kcal/kg
Gas volume	756 l./kg
Explosion temperature approximately	2780°C

Barrère and Moutet [16] suggest the following mixtures which form hypergols with nitric acid:

(1) 25% aniline and 75% furfuryl alcohol
(2) 25% dimethylaniline and 75% furfuryl alcohol
(3) 25% toluidine and 75% furfuryl alcohol
(4) 25–50% xylidine and 75–50% furfuryl alcohol
(5) 25% diethylamine and 75% furfuryl alcohol
(6) 25% triethylamine and 75% furfuryl alcohol

Mixtures (2) and (4) react most easily. They have the shortest induction periods, of 18 and 20 millisec, respectively.

The least reactive are mixtures (5), (6) and particularly (2), with induction periods of 55, 61 and 96 millisec, respectively.

The same authors studied a mixture of nitric acid with furfuryl alcohol. In reactivity it occupies a position midway between the above mentioned groups with an induction period of 33 millisec. Similar results were obtained by Kilpatrick and Baker [17] when studying the reaction of furfuryl alcohol with colourless nitric acid.

Mercaptans. McCullough and Jenkins [18] investigated the possibility of the use of mercaptans, by-products of petroleum refining. The mixture of mercaptans contains as chief ingredients:

Propyl mercaptan	27.8% mol.
Butyl mercaptan	65.3% mol.
Amyl mercaptan	6.6% mol.

and traces of hexyl mercaptan.

They employed 96.5% nitric acid or an acid containing 22% of N_2O_4 and 1% of water. The experiments indicated that mercaptans could be used as the combustible component in nitric acid hypergols.

Hydrazine. Concentrated hydrazine (96%) reacts spontaneously with nitric acid. According to Kilpatrick and Baker [17] reaction with 96% colourless nitric acid occurs with a delay of 5.0 ± 1.7 millisec, whereas with fuming nitric acid (containing 24% N_2O_4) there is a delay of 3.1 ± 1.4 millisec. Hydrazine of 71.5% concentration gives a delay of about 37 millisec with either acid.

In another series of experiments on using a molar ratio $\frac{HNO_3}{N_2H_4} = 2.87$ and a rate of injection of 9.2 m/sec these authors obtained an induction period of 0.2 millisec.

In addition to the foregoing tests they examined the possibility of using liquid ammonia with an admixture of 9 or 14% hydrazine as a combustible component in a mixture with nitric acid containing 24% N_2O_4. The induction period was 14 or 6–10 millisec, respectively.

The properties of hydrazine including its explosive properties will be discussed further.

Ammonia. Lewis, Pease and H. S. Taylor [19] and Altman and Penner [20] showed that the system liquid ammonia–nitric acid may be transformed into a hypergolic system by the addition of an alkali metal, e.g. lithium, to the ammonia.

Surface-active substances. Bernard's [21] investigations showed that the addition of surface-active substances (wetting agents) to the fuel may reduce the induction period prior to the ignition of hypergols.

The author quotes the following figures which illustrate the effect of the addition of sodium alkyl sulphate on the induction period of a mixture of furfural with 98% nitric acid:

Mixture without additions	29.9 millisec
Addition of 0.5% sodium alkyl sulphate to furfuryl alcohol	14.4 millisec
Addition of 0.5% sodium alkyl sulphate to nitric acid	22.7 millisec

TABLE 63

CHARACTERISTIC PROPERTIES OF FUELS WITH NITRIC ACID ACCORDING TO BELLINGER, FRIEDMAN, BAUER, EASTES AND BULL [22]

Composition	Content of combustibles %	Heat of reaction kcal/kg	Density	Pressure in combustion chamber atm	Flash point °C	Specific impulse sec*
Nitric acid (60%)+nitrogen dioxide (40%)+aniline		1535	1.45	20	2707	225
Nitric acid+aniline	26.6	1440		21	2760	218
Nitric acid+furfuryl alcohol	34.5		1.37	21	2620	214
Nitric acid+hydrazine	38.5		1.28	21		243

* The specific impulse I_S is measured in kg (or lb) of pressure exerted by kg (or lb) of fuel per sec. Hence specific impulse is expressed in seconds.

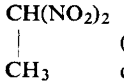
Nitroparaffins. Nitroparaffins, such as nitromethane and tetranitromethane, may also act as constituents of propergols, although there is obviously an essential difference in employing these two substances, resulting from their chemical and explosive properties.

Nitromethane (Vol. I, p. 579) may be used as a monergol propellant. However its negative oxygen balance may be reduced by the addition of liquid oxidants, e.g. of tetranitromethane to form a bipropellant. In practice, however, nitromethane decomposes too slowly, and it is difficult therefore to obtain hypergolic mixtures from it. To facilitate and accelerate the decomposition of mixtures with nitromethane it is necessary to add a catalyst, such as a salt of chromic acid.

Higher nitroparaffins such as nitroethane, and 2-nitropropane may be used as constituents of rocket propellants but rather in the capacity of a fuel, e.g. in mixtures with nitric acid, hydrogen peroxide, or liquid oxygen. Research by Tait, A. E. Whittaker and Williams [23] showed that the combustion of stoichiometric mixture of 2-nitropropane with 98% nitric acid in a closed bomb is maintained spontaneously under pressure above 10 atm. The rate of burning depends on the pressure. For pressures in the ranges 14–70 and 70–140 atm (Fig. 78) the increase in rate of burning as a function of pressure differs significantly. This indicates a difference in the mechanism of the combustion reaction at these two pressure ranges.

Among other nitroparaffins isomeric dinitroethanes are also recommended (Wood [24]):

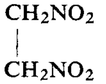
asymmetric



$$\begin{array}{l} CH(NO_2)_2 \\ | \\ CH_3 \end{array}$$

(liquid, b.p. 185°C, density 1.35)

and symmetric



$$\begin{array}{l} CH_2NO_2 \\ | \\ CH_2NO_2 \end{array}$$

(m.p. 40°C, b.p. 135°C, density 1.46)

These substances have explosive properties and may be employed as monopropellent propergols. However, symmetric dinitroethane does not seem to be stable enough (Vol. I, p. 394).

Tetranitromethane is of a different nature, being largely an oxidant.

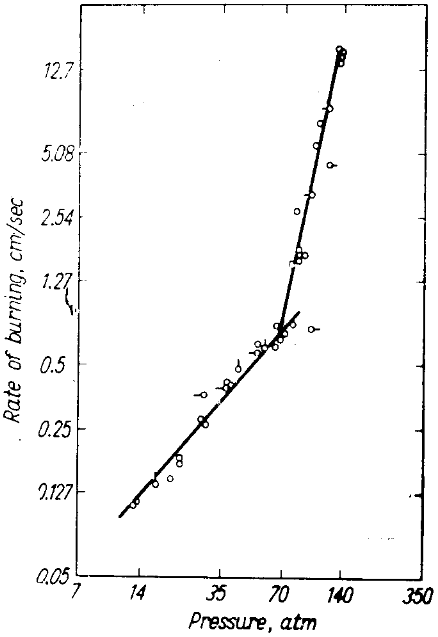


FIG. 78. The relation between the rate of burning of the stoichiometric mixture of 2-nitropropane with nitric acid and the pressure (according to Tait, A. E. Whittaker and Williams [23]).

During World War II the Germans experimented with liquid mixtures consisting of tetranitromethane and combustibles as a liquid fuel for the propulsion of the big V2 rockets.

The greatest advantage of tetranitromethane as an oxidant lies in its high density (1.64 at 20°C). With its high content of oxygen (65.3% by weight) and high density, one litre of tetranitromethane contains 1.07 kg of oxygen, i.e. slightly less than liquid oxygen at a temperature of −183°C (1.14 kg of oxygen per litre). Considering that a molecule of tetranitromethane itself contains a certain amount of combustible material in the form of a carbon atom, it is possible to calculate the oxygen content in the oxidizing part of the molecule only, i.e. in NO_2 groups. According to the calculations of Tschinkel [25] the density of nitro groups in tetranitromethane is 1.484 at a boiling point of 126°C, and the oxygen content 1.16 kg per one litre of nitro groups, i.e. higher than liquid oxygen alone.

Owing to these properties a mixture of tetranitromethane with paraffin is preferable to mixtures containing other oxidizing agents. The explosive decomposition of the tetranitromethane mixtures with petroleum hydrocarbons in stoichiometric proportions gives a high heat effect, viz. 1620 kcal/kg (according to Fedosyev and Sinyaryev [15]).

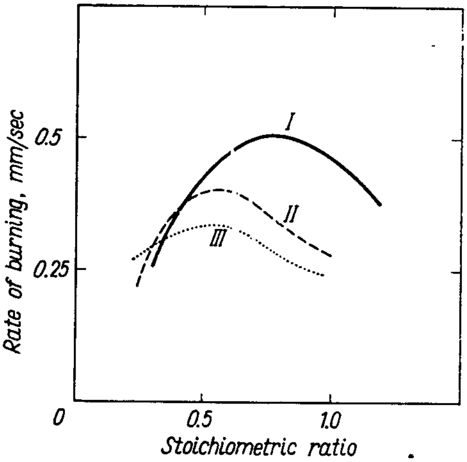


FIG. 79. The rate of burning of mixtures of tetranitromethane with hydrocarbons: *I*—cyclohexane, *II*—iso-octane and *III*—n-heptane (according to Behrens [27]).

The disadvantage of tetranitromethane lies in its high freezing point (+13.8°C). The Germans suggested lowering this temperature by the addition of nitrogen dioxide which, with 20% N_2O_4, freezes at −14°C, and with 35% N_2O_4 at −30°C. Finally, they evolved a mixture for V2 propulsion having a composition: 30% N_2O_4 and 70% tetranitromethane.

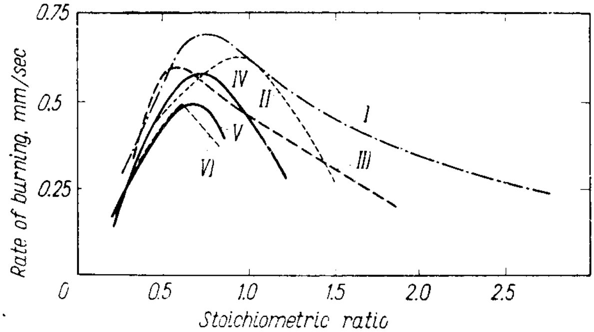


FIG. 80. The rate of burning of mixtures of tetranitromethane with alcohols: *I*—n-hexanol, *II*—n-octanol, *III*—n-butanol, *IV*—n-propanol, *V*—isopropanol, *VI*—isobutanol (according to Behrens [27]).

The disadvantages of this mixture are its high vapour pressure resulting from the low boiling point of nitrogen dioxide, and its erosiveness.

According to Hannum [26] tetranitromethane mixtures with nitromethane are desirable for practical purposes. E.g., a mixture containing 10% nitromethane freezes at 0°C, whereas with 20% nitromethane the freezing point is −14°C, and with 35% nitromethane it is low as −30°C.

Among other additives, methyl nitrate (Tschinkel [25]) may be employed, or substances safer to handle, such as methanol and ethylene glycol monoethyl ether.

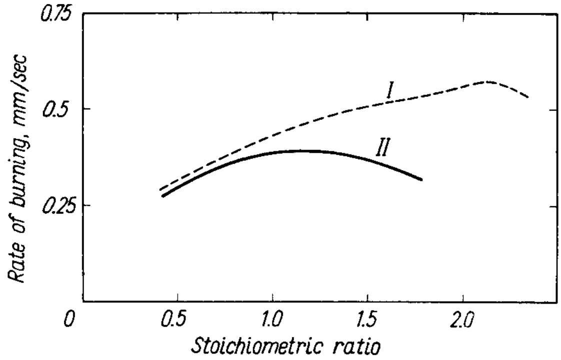


FIG. 81. The rate of burning of mixtures of tetranitromethane with benzaldehyde (*I*) and nitrobenzene (*II*) (according to Behrens [27]).

Behrens [27] examined the rate of burning in glass tubes of 5.5 mm dia. of several mixtures of tetranitromethane with a number of organic substances: hydrocarbons, alcohols and aldehydes. All mixtures showed a maximum of the rate of burning at a certain stoichiometric ratio. Figures 79, 80 and 81 give typical curves of mixtures with hydrocarbons, alcohols and benzaldehyde or nitrobenzene, respectively.

Schwob [28] made an extensive study of burning and detonation of mixtures of tetranitromethane and petrol. He found that burning can pass to detonation when the tetranitromethane content is 65–95%. The burning of these mixtures should be considered as dangerous.

However, the limits of explosibility of the mixtures under the action of detonators or impact are much wider: only the mixtures with tetranitromethane content below 40% should be considered as non-explosive.

Hazards associated with the large-scale manufacture of tetranitromethane seriously hinder its use (the plant at Newark, in the U.S.A., which had produced tetranitromethane on a semi-commercial scale, blew up in 1953 and was never rebuilt, so production had to be discontinued).

HYDROGEN PEROXIDE

H_2O_2

Among oxidants hydrogen peroxide is one of the richest in oxygen. Pure H_2O_2 contains 47% of available oxygen. A method for the preparation of concentrated aqueous solutions of hydrogen peroxide, containing 80–85% H_2O_2, has been worked out since 1943 in Germany by Elektrochemische Werke at Munich. During World War II these solutions were manufactured on an industrial scale under the name of "T-Stoff", either as an oxidant in rocket fuel or (to a less extent) a mono-propellant fuel—cathergol.

The specific gravity of an 80% solution of hydrogen peroxide is 1.34. The solution is fairly stable at room temperature and decomposes only at an elevated temperature (the stability of hydrogen peroxide will be descussed later). To increase the stability of this solution, stabilizing substances such as phosphoric acid and its salts or 8-hydroxyquinoline were added.

The manufacture of 90% hydrogen peroxide was started after World War II in the U.S.A. and Great Britain.

N. S. Davis and Keefe quote the following physico-chemical constants characteristic of 90% hydrogen peroxide [29]:

Specific gravity at 20°C	1.39
Viscosity at 18°C	11.62 cP
Vapour pressure at 30°C	5 mm Hg
Freezing point	−11.1°C
Boiling point	175°C
Heat of formation ($-\Delta H_f$)	
of liquid	45.16 kcal/mole
of vapour (100% H_2O_2)	33.29 kcal/mole
Specific heat (between 0 and 18.5°C)	0.58 cal/g°C
Heat of vaporization	*ca.* 330 kcal/kg
Surface tension at 18°C	75.53 dyne/cm
Conductivity at 25°C	
of the chemically pure product	2×10^{-6}
of a commercial product	10×10^{-6}
Refractive index at 20°C	1.398
Non-volatile residue in a commercial product	0.005%

(Thermal analysis of the system hydrogen peroxide–water is given on Fig. 82.)

Chemically pure hydrogen peroxide can be stored for a long time without noticeable decomposition. Loss on storage of hydrogen peroxide may amount to 1% per annum.

Shanley and Greenspan [31] report the following relationship between the decomposition of 90% hydrogen peroxide and temperature (Table 64).

TABLE 64

Temperature °C	Approximate rate of decomposition
30	1% per annum
66	1% per week
100	2% per 24 hr
140	Rapid decomposition

Slight amounts of impurities may accelerate the decomposition enormously. The effect of various substances on the decomposition of 90% hydrogen peroxide at 100°C is tabulated below.

TABLE 65

Substance added	Quantity added mg/l.	Loss of H_2O_2 over 24 hr at 100°C %
Without additive	—	2
Al^{3+}	10	2
Sn^{4+}	10	2
Cr^{3+}	0.1	96
Cu^{2+}	0.1	85
Fe^{3+}	1.0	15
Zn^{2+}	10	10

(On the accelerating action of hydrogen on H_2O_2—vapour see p. 303.)

Hydrogen peroxide is more stable in an acidic medium than in an alkaline one, and acids are therefore used as stabilizers. Apart from phosphoric acid, already mentioned, boric acid, oxalic acid etc. may also be used.

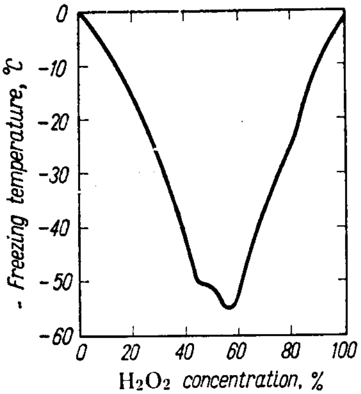


FIG. 82. Freezing temperatures of binary system H_2O_2–H_2O [30].

Experiments have shown that the best construction material for the storage of hydrogen peroxide is high purity (99.6%) aluminium. Aluminium containers should be thoroughly cleaned to remove any traces of organic impurities, and washed first with a solution of caustic soda and then with water and 10% sulphuric acid, over a period of several hours. Finally the acid is washed out with distilled water, after which it is desirable to re-wash the container with hydrogen peroxide. Tanks and containers for hydrogen peroxide should be provided with safety valves, that are ruptured by the excessive pressure produced if the peroxide decomposes.

Special care should be taken to prevent hydrogen peroxide from coming into contact with copper, chromium and lead.

Fittings, pumps, and pipelines can be made of certain types of stainless steels which can be allowed to remain in contact with hydrogen peroxide for relatively short periods, i.e. a few days.

A number of polymers, in particular teflon, polyvinyl chloride and, to a lesser extent, polyethylene do not provoke the decomposition of peroxide.

If, as a result of the presence of some impurities in a vessel containing hydrogen peroxide, decomposition is hastened, it is advisable to add an additional quantity of stabilizer, i.e. phosphoric acid. If this proves inadequate, then, according to Shanley and Greenspan [31], it is necessary to dilute the hydrogen peroxide with water to 67% concentration when it is no longer dangerous, otherwise, violent decomposition may occur and the container may blow up.

When handling large quantities of hydrogen peroxide it is necessary to wear protective goggles, overalls made of protective fabric (an apron of polyvinyl chloride), rubber gauntlets and boots, since severe burns are caused if it comes into contact with the skin.

As previously mentioned, concentrated hydrogen peroxide is used as a cathergol-type monopropellant fuel.

During World War II the Germans employed 80–85% hydrogen peroxide for launching pilotless V2 aircraft and for bringing into operation a mechanism feeding the oxidant and the combustible from their storage tanks into the combustion chambers of V1 aircraft and V2 rockets. This application is based on the decomposition reaction of hydrogen peroxide:

$$H_2O_2 = H_2O + \tfrac{1}{2}O_2 + 23.45 \text{ kcal/mole (690 kcal/kg)} \qquad (1)$$

Decomposition was initiated by the addition of a concentrated aqueous solution of calcium and sodium permanganate to the hydrogen peroxide. The use of potassium permanganate proved ineffective since $KMnO_4$ is insufficiently soluble in water and the solution contains inadequate $MnO_4^{\ominus}$-ions for rapid initiation of the reaction.

According to Ley [32] the British "Sprite" rocket serving the A.T.O. (assisted take-off) of the "Comet" jet aircraft has a similar propulsion unit, i.e. it contains a charge of 136 l. of hydrogen peroxide and about 9.5 l. of a catalyst solution, most probably permanganate.

The use of hydrogen peroxide as a mono-propellant of the cathergol type is based on the following thermochemical data for hydrogen peroxide of 86 and 100% concentration (by weight) (Wood [24], Table 66).

As these characteristics show, the heat of decomposition is considerably higher than the heat of vaporization. The vapour so produced is superheated and, at the same time the temperature of adiabatic decomposition is high enough to make possible a useful expansion of gases. The efficiency of such a fuel, however, is negligible. Its specific impulse does not exceed 130 sec.

A considerable amount of work [33] was dedicated to studying the mechanism of decomposition of hydrogen peroxide in the vapour phase. It was soon recognized that the difficulty of obtaining reproducible results is due to the action of the vessel surface producing the heterogeneous reaction. Baldwin and Mayor [34] have shown that the kinetics of the slow reaction between H_2 and O_2 in aged boric acid-coated vessels could only be explained by assuming that the aged surface was extremely inert to both HO_2 and H_2O_2. Baldwin and Brattan [35] studied the reaction of gaseous decomposition of hydrogen peroxide in an aged boric acid-coated vessel over a range of temperatures 260–520°C. They found the decomposition and the dependence of rate on total pressure being of the first order.

TABLE 66

THERMOCHEMICAL DATA FOR HYDROGEN PEROXIDE

Item	Concentration (%)	
	86	100
Heat of decomposition (kcal/kg)	600	690
Heat of vaporization (kcal/kg)	395	370
Adiabatic decomposition temperature (°C)	650	980
Gas volume on complete adiabatic decomposition (l.)	4900	6400

The results are in agreement with the work of Giguère and Liu [36], Forst [37] and Hoare *et al.* [38].

Baldwin and Brattan also found that the addition of hydrogen to H_2O_2 vapour considerably increases the rate of decomposition of the latter.

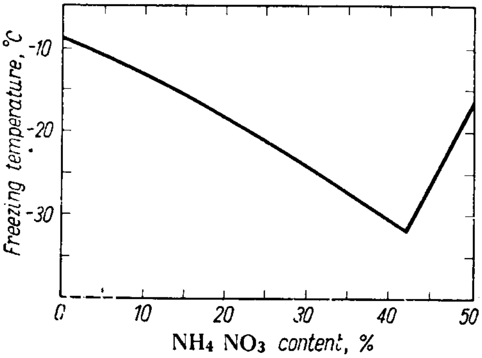


FIG. 83. Freezing temperatures of binary system H_2O_2–NH_4NO_3 [30].

Concentrated hydrogen peroxide was widely used during World War II as an oxidant in a mixture with hydrazine hydrate, for the propulsion of V2 rockets. Hydrogen peroxide mixed with hydrazine reacts spontaneously according to the equation:

$$2H_2O_2 + NH_2NH_2\cdot H_2O \longrightarrow 5H_2O + N_2 + 188\ \text{kcal} \qquad (2)$$

As reaction is preceded by a certain delay, this induction period was reduced by the addition of copper salts, e.g. potassium cuprocyanide $K_3Cu(CN)_4$. This substance was supplied to the system dissolved in the hydrazine hydrate. It was found that potassium cuprocyanide reacts with hydrazine even at room temperature to form metallic copper which, if deposited in the pipelines, may cut off the flow of hydrazine into the combustion chamber. To prevent this the system was modified so that hydrazine hydrate flowed from the tank into the combustion chamber through a cartridge containing cupric nitrate, which dissolved in hydrazine hydrate in a sufficient quantity to accelerate the reaction (hydrazine and its reaction with H_2O_2 will be discussed in more detail further on).

During World War II the Germans used a mixture of hydrogen peroxide with Diesel oil in torpedo and submarine propulsion.

An idea of considerable interest advanced by Paushkin [30] was the use of a solution of ammonium nitrate in concentrated hydrogen peroxide as an oxidant. A solution consisting of 40% NH_4NO_3 and 60% of 92% hydrogen peroxide seems to be particularly attractive. Its freezing point is approximately —30°C (Fig. 83).

Explosive properties of hydrogen peroxide and its mixtures

The exothermic character of the decomposition of hydrogen peroxide indicates that hydrogen peroxide itself may have explosive properties. In fact 99.6% hydrogen peroxide gives a lead block expansion of 75–80 cm³. In a steel tube with 34–40 mm

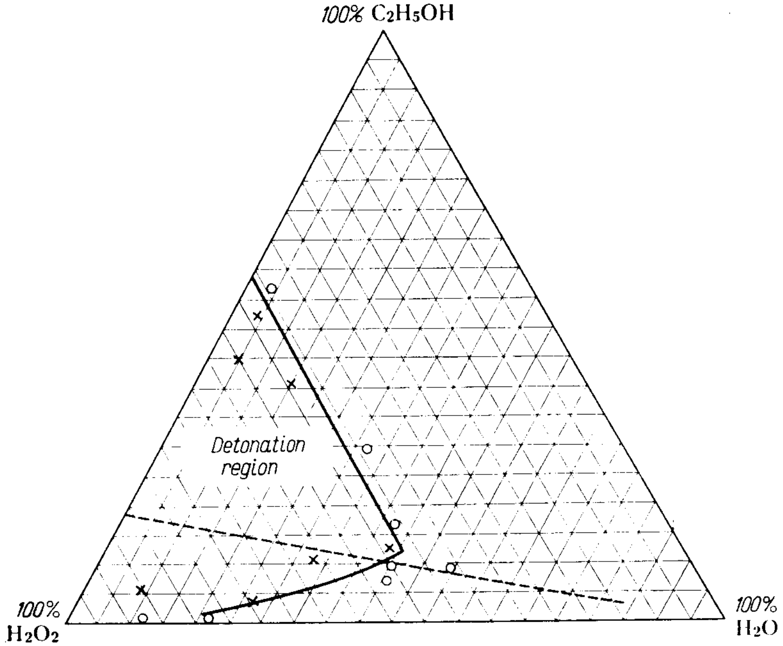


FIG. 84. Diagram of explosive properties of ternary mixtures H_2O_2–H_2O–C_2H_5OH, according to Shanley and Greenspan [31]; × — detonation, ○ — no detonation.

dia. 94–100% hydrogen peroxide detonates completely when initiated with 50 g of compressed pentaerythritol. With 92% hydrogen peroxide, however, detonation is propagated only to 100 mm along the tube, away from the detonator.

Ninety per cent hydrogen peroxide does not detonate at all (Paushkin [30]).

Investigations into the explosive properties of ternary mixtures of hydrogen peroxide and water with various organic substances, carried out by Shanley and Greenspan [31], aroused much interest. On the basis of their results triangular diagrams may be constructed for a number of systems: (a) hydrogen peroxide, (b) water, (c) organic substance (such as ethanol, glycerine, acetone). In Fig. 84 a typical diagram is shown, characteristic of mixtures with ethanol. The other diagrams are very similar. In general, only mixtures containing a limited amount of water possess explosive properties.

All the three organic substances mentioned above, when dissolved in 80% H_2O_2, give mixtures detonated by a detonating cap and a booster with a rate of about 7000 m/sec, which drops to 2300 m/sec as the concentration of hydrogen peroxide is reduced. When weakly initiated they detonate with a rate of 750 m/sec only (Schumb, Satterfield and Wentworth [39]).

A monograph on hydrogen peroxide was written by Schumb, Satterfield and Wentworth [39].

HYDRAZINE

Physico-chemical and explosive properties

Anhydrous hydrazine melts at 2°C and boils at 113.5°C, its density is 1.0253 g/cm^3 (Walden and Hilgert [40]); 1.0231 (Semishin [41]).

With water it forms hydrazine hydrate $NH_2 \cdot NH_2 \cdot H_2O$ with a melting point of -51.7°C and a density d_4^0 of 1.048 (Semishin).

Hydrazine is an endothermic substance. The heats of formation $-\Delta H_f$ of anhydrous hydrazine and the hydrate are, according to Hughes, Gilbert *et al.* [42]:

N_2H_4 liquid -12.0 kcal/mole
$N_2H_4 \cdot H_2O$ -10.2 kcal/mole

Roth [43] found the heat of formation of liquid hydrazine at 25°C to be $-\Delta H_f = 13.8$ kcal/mole.

According to Hughes, Gilbert *et al.* the heat of combustion of the anhydrous substance (liquid) is $-\Delta H_c = 148.6$ kcal/mole.

Anhydrous hydrazine burns in air. On heating hydrazine above boiling point, thermal decomposition of gaseous hydrazine takes place at 250–310°C (Elgin and Taylor [44]; Askey [45]). Bamford [46] ascertained that hydrazine is decomposed by an electrical spark, while Elgin and Taylor established that hydrazine vapour is decomposed by ultra-violet irradiation (also Wenner and Beckmann [47]).

According to Bamford, the thermal decomposition and explosion of hydrazine is expressed by equations in which free radicals are present:

(I)
$$N_2H_4 \rightarrow 2NH_2 \quad (1)$$
$$NH_2 + N_2H_4 \rightarrow NH_3 + N_2H_3 \quad (2)$$
$$2N_2H_3 \rightarrow N_2 + 2NH_3 \quad (3)$$

(II)
$$N_2H_4 \rightarrow 2NH_2 \quad (1)$$
$$NH_2 + N_2H_4 \rightarrow NH_3 + N_2H_3 \quad (2)$$
$$NH_2 + N_2H_3 \rightarrow N_2 + H_2 + NH_3 \quad (3)$$

In addition, side reactions may occur:

(III)
$$N_2H_4 \rightarrow 2NH_2 \rightarrow N_2+2H_2$$

(IV)
$$N_2H_4 \rightarrow 2NH_2$$
$$2NH_2 + N_2H_4 \rightarrow 2N_2 + 4H_2$$

In spite of the ease with which the decomposition of hydrazine has been established, its explosive properties have been not established with certainty.

In relatively recent times Scott, Jones and Lewis [48] made detailed studies of the explosive properties of hydrazine and 85% hydrazine hydrate. In the drop test, neither hydrazine nor hydrazine hydrate were exploded by a very strong blow (5 kg from 1 m height). Hydrazine and its hydrate are also insensitive to friction. The authors' attempts to determine the rate of detonation of hydrazine in pipes also failed since hydrazine is initiated by a detonator with difficulty. The reaction in the ballistic pendulum, of charge of anhydrous hydrazine initiated by No. 8 detonator, was 135% of that produced by TNT. Under these conditions hydrazine hydrate does not detonate at all.

Scott, Jones and Lewis examined the ignitability of hydrazine and hydrazine hydrate by various means.

TABLE 67

Material from which the vessel is made	Atmosphere	Hydrazine		85% hydrazine hydrate	
		Ignition temperature °C	Induction period sec	Ignition temperature °C	Induction period sec
Pyrex glass	Air	270	3.9	292	4.2
	Oxygen	204	4.9	218	5.3
Platinum	Air	226	3.0	338	3.8
	Oxygen	30	6.0	132	19.7
Fe_2O_3 (powdered in a glass vessel)	Air	23	0.0	—	—
	Nitrogen	23	0.0	—	—
Iron	Air	132	0.0	—	—
	Nitrogen	131	0.0	—	—
Stainless steel	Air	160	2.0	—	—
	Nitrogen	415	0.9	—	—

They established that an electrical spark having an energy of 12.5. J when passed through unconfined liquid hydrazine produces no signs of decomposition. Conversely, hydrazine or its hydrate in a confined space undergoes explosive decomposition under the influence of a spark stronger than 2.63 J.

In an atmosphere of oxygen the ignition of hydrazine (but not its hydrate) takes place at a lower temperature than in air. The ignition temperature is strongly influenced by the material of which the hydrazine container is made.

The authors' [48] numerical data are collected in Table 67. They are valuable indications of the safety measures which should be observed in the storage, transportation and handling of hydrazine. It can be contained in vessels of glass and stainless steel, but under no circumstances in those made of iron. Aluminium containers are also acceptable.

The experiments of Scott, Jones and Lewis on the limits of ignitability of hydrazine vapours are also of great importance. The figures obtained by these authors are tabulated below (Table 68).

The ignition of the gaseous mixture was brought about by an electrical spark.

TABLE 68

Composition of gaseous mixture	Content of (%)		Pressure mm Hg	Temperature °C
	Hydrazine	Other component		
Hydrazine–air	4.67	95.33	757–758	92–101
Hydrazine–nitrogen	38.0	62.0	754	109–112
Hydrazine–helium	37.0	63.0	756–758	105–118
Hydrazine–water vapour	30.9	69.1	689–889	130–135
Hydrazine–heptane	86.8	13.2	404–327	104–133

Hydrazine is a highly toxic substance, injurious to the sight, causing temporary blindness. The lethal dose (LD_{50}) for dogs is approximately 0.05 g/kg of body weight. Salts of hydrazine provoke hyperglycaemia, blood clotting due to dehydration and liver damage.

According to Raciborski [49] some moulds can assimilate hydrazine.

A monograph by Audrieth and Ogg [50] is dedicated to hydrazine.

Oxidation of hydrazine by hydrogen peroxide

This most important reaction—the oxidation of hydrazine—has not yet been investigated fully. Work on the subject has consisted mainly of studies of the kinetics of the process in dilute aqueous solutions. Gordon [51], studying the kinetics of decomposition of hydrazine and hydrogen peroxide, found that the reaction rate depends to a great extent on the pH. Its peak value is reached at pH = 10–11.

The addition of cobaltic sulphate to the reaction system raises the reaction rate considerably.

Concentrated hydrogen peroxide does not react instantly with hydrazine hydrate, only after a certain induction period. This has been the cause of a number of explosions and accidents, produced by the accumulation of unchanged components and their sudden reaction after the induction period has elapsed.

As previously stated, the addition of a copper salt to hydrazine reduces the induction period practically to zero. The addition of sodium nitroprusside exerts a similar influence.

According to McLarren [52] a mixture with methyl alcohol has frequently been used in rockets, to react with hydrogen peroxide. E.g. in the HWK-59 jet propulsion engine and BP-20 rocket missiles 80% hydrogen peroxide is used as an oxidant together with a combustible consisting of:

Hydrazine hydrate	30%
Methyl alcohol	57%
Water	13%

0.11% of $K_3Cu(CN)_4$ is added to the fuel.

According to Fedosyev and Sinyaryev [15] a mixture of 80% hydrogen peroxide with hydrazine hydrate diluted with methyl alcohol in the ratio of 1 : 1 has the following physico-chemical constants:

Heat of reaction	1020 kcal/kg or 1330 kcal/l.
Specific gravity	1.30
Gas volume	940 l./g
Temperature of explosion	2330°C
Specific impulse	180 sec

Among the reactions of hydrazine used for rocket propulsion that of hydrazine with nitric acid is known.

It is also possible to use hydrazine hydrate alone as a monergol owing to its high heat of decomposition. Energy and gaseous products are provided by decomposition induced by permanganates, commonly used in the solid form.

1,1-DIMETHYLHYDRAZINE (UDMH)

Among the homologues of hydrazine, asymmetric dimethylhydrazine $(CH_3)_2N\cdot NH_2$ is important. It is obtained from dimethylamine by nitrosation followed by reduction

$$(CH_3)_2NH \xrightarrow{HONO} (CH_3)_2N\cdot NO \xrightarrow{H} (CH_3)_2N\cdot NH_2$$

or by a modification of the Raschig method of preparation of hydrazine in the presence of dimethylamine.

It is a colourless liquid with a freezing point of *ca.* −56°C, a boiling point of *ca.* 63°C and a density of 0.785 g/cm³.

The heat of combustion is *ca.* 3580 kcal/kg.

Under the name of "Dimazine" or the abbreviation of UDMH it is used for hypergols by mixing with nitric acid. It may also be used with liquid oxygen.

In the U.S.A. it is employed in "Nike Ajax", "Rascal" and "Vanguard" rockets (Warren [53]).

MIXTURES WITH LIQUID OXYGEN AND OZONE

When V2 rockets were first used a mixture of liquid oxygen with 70% methyl alcohol was employed as a fuel. This mixture, however, is not capable of self-ignition, and it had to be ignited by means of a pyrotechnical mixture giving a hot flame.

Mixtures containing liquid oxygen are less commonly used now for jet propulsion than mixtures with nitric acid. Nevertheless, for obvious reasons, they have much prospect of success considering that liquid oxygen is a 100% oxidant.

A disadvantage of liquid oxygen is that its boiling point is very low (−183°C), an so is its specific gravity at this temperature (1.14). In view of the low boiling point rockets should be filled with this liquid oxidant just before use.

As a combustible, paraffin or alcohols may be employed. Fedosyev and Sinyaryev [15] quote the following physico-chemical constants for typical mixtures with liquid oxygen.

TABLE 69

Fuel	Heat of reaction		Specific gravity	Volume of gases l./kg	Temperature of explosion °C
	kcal/kg	kcal/l.			
Paraffin	2200	2200	1.00	650	3280
Ethanol (93.5%)	2020	2000	0.998	789	2980

Investigations into the possibility of using liquid ozone or, strictly speaking, mixtures of liquid oxygen with liquid ozone, have recently been carried out by the Armour Research Foundation in Illinois. According to Platz and Hersh [54] liquid ozone or a mixture of liquid ozone and oxygen may be obtained by introducing oxygen, carefully purified from organic impurities, into the ozonizer, where the mixture is irradiated and the ozone liquified (−111.9 °C under atmospheric pressure); the oxygen escapes through an exit pipe. If a mixture of liquid ozone with oxygen is to be obtained the gases discharged from the ozonizer are introduced to the liquid oxygen after being cooled.

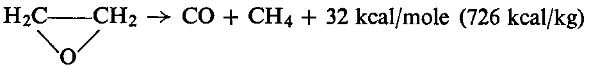
Liquid oxygen (100%) and a mixture of ozone with oxygen are stable enough if the oxygen used for producing the ozone contains not more than 0.002% (calculated on CO_2) of organic material.

NITRIC ESTERS

Liquid and volatile nitric esters, being safer to handle and more stable chemically than nitroglycerine or diethylene glycol dinitrate (DGDN), can be employed as monopropellant jet fuels. Among these compounds methyl nitrate should be mentioned first (Vol. II, p. 160). It was used for jet propulsion by the Germans during World War II under the name of Myrol either in the pure state or as a methyl alcohol solution (30% of methanol and 70% of methyl nitrate). Recently, another nitric ester, i.e. isopropyl nitrate has been suggested but for the time being there is no further information available about its use. Sometimes ethyl nitrate is also mentioned.

ETHYLENE OXIDE

This compound also deserves attention as a monergol. Its physical constants are: boiling point 11°C, freezing point -112°C, density 0.90. It decomposes exothermically according to the theoretical equation:



$$\underset{\diagdown O \diagup}{H_2C\text{——}CH_2} \rightarrow CO + CH_4 + 32\ \text{kcal/mole}\ (726\ \text{kcal/kg}) \qquad (1)$$

In point of fact the reaction is more complicated and proceeds according to the equation:

$$C_2H_4O \rightarrow xCO + yCH_4 + zC_2H_4 + tH_2 \qquad (2)$$

where the coefficients x, y, z and t are less than 1. The heat of this reaction is somewhat lower than for equation (1), but in calorific value, ethylene oxide is on a par with propellants. Table 70 gives the products of decomposition, temperature of explosion and specific impulse according to Glassman and Scott [55] and Kruska [56].

TABLE 70

Pressure in chamber atm	Composition of products (%)				Temperature of explosion °C	Specific impulse sec
	CO	CH_4	H_2	C_2H_4		
20	1.0	0.84	0.16	0.08	1015	159
30	1.0	0.86	0.14	0.07	1027	168
40	1.0	0.87	0.06	0.06	1033	174
60	1.0	0.88	0.06	0.06	1039	181

Ethylene oxide has the advantage of being safe to handle since it is not strictly an explosive.

ATTEMPTS TO INCREASE THE ENERGY OF LIQUID MIXTURES FOR ROCKET PROPULSION

Clearly, attempts to increase the energy liberated by liquid mixtures for rocket propulsion are based, in the first instance, on the use of those components (combustible and oxidant) which release as much heat as possible. E.g. the use of ozone as an oxidant has been discussed above (p. 309).

MIXTURES WITH POWDERED METALS

It has been suggested that powdered metals, e.g. aluminium should be added to the combustible component in the form of a suspension. Stettbacher [57], for example, suggested the following equation for the combustion of a mixture of petrol with aluminium suspended in it in stoichiometric proportions:

$$C_7H_{16} + 2Al + 12\tfrac{1}{2}O_2 \rightarrow 7CO_2 + 8H_2O + Al_2O_3$$

On combustion this mixture gives *ca.* 2545 kcal/kg or *ca.* 2763 kcal/l.

Stettbacher calls attention to the fact that powdered aluminium always contains a certain amount of aluminium oxide (up to 11%), hence the heat of combustion is lower than that theoretically calculated.

The significance of the addition of beryllium to the fuel is still rather theoretical. E.g. paraffin with nitric acid in stoichiometric proportions gives 1440 kcal/kg, whereas the same mixture with 7.2% and 10.0% of beryllium gives a heat effect of 2130 kcal/kg and 2480 kcal/kg, respectively.

BORON, SILICON AND BERYLLIUM COMPOUNDS

The addition of suspensions of metals to the liquid involves difficulty in achieving a homogeneous suspension, and as an alternative the use of organometallic and organometalloid compounds or hydrides has been suggested. These may be combinations of boron with hydrogen, boron with hydrogen and nitrogen, silicon with hydrogen, silicon with hydrogen and nitrogen, which all are predominantly endothermic or only slightly exothermic.

Fedosyev and Sinyaryev [15] report the following properties of the most typical representatives of the above compounds (Table 71).

TABLE 71

Compound		Melting point °C	Boiling point °C	Heat of formation $-\Delta H_f$ kcal/mole	Specific gravity
Name	Formula				
Pentaborane	B_5H_9	50*	60*	0*	0.64*
Diborane amine	B_2H_7N	−66	76	−10*	0.70*
Trisilane	Si_3H_8	−117	53	−20*	0.88*
Trisilicyl amine	$(SiH_3)_3N$	−106	52	−10*	0.895
Beryllium ethyl	$Be(C_2H_5)_2$	12	200*	−35*	0.60*

* Approximate figures.

It is to be noted that boranes react with water in such a manner that the latter acts as oxidant, e.g.:

$$B_4H_{10} + 12H_2O \rightarrow 4H_3BO_3 + 11H_2$$

ORGANOMETALLIC COMPOUNDS

Experiments are also being carried out on the addition of organometallic compounds such as lithium ethyl, aluminium trimethyl or triethyl etc. to the fuel. These compounds ignite on contact with the oxygen of the air or with oxidizing agents—components or propergols—hence they can be valuable constituents of hypergols. At the same time they liberate a large amount of heat on combustion and can thus be used for increasing the energy evolved on the combustion of propergols.

FLUORINE AND ITS DERIVATIVES

Recently, the use of fluorine as an oxidant has been considered feasible. E.g. the reaction of fluorine with hydrazine gives a particularly large theoretical specific impulse (I_s) amounting to 298 sec.

Fluorine with hydrogen gives $I_s = 352$ sec, whereas oxygen with hydrogen has a somewhat lower value (342 sec).

Nevertheless it should be borne in mind that the use of liquid fluorine has considerable disadvantages. Its boiling point is −187°C. To prevent corrosion special vessels of nickel alloys surrounded by a jacket filled with liquid nitrogen (boiling point −199.5°C) are required.

Operating with liquid hydrogen as a combustible also creates exceptional difficulties, due to its exceedingly low boiling point (−253°C).

In addition to fluorine itself, fluorine compounds have also been recommended. Chlorine trifluoride (ClF_3) with a boiling point of 12°C and a density of 1.77 g/cm^3 is the most promising for use in rocket propulsion. Its specific gravity is 1.85, heat of formation $-\Delta H_f = 41.0$ kcal/mole. It is obtainable by the action of fluorine on chlorine in an atmosphere of nitrogen at 280°C, in a reactor of copper or nickel.

During World War II, the Germans developed the production of chlorine trifluoride as an incendiary agent.

Another fluorine compound—nitrogen trifluoride — is interesting theoretically but difficult to manufacture.

Fluorine oxide also merits attention. This is a gas liquefiable at −144.8°C and weakly endothermic. Its heat of formation $-\Delta H_f = -9.2$ kcal/mole [58].

Still another compound of great interest is perchloryl fluoride ($ClO_3 \cdot F$). It was described in Vol. II. Perchloryl fluoride is distinguished by its high stability; it causes no corrosion of commonly used materials. It reacts vigorously with oxidizable organic compounds.

It reacts with hydrazine. In rockets such a mixture gives a specific impulse I_s of 270.

According to Engelbrecht and Atzwanger [59], Jarry [60], and [61] the physical properties of perchloryl fluoride are as follows:

Melting point	$-146°C$ $(-146\pm 2°C)$
Boiling point	$-47.5\pm 0.5°C$ $(-46.8°C)$
Vapour pressure	$\log_{10} P(\mathrm{mm}) = 18.90112 - 1443.467/T - 4.09566 \log_{10} T$ (at -120 to $-40°C$) $\log P(\mathrm{atm}) = 4.46862 - 1010.81/T$ (at -40 to $+95.15°C$)
Heat of vaporization	4.6 kcal/mole
Liquid density	$2.266 - 1.603\times 10^{-3}\,T - 4.080\times 10^{-6}\,T^2$ g/ml T
Critical temperature	95.13°C
Critical pressure	53.0 atm
Critical density	0.637 g/cm^3
Heat of formation at 25°C	$-\Delta H_f^0 = 5.12\pm 0.68$ kcal/mole
Specific heat of liquid	
at $-40°C$	0.229 cal/g°C
$-10°C$	0.244 cal/g°C
$+50°C$	0.290 cal/g°C
$\frac{S_p}{S_v}$ at 24°C	1.12

MIXTURES WITH PERCHLORIC ACID

Perchloric acid ($HClO_4$) is also recommended as an oxidant for rocket fuels. The anhydrous acid is a liquid with a specific gravity at 20°C of 1.767 and a freezing point of −112°C; it decomposes when heated to 9°C. It can be distilled under reduced pressure (at 16°C under a pressure of 18 mm Hg, at 30°C under a pressure of 50 mm Hg).

Perchloric acid forms easily hydrates:

$HClO_4 \cdot H_2O$ (m.p. 50°C, content of $HClO_4$ 84.8%, sp.gr. at 20°C 1.7756)
$HClO_4 \cdot 2H_2O$ (m.p. −17.8°C, content of $HClO_4$ 73.6%)
$2HClO_4 \cdot 5H_2O$ (m.p. −29.8°C, content of $HClO_4$ 69.1%)
α and β hydrates: $HClO_4 \cdot 3H_2O$ (m.p. −37 and −43.2°C respectively, content of $HClO_4$ 65.0%)
$2HClO_4 \cdot 7H_2O$ (m.p. −41.4°C, content of $HClO_4$ 61.5%)

The hydrates of perchloric acid (even lower ones) are judged to be unsuitable as rocket fuels.

The heat of formation of perchloric acid $-\Delta H_f^0$ is 11.1 kcal/mole.

Full decomposition proceeds with heat evolution:

$$HClO_4 \rightarrow \tfrac{1}{2}H_2O + \tfrac{1}{2}Cl_2 + 1.75O_2 + 15.7\ \text{kcal}$$

158 kcal are evolved from 1 kg which is not sufficient to make the substance explosive, but the addition of 3% of organic substance to perchloric acid gives an explosive mixture. Some organic substances (amines, unsaturated compounds, cellulose, wood, rubber) are ignited on contact with perchloric acid.

Elliot and Brown [62] made extensive studies of the inflammability of mixtures of perchloric acid with oxidizable substances. Most of the mixtures of 60% perchloric acid when ignited in a confined space burned to detonation. The mixtures with 70% perchloric acid and some of them with 60% perchloric acid could be ignited by impact. Explosion was induced under action of No. 6 detonator on mixtures with 60% perchloric acid with wood meal or cotton and the rate of explosion was found to be 3000 m/sec.

Exposure to irradiation of sunlight did not seem to affect the mixtures with 40–60% perchloric acid.

A detailed study was made by Jacquet [63] and Jacquet, Médard and Sartorius [64] of the explosive properties of the three-component system: perchloric acid, acetic anhydride and acetic acid. These solutions are widely used in electropolishing baths [65]. However, Merchant [66] drew attention to the explosive properties of such mixtures. Indeed, a number of explosions of electropolishing mixtures occurred, and that in Los Angeles (O'Connor plant) 1947 was particularly disastrous. Two hundred gallons of a solution of 75 vol.% of 72% perchloric acid and 25 vol.% of acetic anhydride exploded. Seventeen men were killed and one hundred and fifty wounded.

By calorimetric measurements [67] the heat of mixing aqueous perchloric acid (69%) with acetic anhydride in glacial acetic acid was found to be 20.6 ± 1.8 kcal/mole. This is the difference between the heats of hydration of acetic anhydride (34.8 kcal/mole) and of 69% perchloric acid (16.4 kcal/mole):

$$2.5(CH_3CO)_2O + HClO_4 \cdot 2.5H_2O \rightarrow 5CH_3COOH + HClO_4 + 18.5\ \text{kcal/mole}$$

The highest explosive power would correspond to the stoichiometric mixture composed of 66 vol.% of 72% perchloric acid and 34 vol.% of acetic anhydride. It could decompose according to equation:

$$CH_3COOH + HClO_4 \rightarrow 2CO_2 + 2H_2O + HCl$$

The calculated thermal effect in this reaction (*ca.* 1250 kcal/kg) would fall between those of the explosive decomposition of nitroglycerine and guncotton, and the calculated temperature would be *ca.* 2500°C.

Jacquet, Médard and Sartorius [63, 64] investigated the process of mixing 62.7% perchloric acid (density 1.59) with 100% acetic anhydride. They found that no explosion occurred when vigorous mixing was applied. This was independent of the order of mixing but addition of the acid to the anhydride was suggested to be the less dangerous procedure.

The stoichiometric mixture (mentioned above) was found to be very sensitive to priming. It was detonated by a primer as weak as 0.6 g of mercury fulminate. The rate of detonation, or more precisely of explosion, was variable (this is typical for liquid explosives): 1300–2000 m/sec. Expansion in the lead block was found to be 85 (picric acid = 100) which is the same value as that of dinitrobenzene (88).

Aptitude to detonation decreased with increasing content of acetic anhydride: mixtures containing less than 57 vol.% of perchloric acid (62.7%) could not be detonated.

The sensitiveness to shock was also examined. 50% explosions were obtained when 1 kg weight fall from 1.40 m on a drop of the stoichiometric liquid in a metal capsule.

The ignition of the mixture by red hot wire or with a flame was difficult. Only those richest in acetic anhydride could be ignited at the boiling point. With increasing perchloric acid content the ignition became more difficult. The stoichiometric mixture did not burn.

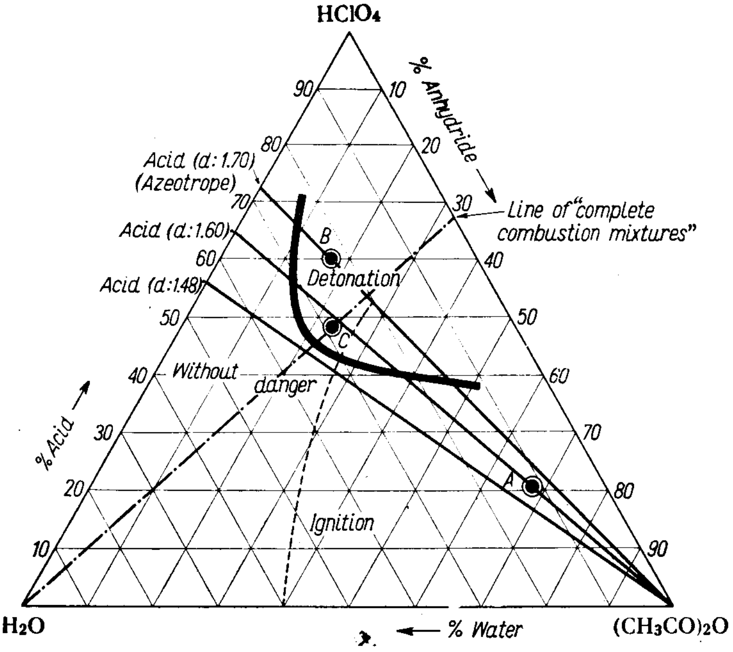


FIG. 85. Explosive properties of perchloric acid–acetic anhydride–acetic acid (and water) mixtures, according to Jacquet [63].

The solutions used for metal polishing (see below) ignited when fine wood shavings were added at 60°C.

Jacquet [63] summarized his results by drawing the triangular diagram (Fig. 85). The stoichiometric mixture is marked by point (*C*) and the mixture which gave the Los Angeles accident is marked (*B*). In the ignition zone but outside the region of detonation are most of the compositions usually applied for electropolishing baths. Point (*A*) corresponds to the mixture in which all the water introduced by 64% perchloric acid reacted with the acetic anhydride to form acetic acid.

Handling and storage of perchloric acid must be done with particular care.

It is well known that anhydrous perchloric acid must never be allowed to come into contact with oxidizable organic substances such as alcohols, wood, cotton, paper, cork and most plastics otherwise ignition or explosion will result.

Anhydrous perchloric acid is liable to explosive decomposition even when free of organic substances. On storage it gradually becomes coloured due to the formation of decomposition products, even in the dark, and in this condition it may explode spontaneously. Anhydrous acid which has become amber coloured (or darker) should therefore be diluted with water immediately and discarded.

Also aqueous perchloric acid may cause fire or explosion [68].

Considerable caution must be exercised in contacting perchloric acid with metals, e.g. the catalytic action has been reported [69] of steel particles in reducing the explosion temperature of mixtures of perchloric acid vapour and hydrogen [69].

REACTIONS OF FREE ATOMS OR RADICALS

Another approach to the problem of increasing the energy of rocket fuels consists of searching for possibilities to operate with combustible (e.g. hydrogen) and oxidizing (e.g. oxygen) elements in the form of atoms (H, O) and not molecules (H_2, O_2) at the moment of combustion, as reaction of atoms would give a much greater heat effect than the reaction of molecules. These attempts are of no practical significance for the present, since methods for producing free atoms sufficiently concentrated and storable are still unknown.

GENERAL CONSIDERATIONS

In publications including those of Latham, Bowersock and Bailey [70], and Wood [24] the following magnitudes of the specific impulse of various mixtures, currently used and prospective (Table 72) are quoted.

A recent publication [71] suggests mixtures of oxygen difluoride as an oxidizer. This substance can give an I_s as high as *ca.* 400 sec when mixed with hydrogen. The mixture of oxygen difluoride and unsymmetrical dimethylhydrazine has a theoretical specific impulse of *ca.* 330 sec.

A high performance can also be achieved with perchloryl fluoride (Vol. II) and tetrafluorohydrazine as oxidizers.

In selecting the constituents of a fuel every effort should be made to attain the optimum conditions likely to be created by the mixture. The optimum conditions are attained by creating:

(1) The highest temperature of reaction
(2) The lowest molecular weight
(3) The lowest $\frac{S_p}{S_v}$ ratio

TABLE 72

Constituents		Oxidant: combustible ratio	Specific gravity	Specific impulse sec	Remarks
Oxidant	Combustible				
100% nitric acid	Turpentine	4.4	–	221	
Fuming nitric acid (FNA)	Ethanol	2.5	–	219	
FNA	Aniline	3.0	–	221	
FNA	Ammonia	2.2	–	225	
FNA	JP-4	–	–	225	
99% hydrogen peroxide	Ethanol	4.0	–	230	
99% hydrogen peroxide	JP-4	6.5	–	233	
99% hydrogen peroxide	Hydrazine	–	–	245	Fuels most commonly used
Liquid oxygen (LOX)	Ethanol	1.5	0.97	242	
LOX	JP-4	2.2	1.02	248	
LOX	Turpentine	2.2	–	249	
LOX	Ammonia	1.3	–	250	
Hydrogen peroxide	Nitromethane	–	–	227	
N_2O_4	Hydrazine	–	–	249	
N_2O_4	Hydrogen	11.5	0.565	279	
FNA	Hydrogen	12.6	0.60	298	
LOX	Hydrogen	2.9	0.23	345	
70% LOX 30% ozone	JP-4	2.3	–	253	
100% ozone	JP-4	1.9	–	266	
100% ozone	Ammonia	1.13	–	267	
100% ozone	Hydrazine	0.63	–	277	
Fluorine	JP-4	2.6	–	265	
Fluorine	Ammonia	2.6	–	288	So-called "Zip-fuels" (high energy fuels in the U.S.A.)
Fluorine	Diborane (B_2H_6)	5.0	–	291	
Fluorine	Methanol	2.37	–	296	
Fluorine	Hydrazine	1.98	–	298	
Fluorine	Hydrogen	4.5	–	352	
Fluorine	Hydrogen	9.4	0.46	371	
100% ozone	Hydrogen	3.2	–	369	
100% ozone	Hydrogen	2.65	0.23	373	

Tormey [72] quotes the following three examples of mixtures which give the optimum conditions.

(1) Mixture giving the highest temperature:

$C_2N_2 + O_3$ (Cyanogen + Ozone)
Flame temperature *ca.* 5240°C
$I_s = 270$

(2) Mixture giving the lowest molecular weight:

$H_2 + F_2$ (**Hydrogen** + Fluorine)
Molecular weight 8.9
$I_s = 373$

(3) Mixture giving the lowest $\frac{S_p}{S_v}$ ratio:

H_2O_2 + petrol
$\frac{S_p}{S_v} = 1.20$
$I_s = 248$

With the reaction of free radicals or atoms much higher magnitudes of specific impulse may be obtained.

TABLE 73

REACTIONS OF HYDROGEN WITH FREE RADICALS

Reagents		Molar ratio H_2/R	Specific impulse sec
Hydrogen	Radical R		
H_2	NH	2.8	410
H_2	BH	2.2	420
H_2	CH	5.0	492
H_2	H	0.5	1040
H	H	–	1280

Still higher magnitudes of specific impulse can be obtained theoretically by using non-chemical reactions, e.g. ions and electrons which arrive in an electric field at a speed close to that of light. Another method is based on the use of photon flux with the speed of light.

Warren [53] quotes the following figures (Table 74):

TABLE 74

Fuel	Specific impulse (sec) max
Chemical	400
Free atoms and radicals	1200
Ions and electrons (from a nuclear reactor)	10^6
Photons (from solar radiation)	10^{10}

FINAL REMARKS

Most of the propulsion systems recorded in Tables 73 and 74 are only suggestions for the future or in development. Some of them would require chemicals which are produced only on a laboratory scale. Others would need chemicals whose properties and methods of production are often insufficiently known.

This is why only a very limited number of liquid compositions is in use.

They are classified into storable and cryogenic liquids [71].

Storable liquids

They remain liquid under normal, ambient operating conditions (moderate temperature, atmospheric pressure). Safety in storage and handling should also be considered. A storable liquid propellant should not have an excessively high vapour pressure at ambient temperature. The leading storable propellant uses dinitrogen tetroxide as oxidizer and a 50/50 mixture of hydrazine–unsymmetrical dimethylhydrazine (UDMH) as fuel [71]. Nitrogen tetroxide and UDMH is another storable propellant mixture in use [73].

Cryogenic liquids

They require a number of additional facilities such as a liquefying plant. The most common cryogenic propellant now in use is liquid oxygen–RP1 (rocket petroleum No. 1, a kerosene-cut hydrocarbon fuel). The higher energetic system liquid hydrogen–liquid oxygen is gradually being introduced.

Dole and Margolis [73] predicted that rocket propellants in use after 1961 would include:

Storable: perchloryl fluoride and hydrazine ($I_s = 268$).

Cryogenic: liquid fluorine and hydrazine ($I_s = 316$) or liquid oxygen and liquid hydrogen ($I_s = 364$).

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CHAPTER III

BLACKPOWDER

HISTORICAL

THE forerunner of all modern explosives, blackpowder, formerly often called gunpowder, is a mixture of potassium nitrate (saltpetre), sulphur and charcoal. The origin of blackpowder is obscure and dates back to very remote times. According to numerous historical works, in particular that of Romocki [1] blackpowder was invented by the Chinese many centuries B.C. The secret of its manufacture penetrated from there to Central Asia and was brought to Europe by the Arabs about the middle of the thirteenth century.

Combustible mixtures containing saltpetre, such as, for example, the famous Greek fire with which the Greeks destroyed the Arab fleet besieging Constantinople in 668, were already fairly widely known at that time. The secret of preparing Greek fire was supposed to have been brought to the Byzantine capital by Kallinikos, a Greek architect from Heliopolis of Syria. The Arab fleet was twice more defeated with this weapon in 716 and 718. The secret of Greek fire has never been disclosed in full but some medieval manuscripts reveal that it was a mixture containing constituents of blackpowder such as saltpetre and sulphur mixed with pitch. Obviously, this was not blackpowder but a mixture akin to it. The possibility that firearms were used for launching the incendiary missiles with a propellent charge can be ruled out since there is no doubt that catapults were used for throwing Greek fire.

Similarly, in a description of the siege of Niebla in Spain (1257) mention is made of the missiles thrown by the Moslems which produced a roar and flash. They were in all probability loaded with a mixture resembling blackpowder. At the battle of Legnica (1241) the Tartars employed another weapon, the so-called Chinese dragon belching fire; this was probably a type of a rocket-like launching device for incendiary missiles.

In the book by Marcus Graecus "*Liber ignium*" translated from Arab sources and published *ca.* 1300, there is a fairly full description of the composition of a combustible mixture called "flying fire" (*ignis volatilis*):

1 part of resin
1 part of sulphur
2 parts of saltpetre

The mixture was kneaded with linseed oil and loaded into a piece of hollow wood, and together these constituted an incendiary missile.

A description of the composition and principles of the manufacture of blackpowder appeared in the works of two of the greatest scientists of the Middle Ages: Albertus Magnus (Saint Albert the Great), a Dominican Monk born in Bavarian Swabia near 1200, and Roger Bacon of the Franciscan Order, born, according tradition, about 1214 at Ilchester in Somerset, England.

Albertus Magnus gave a description of blackpowder in his manuscript "De Mirabilibus Mundi".

As early as 1249 Roger Bacon described blackpowder in his manuscripts "De Secretis" and "Opus Tertium" and gives its composition as follows:

41 parts of saltpetre
29.5 parts of charcoal
29.5 parts of sulphur

It was not until the invention of firearms that the manufacture and use of blackpowder really began to develop. This invention cannot be ascribed with certainty to any particular person, but recent historical research has shown that there is no foundation for the belief that Berthold Schwarz was the inventor. Arab manuscripts written as early as 1320 (e.g. the manuscript in the Leningrad Asiatic Museum by Shems ed Din Mohammed) show tubes employed for shooting balls by means of a charge of powder. It is also known that in 1326 the Republic of Venice ordered firearms and in 1331 cannons were used by the Moors during the siege of Alicante in Spain. Cannons were also employed on a wide scale both by the English and the French at the battle of Crécy in 1346. In Poland the first mention of the use of powder and firearms is to be found in the Statute of Wiślica promulgated by Casimir the Great in 1347 and afterwards, in the description of the battle of Grunwald in 1410, when the Poles employed over 60 guns. In Russia powder and firearms appeared during the reign of Duke Dymitr of Don, in the late fourteenth century. The first references appear in chronicles of 1382 and 1389.

In all probability the first "mills" for making powder in Europe were established at Augsburg (1340), Spandau (1344) and Legnica (1348).

The composition of the powder used in the fourteenth century was:

67 parts of saltpetre
16.5 parts of charcoal
16.5 parts of sulphur

A very detailed study of the history of Greek fire and blackpowder was published more recently by Partington [2]. The book, which is amply provided with full quotations from the original source is the most authoritative and extensive work on the subject.

Blackpowder was also used as a high explosive. According to Kochmyerzhevskii [3] blackpowder was first employed in civil engineering between 1548 and 1572 for cleaning and dredging the Niemen river-bed. In 1627, in Hungary, Kacper Weindl employed blackpowder in a mine for blasting hard coal.

The first published reference to the use of blackpowder in mining was the paper read to the Royal Society in London by Sir R. Moray in 1665 [4]. He referred to "a way to break easily and speedily the hardest rock". According to the same paper the method was invented by du Son in France.

J. Taylor [5] reports that in 1696 blackpowder was utilized to widen a road in Switzerland.

From that time the use of explosives for various engineering operations such as mining, road building, dam building, land improvement etc. became general.

According to Gorst [6] blackpowder is now employed for the following purposes:

(1) as the filling for time-trains in time fuses,

(2) in the manufacture of shrapnel shells to fire the charge that expels the bullets,

(3) as a bursting charge in incendiary and star shells,

(4) in the manufacture of delay pellets and boosters,

(5) in the manufacture of powder pellets for primers,

(6) in the manufacture of primers for igniting charges of smokeless powder and of pyrotechnic mixtures,

(7) in the manufacture of safety fuses in which the cores consist of blackpowder.

In addition, blackpowder is also used (although the practice is decreasing) in sporting cartridges, in opencast coal mining and for blasting in mines where no methane occurs.

D. A. Davies [7] suggested the use of explosive charges for rain-making. The charges, consisting of 15 g of blackpowder plus 1.5% of silver iodide, are sent by balloon into a cloud, where they are exploded by a time fuse. The particles of silver iodide thus released act as nuclei on which the water vapour in a raincloud coagulates, to fall as rain drops.

Blackpowder containing silver iodide is obtained by saturating the blackpowder with an acetone solution of potassium silver iodide and then drying it. The required solution is prepared by dissolving 15 g of potassium iodide and 50 g of silver iodide in 200 g of acetone.

In Great Britain and throughout the Commonwealth blackpowder was used to prove alcohol. In this test alcohol was poured upon a small heap of blackpowder or "proof powder" and a light was applied to burn the heap. If the mixture burnt with explosion it was overproof, if it did not burn or burned with difficulty, the alcohol was underproof. If the mixture burned with "slight" explosion it was proof spirit, i.e. containing 49% alcohol by weight (Tate [8]).

COMPOSITION OF BLACKPOWDER

The blackpowder now most commonly used is composed of:

KNO_3	75%
Charcoal	15%
Sulphur	10%

Charcoal

Charcoal here implies a component with variable properties, not a specific chemical. Hence depending on the method by which the charcoal is prepared powder with various properties could be obtained.

As early as 1848 this attracted the attention of Violette [9], who prepared different types of charcoal in a retort by employing different temperatures of carbonization (Table 75).

TABLE 75

EFFECT OF THE TEMPERATURE OF CARBONIZATION ON THE CHEMICAL COMPOSITION OF CHARCOAL

Temperature of carbonization °C	Colour of charcoal	Yield %	Composition of charcoal (%)		
			C	H	O+N
280–300	brown	34	73.2	4.3	21.9
350–400	black	28–31	77–81		
1000	black	18	82.0	2.3	14.1
1250	black	18	88.1	1.4	9.3

Violette found that the temperature of carbonization of wood is directly related to the ignition temperature of the charcoal obtained (Table 76).

TABLE 76

THE RELATION BETWEEN THE IGNITION TEMPERATURE OF CHARCOAL AND THE CARBONIZATION TEMPERATURE OF WOOD

Temperature of carbonization °C	Ignition temperature of charcoal °C
260–280	340–360
290–350	360–370
432	*ca.* 400
1000–1500	600–800

The ignition temperature of charcoal obviously influences the ignition temperature of the blackpowder. Blackpowder containing "cocoa-", red- or brown-coloured charcoal is most easily ignited, while the heat of combustion of black charcoal, more strongly carbonized, is higher than that of brown coloured material. Thus the power of powder containing black charcoal is greater.

Strongly carbonized (black) charcoal is less hygroscopic, hence the powder from which it is made is also less hygroscopic.

The temperature and ease of ignition of charcoal is influenced not only by the method of carbonization, but also by the type of wood used. A light, porous wood gives more easily ignitable charcoal.

In modern times, the influence of the type of charcoal on the burning of powder has been investigated by T. Urbański and Tęsiorowski [10] and Blackwood and Bowden [11].

Much research has been devoted to the chemical structure of charcoal and has generally been concerned with comparing its chemical properties with those of coal in studying the latter's structure.

As early as in 1869 to classify various coals M. Berthelot [12] treated them with oxidizing agents such as nitric acid, potassium chlorate etc. and obtained a number of organic acids.

Next, Dickson and Easterfield [13] oxidized charcoal with fuming nitric acid in the presence of potassium chlorate and obtained mellitic acid in a yield of about 20% by weight. Finally, Dimroth and Kerkovius [14] made a very important observation: they converted the products of the oxidation of charcoal with nitric acid into barium salts and in turn subjected them to decarboxylation by distillation with barium hydroxide. In the products they detected the presence of benzene, naphthalene and fluorene. The presence of naphthalene and fluorene was the only direct evidence of the existence of condensed aromatic rings in charcoal. On the oxidation of charcoal with nitric acid in the presence of potassium hydrogen sulphate Meyer and Steiner [15] obtained pyromellitic acid. The presence of pyromellitic acid is considered to be indirect evidence of the existence of condensed aromatic rings in charcoal, which constitute an essential part of the chemical structure of charcoal. Nevertheless some authors questioned this view. Philippi *et al.* [16, 17] carried out experiments in which they treated charcoal with sulphuric acid at 300°C and obtained pyromellitic acid in a yield of 1–2%. Later they increased this yield to 6–7%, by conducting the reaction in the presence of mercury. They did not acknowledge this as evidence of the existence of strongly condensed aromatic rings since they had also prepared polycarboxylic aromatic acids by heating such aliphatic compounds as cellulose with sulphuric acid under similar conditions. This opinion, however, is hardly convincing since aromatic rings might have been formed on carbonization, in the course of the treatment with sulphuric acid.

In more recent times Juettner [18] has worked extensively on the oxidation of various types of coal, including charcoal. He examined the action of various oxidizing agents such as potassium permanganate in an alkaline medium and nitric acid. On such oxidation of the charcoal obtained by carbonization of cellulose at 1000°C mellitic acid in a yield of 25% by weight resulted.

Under similar conditions fluorene gives mellitic acid in a yield of about 45%, while hexaethylbenzene yields almost exclusively carbon dioxide, without mellitic acid. The experiments outlined above point to the existence of condensed aromatic rings in charcoal. This structure of charcoal has been definitely proved by infra-red spectroscopic analysis carried out by T. Urbański, Hofman, Ostrowski and Witanowski [19]. These authors investigated the infra-red absorption spectra of the products of thermal decomposition of cellulose and lignin at temperatures from 200–575°C. They showed that heating cellulose to a temperature above 300°C involves breakdown of the aliphatic structure of cellulose which is replaced by condensed aromatic rings. Thus the band 3300 cm⁻¹ of the alcoholic group (bound by a hydrogen bond) weakens with a rise in temperature and disappears at a temperature above 370°C. The band 1640 cm⁻¹ (derived from the water present in cellulose) weakens with a rise of temperature and disappears at a temperature above 245°C.

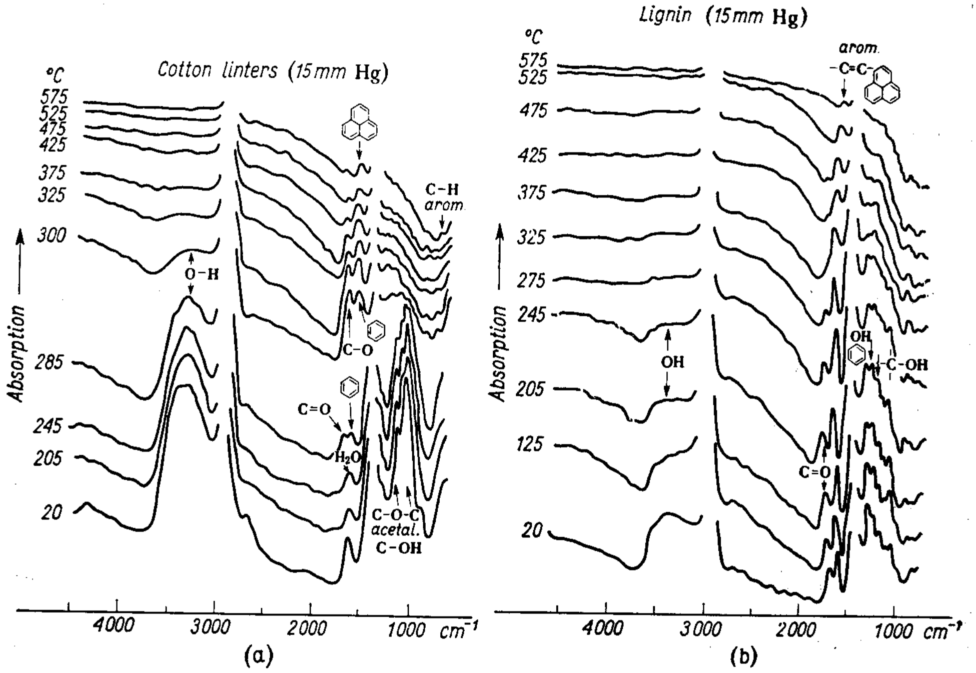

FIG. 86. Thermal decomposition of cellulose (a) and lignin (b) [19].

Cellulose shows the presence of a number of acetal bands (1155, 1105 and 1025 cm⁻¹) which disappear in test samples heated to higher temperatures (370°C or above). Similarly, a band characteristic of the bond C—O between carbon and hydroxyl group weakens with thermal decomposition and disappears at a temperature above 370°C.

In test samples heated to above 300°C there appear bands characteristic of the aromatic system, e.g. 1600–1570 cm⁻¹ (aromatic ring vibrations). Above 400°C the bands appear at 870 and 800 cm⁻¹, characteristic of C—H vibrations in condensed aromatic systems.

The changes in cellulose that occur on heating to various temperatures are shown in Fig. 86. The upper curves of cellulose carbonized at a high temperature (above 500°C) resemble closely those of anthracite or even graphite.

The graph showing the decomposition of lignin is similar, differing from cellulose in that here the change at a temperature of about 350°C is less pronounced since the lignin itself contains aromatic rings in its molecule. Above 350°C the bands characteristic of the aliphatic part of the lignin molecule fade, i.e. the frequencies of alcohol and phenol groups are 3300–3200 cm^{-1}, C—O of phenol 1265 cm^{-1}, C—O of alcohol and ether 1140, 1075 and 1030 cm^{-1}. Here also the general shape of the curves for most strongly carbonized material approximates to those characteristic of anthracite and graphite.

TYPES OF BLACKPOWDER

There are in fact two types of blackpowder classified according to their intended use:

I—for filling fuses,
II—for blasting charges.

With regard to chemical composition the difference between the two types is insignificant and lies mainly in their different rates of burning. In powders belonging to type II the rate of burning should be as high as possible. This is achieved by making the grains of powder of the density as low as possible.

The types of powder also differ in grain size. The powder used in small arms was manufactured in small grains, that for cannons being much larger. Sporting powder, for instance, (cf. Table 79) was manufactured in France in several grades differing in size of grain. Powder No. 0 consisted of the largest grains, powder No. 4 of the smallest, size being classified by the number of grains per gramme.

No. 0	650–950	grains per g
No. 1	2000–3000	grains per g
No. 2	4000–6000	grains per g
No. 3	8000–10,000	grains per g
No. 4	20,000–30,000	grains per g

Blasting powder consists either of grains with a density of about 1.8 or of compressed cylindrical pellets with a density of 1.35–1.50 and a central perforation. Blasting powder must burn vigorously so as to give an effect as close as possible to detonation. It is ignited either by a safety or detonating fuse. The explosive effect of the latter is stronger, and this may be enhanced by the "Herco blasting method" employed by Hercules Powder Co. [20], in which a detonating fuse inserted into the central perforation of the pellets acts as an initiating agent throughout the charge.

The composition of the powders used for mining purposes is given in Tables 77 and 78.

Mixtures with the addition of sodium nitrate (Table 78) are somewhat stronger giving more heat and a larger gas volume than those with potassium nitrate. They are more difficult to ignite and burn more slowly than mixture with potassium nitrate.

TABLE 77

COMPOSITION OF BLASTING POWDERS

Name	Composition (%)			
	KNO_3	Sulphur	Charcoal	$(NH_4)_2SO_4$ and $CuSO_4$
Strong blasting (French "poudre forte" in the form of globules or grains)	75	10	15	–
Slow blasting (French "poudre lente" in the form of globules or grains)	40	30	30	–
No. 1 blasting powder (Germany and Poland, 1924)	73–77	8–15	10–15	–
No. 1 Bobbinite with 2.5–3.5% paraffin (Great Britain)	62–65	1.5–2.5	17–19.5	13–17
No. 2 Bobbinite with 7–9% starch (Great Britain)	63–66	1.5–2.5	18.5–20.5	–

TABLE 78

COMPOSITION OF BLASTING POWDERS WITH SODIUM NITRATE

Name	Composition (%)			
	$NaNO_3$	KNO_3 (instead of $NaNO_3$)	Sulphur	Charcoal
No. 1 black blasting powder (Germany and Poland, 1924)	70–75	up to 25	9–15	10–16
American blasting powder*	70–74	–	11–13	15–17
Petroclastite or Haloclastite, No. 3 black blasting powder	71–76	up to 5	9–11	15–19 of coal-tar pitch
No. 2 black blasting powder	70–75	up to 5	9–15	10–16 of lignite

* Blasting powders in the U.S.A. are marked according to the dimensions of graphitized grains: CCC (*ca.* 14 mm dia.), CC, C, F, FF, FFF, FFFF (1-2 mm dia.).

The mixtures recommended by Raschig [21] similar to those suggested earlier [22, 23] are also worthy of note. They consist of 65–70% sodium nitrate with 30–35% sodium benzenesulphonate or sodium cresolsulphonate, or xylenesulphonate etc. Mixtures of this type have long been used in mining, under the name of Raschit or White Powder. The inventor claimed that the advantage of such mixtures is their safety in manufacture. They were prepared by evaporating an aqueous solution of the ingredients to dryness. Similar mixtures according to the invention of Raschig

[24] were made at Pniowiec in Upper Silesia in 1912. They consisted of sodium or potassium nitrate (*ca.* 70%) and of sulphite liquor evaporated to dryness (*ca.* 30%).

Almost simultaneously Voigt [25] recommended using mixtures of nitrates (mainly sodium nitrate) with salts of nitrophenolsulphonic acids (e.g. mononitrophenol- and mononitrocresolsulphonates) or salts of mononitronaphthalenesulphonic acid. He proposed mixing 25% of the aqueous solution with 75% of sodium nitrate.

TABLE 79

COMPOSITION OF POWDERS USED FOR MILITARY PURPOSES

Name	Composition (%)			Form and size of grains
	KNO_3	Sulphur	Charcoal	
Cannon	75	12.5	12.5	7–21 mm
Sporting	78	10	12	0.1–1 mm
"Normal"*	75	10	15	various
Cannon modified	78	3	19	prisms (p. 360)
Delay fuse powder	75	10–12	13–15	grains 0.3–0.6 mm 4000–7000 per g

* Most commonly used for fire-arms e.g. as rifle powder.

The composition of blackpowder used in France for military purposes is given in Table 79. In many cases they have retained their traditional names in spite of altered application.

In the U.S.S.R. blackpowders for military purposes have a conventional composition: 75% KNO_3, 15% charcoal and 10% sulphur. Their grades differ in grain size. No. 1 cannon and rifle powder has large grains, No. 2 shrapnel of rifle powder has smaller ones, the finest being No. 3 rifle powder. In addition sulphurless powder composed of 80% KNO_3 and 20% charcoal is used in the U.S.S.R. as a priming composition.

Blackpowder for small rockets (chiefly sea rescue signal rockets) is characterized by its high content of charcoal.

It consists of:

	German rockets	American rockets
Potassium nitrate	60%	59%
Charcoal	25%	31%
Sulphur	15%	10%

MODIFIED BLACKPOWDER

Prior to the invention of smokeless powder various attempts had been made to improve blackpowder. In particular experiments were carried out: to obtain **sulphurless powder, ammonium powder (with ammonium nitrate instead of potas-**

sium nitrate), to replace potassium nitrate with potassium chlorate and, finally, to introduce a powder in which potassium or ammonium picrate was the combustible (and explosive) constituent instead of charcoal and sulphur.

Sulphurless powder

Andrew Noble [26] suggested the omission of sulphur in powder mixtures. He found a mixture of 80% KNO_3 and 20% charcoal to be somewhat stronger than blackpowder of normal composition, i.e. containing 10% sulphur. At Noble's suggestion sulphurless powder was introduced into England. This type of powder consisting of 80% KNO_3 and 20% charcoal is now used in Great Britain and the U.S.S.R. in igniters for firing pyrotechnic mixtures.

A stoichiometric mixture of potassium nitrate and charcoal contains 87.1% potassium nitrate and 12.9% charcoal. The decomposition is expressed theoretically by the following equation:

$$4KNO_3 + 5C \longrightarrow 2K_2CO_3 + 2N_2 + 3CO_2$$

In this reaction 779 kcal/kg is evolved, the gas volume V_0 amounts to 240 l./kg, and the calculated temperature is 2700°C. For mixture consisting of 70% potassium nitrate and 30% charcoal (Sulphurless Gunpowder SFG.12) the heat of reaction is 670 ± 20 kcal/kg, according to Thomas [27].

Langhans [28] found that a mixture in which sulphur is replaced by selenium in no way resembles blackpowder. It is slow-burning and has no practical application.

Ammonium powder

Ammonium powder (formerly termed amide powder) was obtained in attempts to increase the power of blackpowder. One of the causes of the relatively low power of blackpowder lies in the fact that on explosion it produces a great quantity of solid matter, but only a relatively small volume of gas. In working for an increase of the volume of the gaseous products in the middle of the nineteenth century, attempts were made to substitute ammonium nitrate for potassium nitrate. The observation of Reiset and Millon [29] that a mixture of ammonium nitrate and charcoal has explosive properties and explodes on being heated to 170°C was the starting point for this work.

Gaens [30] obtained amide powder with the following composition:

KNO_3	40–45%
NH_4NO_3	35–38%
Charcoal	14–22%

This proved to be a more powerful explosive than blackpowder and burned with less smoke. Shortly afterwards it was used in Germany for small calibre naval guns.

Next, a similar powder was used for naval guns of larger calibre; this achieved great success as a greater muzzle velocity was obtained with a smaller charge of powder. Powder of this type was employed in Great Britain under the name of Chilworth Special Powder.

Ammonium powder obtained from ammonium nitrate and charcoal was also used successfully in guns of the Austrian navy between 1890–1896. It had however many disadvantages, since it was difficult to ignite, gave uneven results and was highly hygroscopic. This limited its use until it was withdrawn in all countries.

It was not until World War I that, due to the shortage of cellulose and acids for nitration, an ammonium powder with a composition of:

NH_4NO_3	85%
Charcoal	15%

was used for filling cartridges for Russian and German field artillery. In Russia it was termed SUD (Selitrougolnyi Dobavok) and in Germany Ammonpulver. The powder was manufactured in the form of rings with the outer diameter equal to the inner diameter of the cartridge case.

The main new feature introduced here was the use of combined charges i.e. of nitrocellulose and ammonium powder, the latter constituting 1/3 (exceptionally 1/2) of the whole charge. Here, nitrocellulose powder not only played the role of a propellent charge, but also acted partly as a secondary primer regulating the burning of the ammonium powder. The greatest disadvantage of ammonium powder, viz. the difficulty of ignition and burning, was thus overcome. It also turned out that ammonium powder possesses the advantages of being only slightly erosive and producing only slight muzzle flash. The hygroscopicity of ammonium powder was overcome by employing a special packaging with hermetically sealed cartridge cases.

Ammonium powder has the important disadvantage that ammonium nitrate occurs in various crystallographic forms with different specific gravities, one of the transitions taking place at +32°C, i.e. only just above room or summer temperature (Vol. II). When a charge of ammonium powder is heated to this temperature a decrease in density occurs and in consequence there is an undesirable increase in rate of burning.

During World War I 3000 tons of ammonium powder was produced monthly in Germany.

Towards 1934 a number of patents were filed on mixtures approximating in composition to ammonium powder and containing ammonium nitrate and guanidine nitrate or nitroguanidine with the addition of ammonium bichromate. In many cases gelatinized nitrocellulose was added as a binding agent. Compressed charges of these mixtures had a low rate of burning and a low calorific value. They could be applied to small jet engines, e.g. in World War II they were recommended for torpedo propulsion and for driving certain engines and various mechanical devices. These will be dealt with in later sections.

As a result of this work general conclusions were made as to the value and significance of certain constituents.

It was established that the addition of kaolin to mixtures containing ammonium nitrate raises the level of pressure at which burning is stabilized and facilitates uniform burning of the mixtures.

The presence of guanidine nitrate proved to be preferable to that of nitroguanidine since the former permits the charges to be compressed to a great density.

2,4-Dinitroresorcinol proved to be an important constituent of these mixtures as an sensitizing agent i.e. facilitating uniform burning under low pressure.

Asbestos, which increases the burning surface of powder mixtures, is also added and a small amount of vanadium pentoxide which exerts an advantageous influence on the uniformity of burning of a mixture.

By 1949, pressed charges began to come into use for a variety of purposes such as operating reciprocating engines, turbostarters for aircraft, starter motors for Diesel engines, etc. For example, a typical solid gas-generating charge for the "Williams and James" motor, designed for starting bus engines, was made from compressed pellets: 10 g of guanidine nitrate plus 15% 2,4-dinitroresorcinol, with a burning time of approximately 1 sec [5].

A similar mixture was used for starting the turbo starters of Armstrong-Siddeley Sapphire turbojet engines. The charge weighed 5 lb and burned one-sidedly from the central hole. The burning time was 10 sec, and the pressure developed was 750 lb/in^2.

A mixture of similar composition in the form of pellets weighing 12 g each and burning "cigar" fashion was introduced in 1949–1950 to start up 2 gallon fire extinguishers manufactured by General Fire Appliance Company. The burning time of the charge was 1 min. A charge weighing 1.3 lb and burning for 3 min was also designed for a 34 gallon extinguisher [5].

A different type of ammonium powder containing ammonium bichromate was also used to activate the "Williams and James" reciprocating engine.

This was composed of:

NH_4NO_3	78.5%
KNO_3	9.0%
Ammonium oxalate (anhydrous)	6.9%
Ammonium bichromate	5.6%
China clay	0.7%

The 15 lb charge was pressed in increments, under a pressure of 5550 lb/in^2 (370 kg/cm^2) into an internally-insulated steel tube so that it formed a continuous solid column. The charge was ignited by means of an electric powder fuse comprising a small charge of *ca.* 0.32 g (5 grains) of blackpowder. The gases drove the engine for 3 min 20 sec. The operating gas pressure rose to 280 lb/in^2.

For larger engines a charge of 149 lb was pressed at 12,000 lb/in^2 into a container 17 in. dia. The gases drove the engine for 2 min at an average pressure of 530 lb/in^2.

The same composition was used for driving a rotary blower motor. For this purpose an 8 lb charge was pressed into a 3.5 in. internal diameter steel tube lined with insulating material.

Another charge used for engine-starting had the composition:

Nitroguanidine	56.0%
Guanidine nitrate	28.0%
Ammonium chromate	8.0%
Dimethyl diphenyl urea	4.0%
Beech charcoal	4.0%

8 lb of this powder, pressed under a pressure of 6000 lb/in^2 (400 kg/cm^2), gave a charge that ran the "Williams and James" engine for 3 min 20 sec at a pressure rising slowly from 100 to 190 lb/in^2. The gas temperature leaving the charge tube was 600°C and at the engine inlet 340°C.

Another composition was:

Guanidine nitrate	94.5%
Vanadium pentoxide	0.5%
Cuprous oxide	5.0%

This charge was ignited by *ca.* 0.32 g (5 grains) of blackpowder igniter and a nitrocellulose–red lead oxide–silicon mixture.

For more information see J. Taylor [5].

A quasi-powder consisting of ammonium nitrate, guanidine nitrate and nitroguanidine with an admixture of potassium or ammonium chromate was employed as an agent for dispersing pesticides. This mixture burns slowly evolving a relatively small amount of heat. When mixed with a pesticide in equal proportions, the smoke formed on burning is rich in the pesticidal substance. Gammexane (BHC) DDT, Parathion, azobenzene etc. may be dispersed in this way (Marke and Lilly [31]).

Recently, mixtures containing ammonium nitrate have been recommended as materials for rocket propulsion (p. 383).

Chlorate powder

The first attempts to substitute potassium chlorate for potassium nitrate undertaken by Berthollet [32], who discovered potassium chlorate, were unsuccessful. It was immediately evident that a mixture of potassium chlorate, sulphur and charcoal was exceptionally sensitive to impact and friction, and was therefore too dangerous to manufacture. The removal of sulphur from the mixture did not increase safety and thus the powder has never found practical application.

Picrate powder

In 1861 Designolle [33] suggested using potassium nitrate mixed with metal picrates, mainly potassium picrate, as a propellant substitute for ordinary blackpowder. It was manufactured on a rather large scale in Le Bouchet in France and used during the Franco-Prussian War of 1870–71.

Blackpowder and small arms powder contained 9–16% and *ca.* 23% potassium picrate, respectively.

In 1869 Brugère [34] and independently F. Abel [35] suggested the use of ammonium picrate in a mixture with potassium nitrate instead of blackpowder. By employing virtually the same procedure as in the manufacture of blackpowder grains were obtained and then slightly polished. When examined in France in 1881 this powder gave good results for use with rifles and cannon, considerably surpassing blackpowder in strength. Brugère powder (Poudre Brugère) consisted of:

Ammonium nitrate	43%
Potassium nitrate	57%

The new propellant was promising but the nitrocellulose smokeless powder invented soon afterwards superseded all mixtures containing potassium nitrate and similar salts, that give a number of solid particles when exploded. For a time in the United States various mixtures were still used instead of blackpowder—chiefly for sporting purposes. E.g. Gold Dust Powder (Starke [36]) consisted of 55% ammonium picrate, 25% potassium picrate and 20% ammonium bichromate. Soon, however, early in the nineteenth century, the use of these mixtures was discontinued.

In World War II a variety of picrate powder consisting of ammonium picrate, potassium or sodium nitrate and a binding agent was introduced in Great Britain and in the U.S.A. as the propellant charge for small rockets. This was reported more fully in a chapter devoted to mixtures for rocket propulsion (p. 365).

THEORY OF THE BURNING OF BLACKPOWDER

For a long time attempts have been made to explain why three non-explosive substances, viz. potassium nitrate, charcoal and sulphur, when combined together should form an explosive mixture. It was particularly incomprehensible that binary mixtures of potassium nitrate with charcoal or with sulphur should be non-explosive or only poorly so. The problem was the more difficult to elucidate since it involves a reaction in the solid phase.

A number of outstanding scientists such as Descartes (1644) [37], Newton (1705), Lomonosov (1750) endeavoured to explain the course of the reaction that occurs when blackpowder burns. Both these and later investigators tried to analyse the explosion products of blackpowder and to derive equations for the decomposition process.

Gay-Lussac [38] found that the gases were composed of 52.6% CO_2, 5% CO and 42.4% N_2, their volume, when the density of the powder was 0.9, being 450 times the volume of the explosive. Piobert [39] disagreed with these results, finding a much lower value for the gas volume which he asserted was 250 times the volume of the charge.

Chevreuil [40] reported that in the bore of a gun barrel the powder decomposes according to the equation:

$$2KNO_3 + S + 3C = K_2S + N_2 + 3CO_2$$

If the powder burns in the open potassium sulphide is oxidized to sulphate. When blackpowder burns slowly the products, apart from carbon, include such components as potassium sulphide, sulphate, carbonate, cyanide, nitrate and nitrite.

A classical paper on the composition of the explosion products of blackpowder and of the heat of reaction was published by Bunsen and Shishkov [41]. They ascertained that the gases formed constitute 31% of the charge and contain approximately 50% CO_2, 40% N_2, 4% CO and lesser amounts (0.5–1.5%) of H_2, O_2, H_2S. Solid products consist of potassium carbonate, sulphate, thiosulphate, sulphide and nitrate with traces of potassium rhodanate, sulphur and carbon. These authors also detected the presence of ammonium carbonate.

These investigations were repeated by Linck [42], Karolyi [43] and Fiodorov [44]. Fiodorov's works are orginal in character: he examined the composition of the solid products of the explosion of blackpowder in a pistol or gun barrel, and arrived at the conclusion that the composition of these products depends on the conditions of firing, for instance on the calibre of the gun or pistol. He also established that the primary solid products of explosion consist of potassium sulphate and carbonate, which then undergo reduction under the influence of the excess carbon.

Extensive work on the products of the explosion of blackpowder in a confined space were carried out by Andrew Noble and F. Abel [45]. They showed that there is considerable variability in the composition of the products, depending on the conditions under which the powder explodes.

On the basis of Bunsen and Shishkov's investigations, Berthelot [46] derived the following equation for the decomposition of the powder:

$$16KNO_3 + 6S + 13C = 5K_2SO_4 + K_2S + 6N_2 + 11CO_2$$

A further advance was the development of the first theory about the explosion of blackpowder by Berthelot, who for this purpose drew largely on the experimental work described above.

Berthelot assumed two limiting cases for the decomposition of powder:

(1) With the formation of K_2CO_3 as a chief product of decomposition and of K_2SO_4 as a by-product;

(2) With the formation of K_2SO_4 as a chief product of decomposition and of K_2CO_3 as a by-product.

In the first case the decomposition proceeds according to the following three equations:

$$2KNO_3 + 3C + S = K_2S + 3CO_2 + N_2 \quad (1)$$

$$2KNO_3 + 3C + S = K_2CO_3 + CO_2 + CO + N_2 + S \quad (2)$$

$$2KNO_3 + 3C + S = K_2CO_3 + 1.5CO_2 + 0.5C + S + N_2 \quad (3)$$

so that $\frac{1}{3}$ of the powder decomposes according to equation (1), a half according to equation (2) and the rest ($\frac{1}{6}$) according to equation (3).

In the second case the decomposition runs according to the four equations, namely (1), (3), (4) and (5) so that $\frac{1}{3}$ of the powder decomposes according to equation (1), a half according to equation (3), $\frac{1}{8}$ according to equation (4) and the rest ($\frac{1}{24}$) according to equation (5).

$$2KNO_3+3C+S=K_2SO_4+2CO+C+N_2 \tag{4}$$
$$2KNO_3+3C+S=K_2SO_4+CO_2+2C+N_2 \tag{5}$$

Debus [47] came to the conclusion that the burning of blackpowder is a two-stage process. In the first oxidation occurs according to the exothermic reaction:

$$10KNO_3+8C+3S=2K_2CO_3+3K_2SO_4+6CO_2+5N_2+979\ \text{kcal}$$

The products so formed are then reduced according to the following endothermic reactions:

$$K_2SO_4+2C=K_2S+2CO_2-58\ \text{kcal}$$
$$CO_2+C=2CO-38.4\ \text{kcal}$$

Potassium sulphide so formed may undergo further reactions, viz.:

$$K_2S+CO_2+H_2O=K_2CO_3+H_2S$$
$$K_2S+CO_2+\tfrac{1}{2}O_2=K_2CO_3+S$$

A part of the unburnt potassium sulphide and sulphur gives K_2S_2.

Much later K. A. Hoffmann [48] resumed work on the mechanism of explosion of blackpowder. On examining the behaviour of mixtures of charcoal with sulphur he found that the reaction in blackpowder starts above the melting point of sulphur, at approximately 150°C, with a reaction between hydrogen present in charcoal and sulphur. Hydrogen sulphide thus formed reacts at temperatures between 285–290°C with potassium nitrate to yield K_2SO_4. Heat is then emitted which causes the KNO_3 to melt. This is an essential moment in the overall reaction since molten saltpetre reacts with molten sulphur and with carbon. The reaction proceeds the more readily the lower the melting point of the saltpetre, so that a powder with the addition of $NaNO_3$ (m.p. 313°C) ignites and burns more readily than a mixture with KNO_3 alone (m.p. 340°C). Blackpowder containing a mixture of potassium nitrate with sodium nitrate ignites still more readily since a eutectic mixture of KNO_3 and $NaNO_3$ melts at a temperature of about 220°C.

To prove the soundness of his theory Hoffmann refers to the fact that blackpowder is relatively difficult to ignite (as compared with nitrocellulose, for instance), not taking fire even from a strong electric spark but only on being heated to the temperature at which the above described reactions begin to take place.

Hoffmann also performed many experiments on the significance of sulphur in blackpowder mixtures (this problem was previously raised by Andrew Noble [49]) to substantiate his statement that blackpowder is well fitted for use when composed only of potassium nitrate and charcoal, hence without sulphur or with a smaller content of sulphur, e.g. 2%. From these experiments he drew the following conclusions:

(1) Sulphur facilitates an increase in the quantity of gases evolved on explosion. In the absence of sulphur potassium nitrate with carbon gives only K_2CO_3, but in the presence of sulphur CO_2 is evolved and potassium forms K_2SO_4 and K_2S.

(2) Sulphur reduces the initial decomposition temperature. For instance a mixture of two moles of KNO_3 and three gramme-atoms of carbon (in the form of 71% charcoal) begins to decompose at 320°C and explodes at 357°C, while a mixture of two moles of KNO_3 and one gramme-atom of sulphur begins to decompose at 310°C and explodes at 450°C. Finally, a mixture of two moles of KNO_3, one gramme-atom of sulphur and three gramme-atoms of carbon begins to decompose at 290°C and explodes at 311°C.

(3) Sulphur intensifies the sensitiveness of mixtures to impact; a mixture of KNO_3 and charcoal does not explode while a mixture of KNO_3 and sulphur decomposes when struck by a 2 kg weight falling from 45–50 cm. On the other hand, a mixture of KNO_3, charcoal and sulphur is exploded by a 2 kg weight from a drop of 70–85 cm

(4) Sulphur counteracts the formation of carbon monoxide in the products of explosion. CO and KCN occur in the products of decomposition of a mixture of KNO_3 with charcoal, due to the reaction of charcoal with K_2CO_3:

$$K_2CO_3+2C=2K+3CO$$

$$2K+2C+N_2=2KCN$$

On the other hand, in the presence of sulphur a reaction with K_2SO_4 takes place:

$$K_2SO_4+2C=K_2S+2CO_2$$

As there is no CO in these products no hydrogen evolves since the following reaction does not take place:

$$CO+H_2O=CO_2+H_2$$

When there is little sulphur in the powder, toxic CO is formed so that in blackpowder for mining purposes the content of sulphur should be not less than 10%.

Reactions between potassium nitrate and charcoal have also been investigated by Oza and Shah [50].

Blackwood and Bowden [11] have more recently published extensive studies on the mechanism of the initiation and burning of blackpowder and on that of the reactions of binary mixtures, viz. KNO_3+sulphur; sulphur+charcoal; KNO_3+ +charcoal.

It may be concluded from their experiments that burning occurs in a place heated to a temperature of 130°C or higher. Heat may be applied either by the direct effect of flame or by a hot metallic surface (e.g. glowing wire); heating may also result from impact, adiabatic compression of the air in the spaces between the grains of powder and finally, by mutual friction between the grains. The temperature of 130°C is considerably lower than the usual ignition temperature, nevertheless it may be sufficient to provoke an explosion if the grains are confined.

When the grains of blackpowder are subjected to a pressure of about 150 atm explosive decomposition may start at a temperature considerably lower than usual.

The propagation of flame from grain to grain is caused by an emission of hot molten potassium salts projected from one grain to another as the powder burns.

The ease of ignition of blackpowder and its rate of burning are influenced by the type of charcoal used, the decisive agents in this respect being in the opinion of Blackwood and Bowden those constituents of charcoal which can be extracted with organic solvents. Depending on the content of these constituents in the charcoal the properties of the blackpowder can be varied, i.e. the smaller the content of soluble constituents in the charcoal, the easier is the ignition and the faster the rate of burning of the powder.

Blackwood and Bowden formulate the following mechanism for the ignition and burning reactions of blackpowder. First sulphur reacts with organic substances present in charcoal:

$$S + \text{organic compounds} \rightarrow H_2S \tag{1}$$

Almost simultaneously saltpetre reacts with these compounds:

$$KNO_3 + \text{organic compounds} \rightarrow NO_2 \tag{2}$$

The following reactions may also occur:

$$2KNO_3 + S \rightarrow K_2SO_4 + 2NO \tag{3}$$

$$KNO_3 + 2NO \rightarrow KNO_2 + NO + NO_2 \tag{4}$$

$$H_2S + NO_2 \rightarrow H_2O + S + NO \tag{5}$$

Reaction (5) proceeds until all the hydrogen sulphide is used up when NO_2 appears and begins to react with the still unconsumed sulphur according to equation (6):

$$2NO_2 + 2S \rightarrow 2SO_2 + N_2 \tag{6}$$

The sulphur dioxide so formed may immediately react with potassium nitrate:

$$2KNO_3 + SO_2 \rightarrow K_2SO_4 + 2NO_2 \tag{7}$$

Reactions (5) and (6) are endothermic, but reaction (7) is strongly exothermic. Reactions (1)–(7) constitute the ignition process. According to Blackwood and Bowden the chief reaction when the powder begins to burn is the oxidation of charcoal by potassium nitrate.

EXPLOSIVE PROPERTIES OF BLACKPOWDER

From a comprehensive analysis of the products of explosion of blackpowder Kast [51] derived the following equation:

$$74KNO_3+30S+16C_6H_2O \text{ (charcoal)}=56CO_2+14CO+3CH_4+2H_2S+$$
$$4H_2+35N_2+19K_2CO_3+7K_2SO_4+2K_2S++8K_2S_2O_3+2KCNS+$$
$$(NH_4)_2CO_3+C+S+665 \text{ kcal/kg}$$

The heat of explosion and gas volume naturally depend on the composition of the powder. Noble and Abel [45] in the work quoted above give the following figures (Table 80):

TABLE 80

DEPENDENCE OF THE PROPERTIES OF BLACKPOWDER UPON THE COMPOSITION

Blackpowder	Composition			Heat of explosion kcal/kg	Gas volume V_0 cm³/g
	KNO_3	Sulphur	Charcoal		
Coarse-grained	75	10	15	726	274
Fine-grained (sporting)	75	10	15	764	241
Blasting	62	16	22	516	360
"Cocoa" powder	80	2	18	837	198

The latest studies of H. Thomas [27] quote the following figures for "Normal Gunpowder G.12":

Potassium nitrate	75.3%
Charcoal	14.4%
Sulphur	10.3%

Heat of explosion is 735 ± 15 kcal/kg at a moisture content of 0.85%. In dry powder heat of explosion is 740 ± 15 kcal/kg.

According to Kast, the gas volume V_0 is 280 l./kg, the specific pressure f is 2800 m and the temperature of explosion t is 2380°C (Noble and Abel found this value to be 2100–2200°C, Will [52]—2770°C).

The specific gravity of blackpowder may vary within the limits of 1.50–1.80 depending on its intended use. Its apparent density is 0.900–0.980.

Blackpowder is highly sensitive to impact and friction. It explodes when struck by a 2 kg weight falling from 70–100 cm. Its ignition temperature is 300°C. A sack filled with blackpowder takes fire when penetrated by a rifle shot.

The rate of burning of blackpowder at atmospheric pressure is much greater, than that of smokeless powder, but the rate and mode of burning at a pressure higher than atmospheric depend on its compression pressure. Grains of blackpowder do not burn by parallel layers but all over the mass of charge, if their density is lower than 1.75. Above this density they burn by parallel layers and the burning time then depends on the grain size (Vieille [53]). E.g. blackpowder with a density of

1.8 shows a rate of burning of about 10 cm/sec at a pressure of 1660 kg/cm^2 while nitrocellulose or nitroglycerine smokeless powder has a rate of burning of 15–30 cm per sec.

According to Blackwood and Bowden [11] a single grain of blackpowder burns with a rate of 0.4 cm/sec at atmospheric pressure. The flame is propagated along the line of grains at a rate of 60 cm/sec at atmospheric pressure.

Blackpowder for demolition charges or as a mining explosive has a lower density (about 1.67) and therefore burns very fast while blackpowder with a higher density (about 1.87), used as a propellant, burns slowly in parallel layers (Fig. 87). It is very important for the blackpowder to be of adequate density since this makes it possible to control its burning rate. The pressures required for obtaining charges of suitable density are listed below (according to Rinkenbach and Snelling [54]).

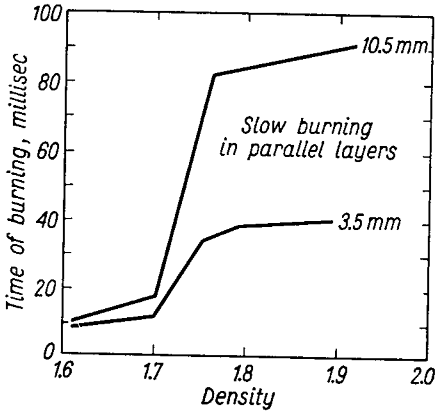

FIG. 87. The relation between the time of burning of blackpowder and its density (for grains 3.5–10.5 mm dia.).

Pressure kg/cm^2	Density
200	1.32
330	1.41
660	1.55
1330	1.695
2000	1.775
3330	1.84
5000	1.88
6660	1.88

Blackpowder may explode violently if it is confined in an air-tight container and initiated with a strong initiator. Its lead block expansion scarcely amounts to 30 cm^3 due to the "non-hermetic" effect of sand stemming. In an iron tube 35–41 mm dia. it gives a rate of explosion of 400 m/sec.

Andreyev [55] has made extensive studies on the transition of the burning of blackpowder into explosion. He used for this purpose a device composed of an iron tube, 40 mm in inner diameter and 200 mm in length, containing a 50 g charge of blackpowder and hermetically sealed. When the charge is ignited, if the blackpowder undergoes deflagration only, it ejects the steel base of the tube, whereas if the deflagration passes into explosion, the tube is blown into several pieces.

According to Andreyev blackpowder may burn at a pressure lower than atmospheric. Burning, however, is the more difficult, the lower the surrounding pressure. The limiting pressure at which blackpowder still burns is 0.1 kg/cm^2. From 2–30 atm the dependence of the rate of burning on the pressure may be expressed by the equation $U=72p^{0.24}$, where U is a linear rate of burning in cm/min and p the pressure in atmospheres.

THE MANUFACTURE OF BLACKPOWDER

RAW MATERIALS

Saltpetre

Potassium nitrate is obtainable from natural deposits in hot countries e.g. Ceylon, Egypt, Mexico, India, Iran and some areas of the U.S.S.R. It occurs there as the result of the microbiological oxidation of organic nitro compounds and of the reaction of the products with the alkaline components of the soil. On being refined by crystallization such saltpetre was (and partly still is) used for the manufacture of blackpowder. In Great Britain for instance until relatively recently the only source of potassium nitrate was saltpetre from India.

At one time potassium saltpetre was also obtained from manure and wood ash. Here potassium nitrate forms as a result of microbiological processes followed by reaction with potassium carbonate. Descriptions from various periods of history may also be found that refer to the collection of saltpetre from the walls of cellars situated in the vicinity of sewers. In this way, for instance, saltpetre was acquired in Poland for the manufacture of blackpowder during the insurrections of 1830 and 1863.

From the middle of the nineteenth century potassium nitrate began to be manufactured from Chilian saltpetre containing 20–35% $NaNO_3$. The Chilian saltpetre was first refined to increase the content of $NaNO_3$ to 95% and afterwards subjected to the exchange reaction:

$$NaNO_3+KCl \rightleftarrows KNO_3+NaCl \tag{1}$$

Reaction (1) is conducted in an aqueous solution at a temperature of 100°C. It takes the desired course due to the poor solubility of NaCl at this temperature. The sodium chloride is then precipitated and the reaction therefore shifts to the right. The potassium nitrate so obtained was termed "converted saltpetre".

Another method of manufacturing KNO_3 was based on double decomposition with potassium carbonate.

At present, reaction (1) is most frequently used to obtain potassium nitrate although the sodium nitrate used is now of synthetic origin.

Another method now employed consists in the treatment of potassium carbonate or caustic potash with nitrogen dioxide. The course of the reaction is:

$$N_2O_4+H_2O=HNO_2+HNO_3 \tag{2}$$

$$HNO_2+HNO_3+2KOH=KNO_2+KNO_3+2H_2O \tag{3}$$

A mixture of potassium nitrite and potassium nitrate is treated with nitric acid to oxidize nitrite to nitrate:

$$3KNO_2+2HNO_3=3KNO_3+2NO+H_2O \tag{4}$$

Still another method for the preparation of KNO_3 directly from KCl and nitric acid was used recently. Reaction proceeds at temperatures between 75–85°C according to the approximate equation:

$$4KCl+5HNO_3=NOCl+Cl_2+2H_2O+4KNO_3+HCl \tag{5}$$

Potassium saltpetre prepared by any of these methods is refined i.e. it is recrystallized from water by a method chosen in accordance with the impurities known to exist in the product.

Crystallization is facilitated by the great difference in solubility of potassium nitrate at high and low temperatures (it is ten times more soluble at 100°C than at 10°C).

Potassium saltpetre for the manufacture of blackpowder must be of high purity. The technical specification for the synthetic product according to the U.S.S.R. standard (GOST 1939–43) is summarized in Table 81.

TABLE 81

TECHNICAL SPECIFICATION FOR SYNTHETIC KNO_3 USED IN THE MANUFACTURE OF BLACKPOWDER (GOST 1939–43)

Requirements	Class	
	I	II
Appearance	white crystals	white crystals
Min. content of KNO_3, %	99.8	99.0
Max. content of moisture, %	0.1	0.2
Max. content of chlorides, calculated as NaCl, %	0.03	0.1
Max. content of carbonates, calculated as K_2CO_3, %	0.03	0.5
Max. content of water-insoluble substances, %	0.04	0.04
Max. content of substances insoluble in hydrochloric acid, %	0.005	0.02

Potassium saltpetre manufactured from Chilian saltpetre may also contain potassium perchlorate and potassium iodate, which are very detrimental since they increase the sensitiveness of blackpowder to friction and impact. A great many explosions which have occurred during the manufacture of blackpowder have been ascribed to the presence of these salts in saltpetre, although it has not been ascertained experimentally that small admixtures of $KClO_4$ increase the sensitiveness of blackpowder to impact and friction. Nevertheless, for the sake of safety potassium nitrate manufactured from Chilian saltpetre must not contain perchlorates and iodates in analytically detectable quantites.

Chilian saltpetre

Some types of blackpowder used for blasting contain sodium instead of potassium saltpetre. Such a mixture is sometimes termed "explosive saltpetre" and is considered a cheap substitute for blackpowder. The advantage of Chilian saltpetre as an oxidizing agent lies in the fact that by weight it contains more oxygen than potassium saltpetre. Its disadvantage consists in its relatively high hygroscopicity, although this is caused by the presence of calcium salt since chemically pure sodium nitrate is only slightly hygroscopic.

According to Soviet Standards GOST 828–41 sodium saltpetre for the manufacture of blackpowder mixtures should contain not less than 98% $NaNO_3$ and less than 2% moisture.

Sulphur

For the manufacture of blackpowder the sulphur used should be of highest purity, refined by distillation. Crude sulphur (which usually contains 2–5% of impurities) is distilled from retorts heated to a temperature of 400°C. The receiver should be maintained at a temperature above 115°C (120–130°C), i.e. above the melting point of sulphur (114–115°C). Under these conditions the distillate condenses to a liquid which is then cast into sticks or blocks. This is the only form of sulphur suitable for the manufacture of blackpowder. If the receiver temperature is lower, the sulphur distilled from the retort condenses as flowers of sulphur which always contain a little SO_2, and even traces of H_2SO_4 (the substance is easily oxidized due to its large surface area). Sulphur in this form is therefore slightly hygroscopic and acidic, and is unsuitable for the manufacture of blackpowder.

Charcoal

It is very important to select a suitable type of wood for the manufacture of the charcoal used in blackpowder. It must be soft, but not resinous and should be prepared from "white wood" of such trees as alder, poplar, willow, hazel etc. Before carbonization the wood must be de-barked and cut into pieces 10–30 mm thick. In some countries where hemp is plentiful the stems of this plant are used for making charcoal.

The material to be carbonized is placed into sheet-iron retorts, approximately 1 m dia. and 1.5–3 m long, one end of which is closed with an air-tight lid and the other fitted with an offtake for the gaseous products of distillation. These products are usually burnt since it is not worth while recovering them. The combustion of CO is particularly important, otherwise it may poison the atmosphere. The retorts are heated either by exhaust gases or by superheated steam. Carbonization lasts for 3–8 hr depending on the construction of the furnace and retorts, the temperature, and the type of material to be carbonized. After carbonization the retorts are taken out of the furnace and allowed to cool down (with the offtake closed). The charcoal is removed from the retort when it is cool—hot charcoal easily ignites. The charcoal should not be milled until the fourth day after its removal from the retort since charcoal which is too fresh may catch fire during milling.

Three types of charcoal are obtained depending on the temperature of carbonization (Table 82).

TABLE 82

TYPES OF CHARCOAL

Type	Temperature of carbonization °C	Content of C %
"Cocoa" (red)	140–175	52–54
Brown	280–350	70–75
Black	350–450	80–85

In some blackpowder type mixtures, especially those for mining purposes, charcoal is partially or wholly replaced by carbon black, brown coal, pitch from coal tar, coal tar itself, naphthalene, paraffin, wood bark, cellulose or wood meal, starch, resin etc. Thus mixtures are obtained with properties similar to blackpowder. Generally, however, they burn more slowly and are more difficult to ignite.

MILLING THE INGREDIENTS

The manufacture of blackpowder consists in thoroughly mixing the well-milled ingredients to obtain the required particle size and density. (Fast-burning blackpowder is fine-grained while the slower-burning type has larger grains of high density.) Manufacture consists of the following operations:

(1) Milling of the ingredients;
(2) Mixing of the ingredients;
(3) Pressing;
(4) Corning and finishing (drying, polishing and screening).

The methods of manufacture depend upon the trend of development traditional in a given factory or country. The variety of methods arises partly from the fact that the manufacture of blackpowder is highly dangerous so that different countries

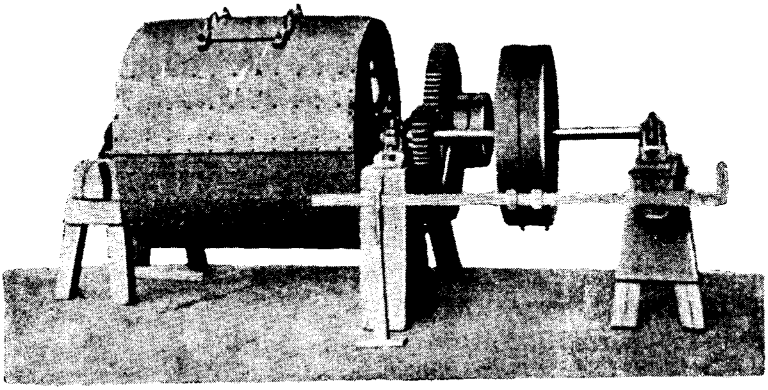

FIG. 88. Iron ball mill.

have worked out their own methods of reducing risks. Nevertheless, there are certain agreed methods observed everywhere.

The ingredients of blackpowder may be milled by two methods:

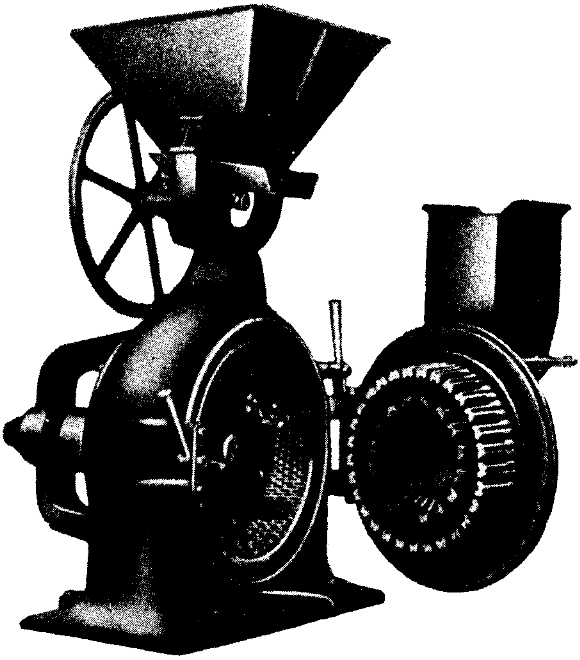

FIG. 89. Disk mill.

(1) Each ingredient may be milled separately;

(2) Two ingredients may be milled together: charcoal with sulphur and charcoal with saltpetre.

Saltpetre (dried at temperatures ranging from 100–110°C if necessary) is milled either in ball mills, using iron balls (Fig. 88), in disk mills (Fig. 89), or in disintegrators.

Charcoal is usually milled in either ball mills or disintegrators. It may be given a preliminary treatment in edge runners.

Sulphur is milled in similar equipment, but in some countries edge runners or rollers are used. Since sulphur is strongly electrified on milling it is advisable to add to it a slight amount of saltpetre to increase its electrical conductivity and reduce the danger of an explosion of sulphur dust suspended in air. Until 1881 such dust explosions were frequent. For the same reason all the equipment used for milling, especially for milling charcoal and sulphur, should be well earthed.

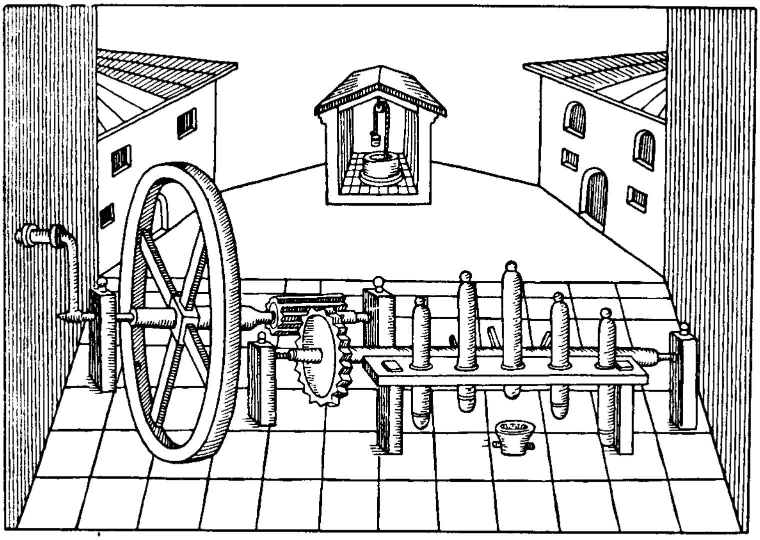

FIG. 90. A sixteenth-century stamp mill (the stamps and one of the mortars are shown).

Up to the end of the eighteenth century the ingredients of blackpowder were milled in stone or wooden mortars in which the wooden pestles were fitted with power drive (Fig. 90). The production capacity of such devices was, of course, rather low. They were used too, for mixing the mass of powder, but this proved to be dangerous, and in several countries (e.g. Great Britain) it was prohibited by law (about 1772).

In some countries (France and Switzerland) it is believed that it is more dangerous to mill charcoal and sulphur separately than together in the correct proportions. Saltpetre is also milled together with charcoal since the addition of such a mixture to a mixture of charcoal and sulphur is supposed to be safer than the addition of saltpetre alone if the ratio of charcoal to saltpetre in the mixture added does not exceed 1:15.

Thus in France binary (two-component mixtures called "binaires") are formed:
Binary mixture containing sulphur (sulphur with charcoal);
Binary mixture containing saltpetre (saltpetre with charcoal).

Binary mixtures of charcoal with sulphur or with saltpetre, being insensitive to friction and impact, are prepared in iron ball mills composed of drums (1.2 m dia. and 1.5 m in length) with bronze balls. The drums (Fig. 91) are fitted inside with humps (*1*) which increase mixing and milling efficiency of the bronze balls. The drums are fitted on their cylindrical surface with a door (*2*) for loading and unloading. To prevent escape of dust into the premises they are enclosed in a tin casing (*3*), with a funnel for unloading on its lower end. The mouth of the funnel is closed by a coarse stationary screen (*4*) and, situated below this, there is a fine vibrating screen (*5*) with a clearance of 0.65 mm. Screen (*5*) is connected with the mouth of the funnel by a leather sleeve (*6*).

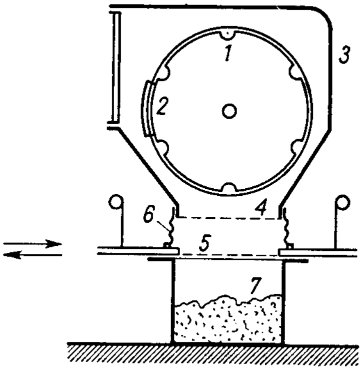

FIG. 91. Iron drum for preliminary milling of the ingredients of blackpowder in the form of two-component mixtures.

The drum charge ranges from 80 to 180 kg:

Binary mixture containing sulphur:	sulphur 50 kg
	charcoal 35 kg
Binary mixture containing saltpetre:	saltpetre 155 kg
	charcoal 10 kg

In addition 100–150 kg of bronze balls 8–15 mm dia. are loaded into the drum, which rotates with a rate of 18–20 r.p.m.

The binary mixtures are mixed and milled for 4–6 hr, after which the drum is stopped, the door is opened and the contents are poured out by slow rotation. The balls are retained by screen (*4*) while the material sifted through screen (*5*) falls into the tin container (*7*) which can be hermetically sealed.

Separate drums should be used for the preparation of these binary mixtures. Special care must be taken to ensure that the container for the sulphur mixture is properly sealed, otherwise the sulphur which has been finely milled and heated on milling may oxidize and even ignite in contact with air.

In the German factories at Spandau, Hanau, Ingolstadt and Gnaschwitz, milled saltpetre, milled charcoal and a mixture of equal amounts of sulphur and saltpetre were prepared in separate operations.

MIXING THE INGREDIENTS

The mixing of the three ingredients is one of the most dangerous operations in the manufacture of blackpowder. If mealed powder is to be produced for pyrotechnic purposes (e.g. for signal or rescue rockets), or for initiators, mixing in a drum is sufficient. For the manufacture of granulated or pelleted powder, the ingredients must be mixed in an edge runner, though sometimes drums with wooden balls may be employed.

Mixing in a drum

When mixing the three ingredients to obtain mealed powder, wooden drums 1.5–1.7 m dia. are used in a drum, provided with wooden humps. The humps enable the drums to be rotated with a speed of 17–19 r.p.m.; without them the speed would have to be increased to 25–26 r.p.m. On completion of the mixing process the lid is taken off the outlet, which is covered with the screen, the contents are turned out by slowly rotating the drum, and sifted through the screen. Such a mixture is ready for use in pyrotechnics. In some factories drum mixing is carried out as a preliminary to kneading in edge runners.

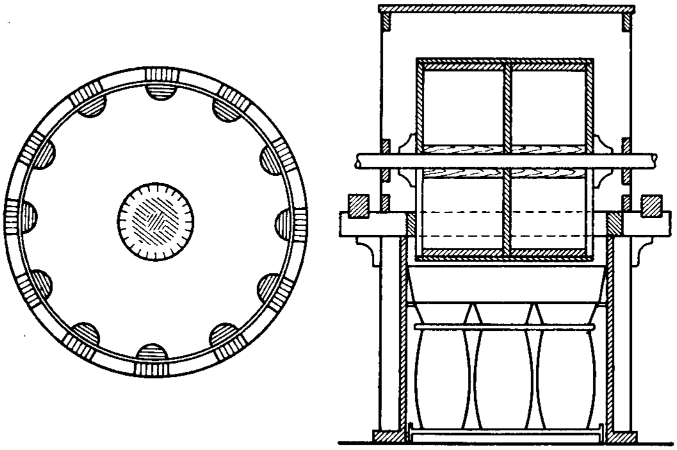

FIG. 92. Wooden drum for mixing three ingredients of blackpowder.

In some factories the three ingredients are dampened with 8–10% of water and then mixed in wooden drums with wooden balls (Fig. 92). The balls work by a kneading action so that to some extent they replace mixing in an edge runner. The required quantity of water is introduced into the drum by a special pipe. After being removed from the drum, the damp mass is pressed into cakes in the same way as the product from the edge runners.

Mixing in an edge runner

The edge runner (Figs. 93 and 94) consist of two heavy (500–600 kg) cast-iron wheels approximately 1.5 m dia. and [illegible].5 m wide. The wheels rotate around horizontal shafts connected by a clutch with a vertical axle (*1*) so as to enable clutch (*2*) to be lowered or raised together with the suspended wheels (*3*). The vertical axle butts against the bearing (*4*) situated in the centre of an iron tray (*5*). Near the wheels and along the vertical axle there are bronze scrapers which push the mixture under the wheels (the scrapers near the wheels push the material towards the centre of the tray, those along the vertical axle push it away from the centre of the tray). The material is thus continuously raked under the rolling wheels. The level at which the scrapers are fixed can be regulated. The wheels may rotate about the vertical axle at two speeds: a high speed of 10–15 r.p.m. and a low one of $\frac{1}{4}$–$\frac{1}{2}$ r.p.m. As a safety precaution, all the nuts and other parts which might be loosened by the continuous motion are split-pinned or fastened with copper wire to prevent them from falling into the mass of blackpowder and thus causing an explosion. To prevent electrification of the charge the equipment must be well earthed.

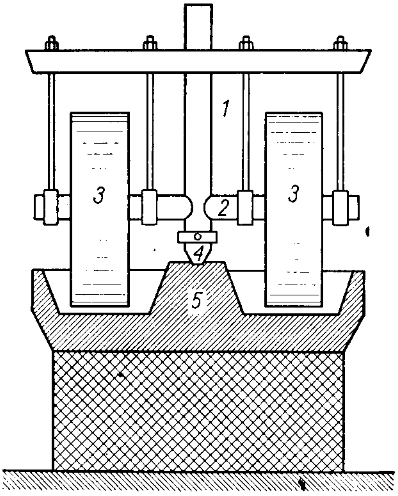

FIG. 93. Diagram of an edge runner.

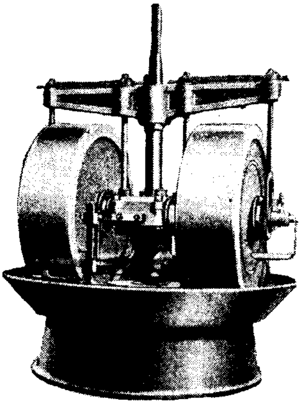

FIG. 94. General view of an edge runner.

Near the vertical axle of the edge runner there is a tube for supplying the charge with the necessary amount of water. In modern factories the water storage tank and the cock regulating the water inflow are situated in an adjacent room from which the apparatus is operated.

During mixing, the gap between the surface of the wheels and the tray must not be less than 4 mm, so as to avoid the danger of seizing. This gap is regulated according to the size of the charge and the density of mixture required. The greater the required density the less should be the gap: the pressure of the wheels on the mixture is then higher.

This principle of mixing by means of suspended wheels was not introduced until the end of the nineteenth century; before then the kneading process in edge runners was the most dangerous operation in the manufacture of blackpowder. Wooden trays were introduced in some factories to increase safety, but they wore out too quickly. In many factories the use of edge runners, which caused such frequent explosions, was completely abandoned in favour of drum mixing and the edge runners have only been re-introduced in very few instances.

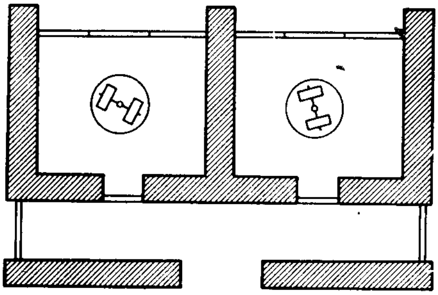

FIG. 95. Lay-out of a building in which edge runners operate.

A lay-out of a factory building in which edge runners are operated is shown in Fig. 95. The building has a "blow-out" construction, i.e. the three walls are stout and the fourth together with the roof is light-weight with a door. One edge runner is placed in each compartment. There is also an engine room in which the engines and transmission gear are mounted (the edge runners usually have an overhead drive comprising bevel gearwheels). There is a window in the wall protected by thick panes, through which a worker operating the edge runner can watch the run of the machine. Switches regulating the run of the edge runner and the cock which controls the water inflow are within arms reach. Admittance to the room where the edge runners operate is prohibited except for the loading and unloading of material. Special felt-soled slippers, left standing by the door, should then be put on to prevent sand from being carried in from outside. When the edge runner is operating at high speed there is no admittance whatever into the premises.

Mixing proceeds in the following way: The ingredients, milled separately or in binary form, are weighed out into wooden boxes or barrels fitted with grips, and following the addition of *ca.* 8% of water (10% on hot and dry summer days) they are mixed by hand with a wooden paddle. The damp material is spread evenly over the tray of the runner. The layer of the material should not be less than 1 cm thick.

The wheels are then set in motion, the rotational speed of the vertical axle being increased gradually so that rolling is carried out with an angular-translatory motion.

Thus the wheels knead, grind and mix the material and at the same time press it by their dead weight.

Due to friction the temperature rises to 30°C, and water evaporates so that further addition should be made from time to time i.e. whenever the mass begins to form dust, which indicates a drop in water content to 2–4%.

If the wheels cease to rotate about their axle, friction develops between the surface of the wheels and the mixture which, apart from lowering the efficiency of the runner, may lead to the ignition of the mixture (e.g. after the surface has dried). To prevent this the runner is adjusted to run at slow speed (which is quite safe) and leather is inserted between the wheels and the kneaded mixture. With the pressure of the wheels on the thickened layer the friction increases and the wheels begin to rotate. The leather may then be removed and the runner switched over to high-speed motion.

The runners are costly to operate since they consume much energy. Care should be taken therefore that they work for as short as possible a time. The maximum density of material is obtained after 1–1.5 hr; further kneading reduces the density of the mixture until a limit is reached.

Escales [56] gives the following figures characterizing the influence of duration of kneading on the density of the product (according to data obtained from the powder factory at Spandau).

Duration of kneading	Density
1 hr 48 min	1.63
2 hr 40 min	1.42
5 hr 24 min	1.36
7 hr 12 min	1.36

The French data, however, are somewhat different (Pascal [57]), namely:

Duration of kneading	Density
Mining powder 30 min	1.57
Military powder F_3 2–2.5 hr	1.47
Sporting powder (78% saltpetre) 1.5 hr	1.725
Sporting powder (78% saltpetre) 5 hr	1.80

If the dust sifted during the later operations is re-used for kneading, the process may by shortened since the material is already partly kneaded. Kneading is carried out with a moisture content of 2–4%.

PRESSING

After the kneading has been completed the mass is pressed to form press cakes which are then dried. These cakes are hard and give a conchoidal fracture. Pressing is done either: (a) in the same edge runners; (b) in hydraulic presses.

Pressing in edge runners

Pressing in edge runners as carried out in France is effected by lifting the scrapers after mixing has been completed, with the runner in slow-speed motion. The wheels knead the mass which is not now raked by the scrapers. The material thus obtained is in the form of a hard press cake which is then air-dried at temperatures from 20 to 30°C.

Pressing in hydraulic presses

The damp mass of powder removed from the edge runners is spread in an even layer up to 9 cm thick over bronze or copper plates. Several layers are thus superimposed and compressed in a press (Fig. 96) at a pressure from 25 to 35 kg/cm^2 for 30–40 min. At this pressure the density of the grains obtained amounts to 1.7. By applying a pressure of 100–110 kg/cm^2 for 1.5–2 hr a density of 1.8 may be achieved. The valves of the press must be handled at a safe distance, from behind a strongly built protective wall, since pressing entails some danger e.g. a slight sliding movement, under the effect of high pressure, may cause an explosion. After pressing, the press cakes are dried, as described above.

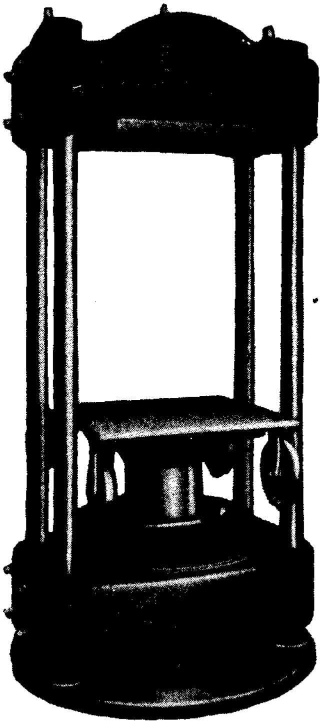

FIG. 96. Blackpowder press, hydraulically operated.

CORNING

Corning is accomplished by breaking up the press cakes into grains, usually in roll corning mills. Drum corning mills are also used but less frequently. For some types of quick-burning powders combined corning is applied using grains from the corning mill together with meal powder (granulation).

Roll corning mill

The dried press cakes are broken up with a mallet into smaller lumps and thrown continuously into the corning mill (Figs. 97 and 98) consisting of several pairs of bronze rollers arranged one above the other. After being crushed between the upper pair of rollers the material passes over an automatic sieve, which separates out the dust. The coarse pieces are crushed by the next pair of rollers, that operate at slower speed, so as to form smaller grains. This process of sieving and crushing is repeated in the following series of rollers and sieves until the material from the last pair of rollers produces grains of the desired size. Any grains that are still too large are recycled.

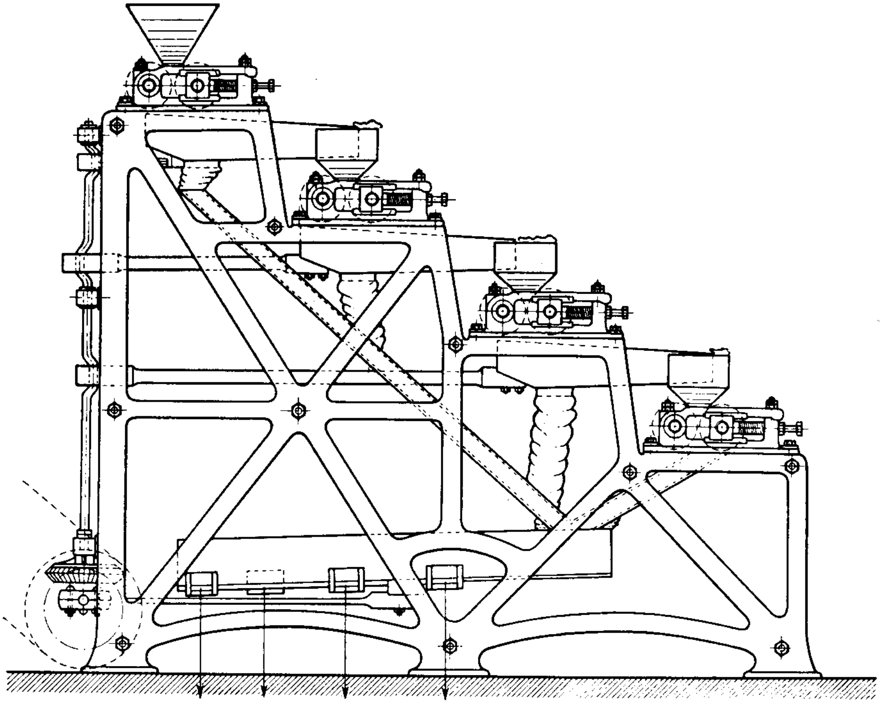

FIG. 97. Corning mill for granulating blackpowder.

The brass sieves under the rollers are stretched on frames so that they can be easily taken out and, if necessary, replaced by sieves of different mesh size. The sieves and rollers are enclosed in a plywood casing, to prevent the escape of dust. Sometimes dust absorbers are fitted (Fig. 98).

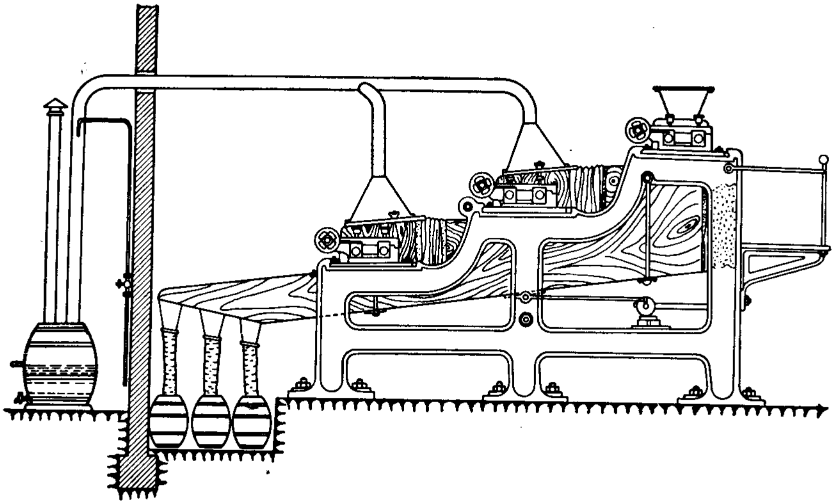

FIG. 98. Corning mill with dust remover.

Since the corning process may be dangerous, the mill is never approached while the machinery is in operation. In modern factories loading is performed by placing the feed pipe of the charging hopper over the corning mill in a separate cage, shielded by a ferro-concrete barrier. Corning mills should be well earthed. The danger is particularly great if foreign bodies e.g. metal fragments or nails, are caught between the crushing rollers. The presence of such objects in the corning mill has caused a number of explosions.

Drum corning mill

The drum corning mill (Fig. 99) comprises two concentric drums (*1*) and (*2*), 1.15 and 1.25 m dia. made of brass net stretched on a wooden frame with wooden ribs inside. The inner drum (*1*) is made of 7.5 mm mesh net while the outer drum (*2*) is of smaller mesh corresponding to the required grain size. The drums are located in a casing (*3*) made of plywood. The casing is connected with the vibrating screens (*5*) by a leather sleeve (*4*). The mesh sizes for different grain sizes (denoted by number of grains per gramme) are:

Sizes of screen meshes (mm)		Number of grains per gramme
I	II	
1.6	1.2	650–950
1.2	0.8	2000–3000
Silk muslin		20,000–30,000

The press cakes, broken into pieces with a mallet, are loaded continuously through a hole in the drum near the axle. As the drum rotates the particles are broken down until grains of the right size are obtained. They are then separated by sieving.

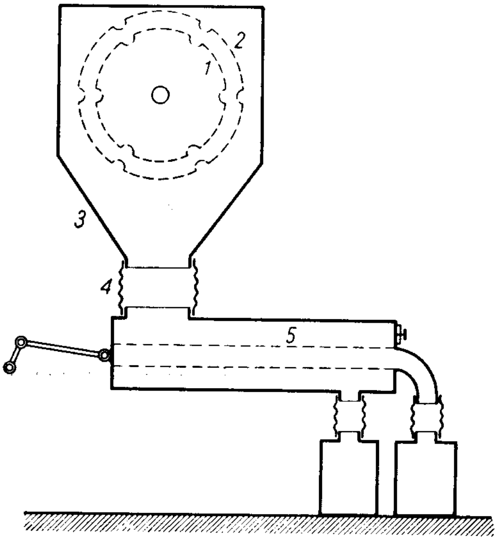

FIG. 99. Diagram of drum granulation.

Granulating in drums. In some countries (e.g. France) the manufacture of very fast-burning low density blackpowder for use in mining is carried out by granulating moistened mealed powder. In the granulating process, a wooden drum 1.6 m dia. and 0.6 m long is employed. A definite number of powder grains are taken from the corning mill, and moistened to a 10% water content with mealed powder produced by mixing of the three ingredients. They are then poured into the drum. As the drum rotates the mealed powder sticks to the surface of the grains to form spherical granules. External wooden hammers are used to prevent the mass from sticking to the inner surface of the drum. The mass heats up by friction and part of the water evaporates, hardening the grains. The granulated powder is sieved to obtain grains in the size range 3–6 mm. The undersized grains are recycled and the oversized ones are ground in the corning mill and granulated again.

FINISHING

The powder from the corning mill is then finished. This consists mainly of polishing, drying and grading the grains. If cylinders are required (blasting powder of the German type) finishing is limited to pressing the grains into cylinders.

Polishing, drying and grading

After corning the grains have an irregular and rough surface which prevents them from flowing freely and from filling a space without voids, so that their density is rather low. To overcome this, the powder grains are polished and thus acquire a smooth, slippery surface. The powder from a corning mill subjected to polishing contains *ca.* 1.5–3% (according to German data) or 4% (according to French data) of moisture. The tumbling drums are constructed similarly to that shown in Fig. 92. They may be made of leather stretched on a wooden frame (Fig. 100). The rate of rotation of the drum, dependent on its dimensions, is 7–16 r.p.m. (smaller drums rotate more quickly to reach the peripheral velocity required). The drum can be charged with 100–240 kg of powder.

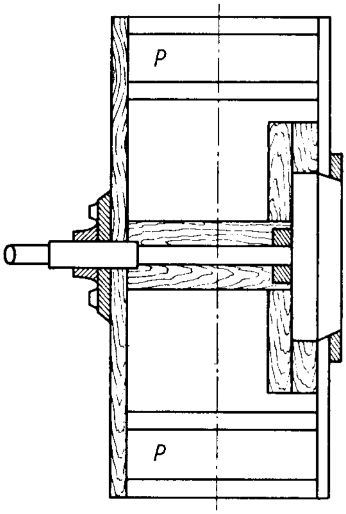

FIG. 100. A leather drum for polishing (the latter is stretched on a wooden frame). *P* indicates the wooden ribs.

At first, the work is carried out with the side door closed so that the powder retains enough moisture to facilitate the polishing process. After a few hours 0.1–0.5% of graphite is added to the charge and polishing is continued for several more hours. The graphite fills the pores in the surface of the grains and coats them with a thin layer, giving them their characteristic brightness.

During the last hours of polishing the side door in the drum is opened so that some of the moisture escapes. The overall polishing process lasts for 4–24 hr, depending on the type of powder. The finished grains are more slippery, pour more easily and fill space better than the unpolished product.

The fine-grained powder used for filling time-trains in time fuses is sometimes polished by coating the grains with a layer of shellac. For this an alcoholic solution of shellac (1–2% shellac by weight) is sprayed into the drum. Powder grains coated with this material burn more slowly than usual. The rate of burning can be regulated by the amount of shellac used.

The polished powder is dried at 50°C to 0.5–1.0% moisture content (in countries with a damp climate the permissible moisture content is higher and in countries with a dry climate—lower). Shelf driers with a natural stream of warm air are usually employed. The use of a pressurized air stream is permissible provided that it is warmed. The use of suction fans is inadvisable since dust from the powder may penetrate their mechanisms and ignite.

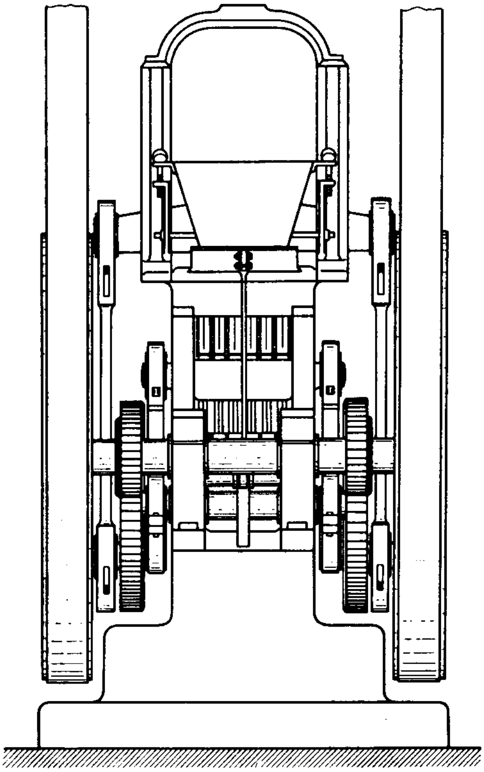

FIG. 101. A multistroke press of the Vyshnegradskii type.

The polished, dried powder is finally graded by sieving out the dust. Revolving or various types of vibrating sieves, often hand driven for safety (see Fig. 99) are used for this purpose.

The sieve frames should be made of wood to avoid the danger of friction and impact. Brass mesh (formerly perforated parchment) or silk muslin is used, stretched on frames so that the sieves can be easily arranged according to the grain sizes required. Dust separated out by sieving is sent back to the edge runners.

After all these operations, i.e. corning, polishing, drying and grading, have been completed 50 kg of the powder, ready for use, is obtained from 100 kg of mixture supplied to the edge runner. All the waste material accumulated during processing is returned to the edge runners. The yield is higher in the manufacture of coarse-grained powder than in that of fine-grained powder.

Final pressing

Final pressing is applied to blasting powder of the German type which is obtained in the form of cylindrical pellets 30 mm dia. and *ca.* 40 mm long with a central hole 10 mm dia. along the axis of the charge. The hole serves for the insertion of a detonating cup or a detonating fuse (p. 328).

Unpolished or polished powder grains containing moisture (up to 4%) are pressed for a short period (e.g. 30 min) in a mechanical press using two pistons: one applied from above, the other from below in order to achieve a highly uniform density. Vyshnegradskii [58] designed this technique. The press is usually a multistroke unit in which six to twelve pellets are compressed at the same time (Fig. 101).

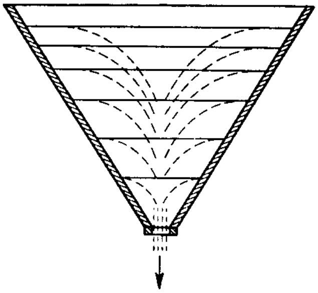

FIG. 102. Diagram showing the working principle of a funnel in powder blending.

The compressed pellets are finally dried at 50°C to increase their resistance to mechanical shock. On drying, the moisture content falls below 1%. Blackpowder in the form of cylindrical pellets is the most suitable type of explosive for blasting. Cannon blackpowder was also once produced in the form of prisms; (this will be discussed later, in the chapter on cannon blackpowder).

BLENDING

To obtain a uniform lot of granular powder several batches are blended in a wooden funnel. The powder is poured into the funnel in layers after which the bottom outlet of the latter is opened. As the contents pour out, like liquid, they are blended (Fig. 102).

CANNON POWDER

Blackpowder for the manufacture of propellent charges has long been obsolete although some types are still produced for other purposes. Thus the French "cube" powder, poudre C or poudre SP, is employed as an igniter in bag cartridges.

Cannon powder is manufactured by kneading in an edge runner followed by pressing the cake to a high density. Afterwards the mass is corned, moistened to 3–3.5% water content and pressed again into cakes at a pressure of 100 kg/cm^2.

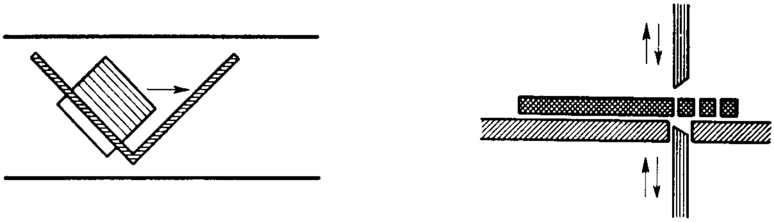

FIG. 103. Cubing sheets of blackpowder.

The sheets are then sliced on a cutter (first into strips, then into cubes) using a rectangular blade (Fig. 103).

After a short polishing period to smooth over and round off the sharp and irregular edges, the cubes are separated from dust and dried to the less than 1% water content.

At one time prismatic powder with a very high density, burning in approximately parallel layers, acquired an importance, but now it is only of historical interest.

It was invented in the United States by Rodman [59] and improved during the period 1868–1882. It had the form of a hexagonal prism (Fig. 104) with a central channel and was manufactured in the usual way with the distinction that the grains from the corning mill were finally compressed into prisms by the Vyshnegradskii hydraulic press (p. 358). It was used for long-range gun fire. Since powder for this purpose must burn as slowly as possible the following measures were taken to reduce the rate of burning:

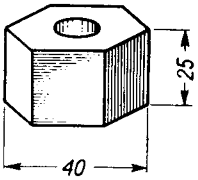

FIG. 104. Blackpowder in prism form.

(1) Brown charcoal was used in the mixture.

(2) The sulphur content in the mixture was reduced. This gave the following compositions:

	In Germany and France	In Russia	In Belgium
KNO_3	78%	75.5%	52%
Sulphur	3%	8.5%	9%
Charcoal	19%	16%	39%

(3) Powder cakes (before corning) were pressed in a hydraulic press to a density of 1.80 and after separating 2.5 mm grains, were pressed again into prisms with a density of 1.86.

(4) The prisms were dried as slowly as possible (3–7 days) and at a low temperature (35–40°C) to avoid the formation of internal fissures due to over-rapid drying.

Mention should also be made of another method of reducing the rate of burning of the powder, i.e. the addition of paraffin. In some French cube powders, paraffin was substituted for 5% of charcoal.

SAFETY IN BLACKPOWDER FACTORIES

The manufacture of blackpowder is one of the most dangerous in the production of explosives.

The individual operations are carried out in "danger buildings", separated by safety distances. These distances are reduced if the buildings are mounded. For unmounded buildings the average safety distance is 50 m. A blow-out construction is usual: three walls are of stout brick while the fourth wall and the roof are of light-weight construction, e.g. of wood or asbestos tile. Alternatively, the whole building may be constructed of light-weight boards.

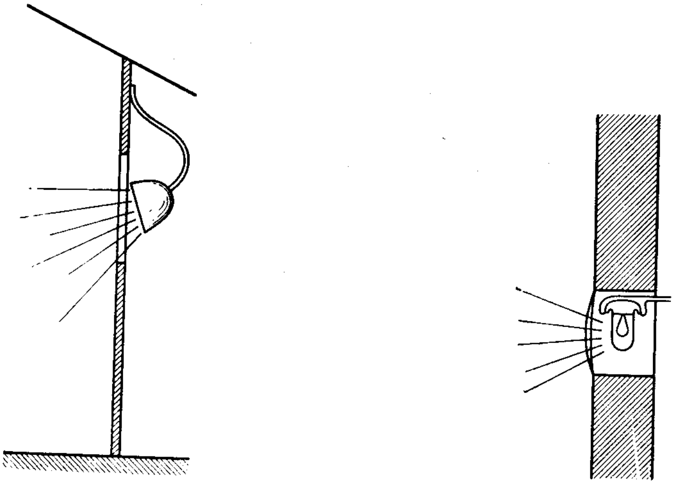

FIG. 105. System for illuminating buildings in which blackpowder is manufactured.

Shelters for the workers should be set up in the vicinity of each building. These are huts covered with earth at the side of the operating building. If the buildings have three stout walls the shelter may be located behind one of them. Doors and windows should be large to give plenty of light, and closed from outside with a wooden shutter. Except for windows facing north the glass should be opaque or coloured. Doors and windows are fitted with overhanging eaves to protect the interior of the building from rain. Inside the building, the floor may be either of wood (all crevices being sealed with pitch) or of asphalt or concrete, close-covered with linoleum. It is also desirable that a wooden barrier should be erected at the entrance forming an anteroom in which those who enter the danger building put on clean felt over-boots.

Electric cables should be carried in steel conduits on the exterior of the walls. Incandescent lamps inside the building should be recessed into the walls and protected by safety glass. Alternatively, the buildings may be lit through the windows by reflector lamps (Fig. 105). The buildings may be heated only by hot water (not by steam) and the radiators must be dusted frequently.

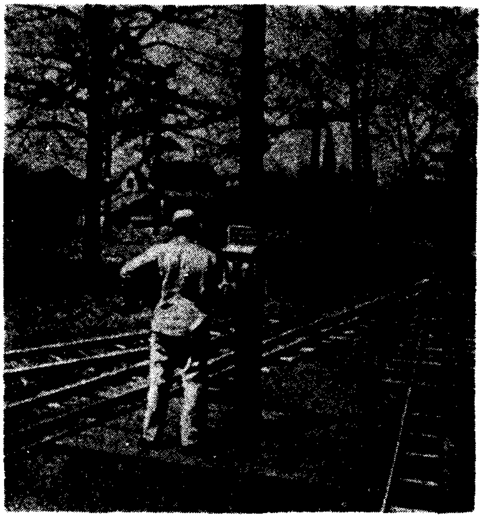

FIG. 106. Remote control of a machine dangerous to operate (corning mill) in a blackpowder factory [60].

All machines must be well earthed, all their frictional parts being made of bronze, wood etc. If steel parts must be used they should be lubricated profusely, if possible, with solid grease (vaseline, cup grease). Particularly dangerous machines (e.g. corning mills) must be operated by remote control (Fig. 106).

In front of the building a timber floor protected by a eave should be laid. Trucks coming and going with materials should be moved by hand. Trucks with pneumatic-tyred wheels or barrows with bronze wheels are best for this purpose. If a narrow-gauged track is to be used, in the vicinity of buildings holding blackpowder, the rails should be of wood and the trucks should be fitted with bronze wheels.

Blackpowder must be packaged for transport in cloth or rubber bags and placed in tightly closed wooden boxes.

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CHAPTER IV

COMPOSITE PROPELLANTS FOR ROCKETS

GENERAL INFORMATION

Blackpowder was the oldest known and the only propellant used in rockets up to time of World War II. It is a slow-burning powder with a high content of charcoal (p. 330).

Blackpowder is still used in small rockets (e.g. signal or rescue rockets for carrying the rope from shore to ship or vice versa). Its limited application is due to the fact that blackpowder gives a very low specific impulse: I_s = from 40 to 80 sec, which is much lower than that of modern composite propellants and smokeless rocket powders which give a specific impulse of 180–200 sec.

Smokeless (double base, i.e. nitroglycerine) powder, however, has some disadvantages which limit its use. It is difficult to produce in large-size charges and production involves costly investments. It is also dangerous to manufacture due to the use of nitroglycerine as an ingredient. In addition the powder requires periodic testing of the stability. It was for this reason that during World War II and afterwards composite propellants were introduced consisting of two essential ingredients: solid oxidant and solid fuel.

Solid composite propellants are usually rich in combustible ingredients and the amount of oxidant is usually limited by the mechanical properties of the mixtures. Careful choice of components is needed to obtain high loadings without jeopardizing fluidity in mixing and creating discontinuities in the binder. A common procedure consists of using oxidants in two or more sizes.

Mishuck and Carleton [1] classify rocket propellants into:

(1) Polymerizable, castable (e.g. polysulphide–ammonium perchlorate mixtures);

(2) Nonpolymerizable, castable, gel-type (cast double base powder);

(3) Vulcanizable, non-castable (rubber–ammonium nitrate).

The most popular are the polymerizable, castable systems (group 1). They offer a great versatility in the choice of polymerizable monomers.

Rheological properties are very important in mixing and processing the compositions. Thus sedimentation of suspended solid before curing ought to be negligible. Casting must be sufficiently fluid to allow the escape of gas-bubbles. It is necessary to know how the viscosity of a homogeneous liquid is modified by high loading with suspended solids.

A general discusion of the factors important in choosing the composition and methods of manufacture of the composite propellants was given by Mishuck and Carleton [1].

The following salts are commonly used as oxidants: potassium, sodium or ammonium nitrates and potassium or ammonium perchlorates. Lithium perchlorate was also suggested but seems to be used in an experimental scale only.

Solid fuels are mainly plastics or elastomers which, apart from functioning as combustibles, also serve to provide the rigidity. Occasionally a combustible and explosive substance such as nitrocellulose in a colloid form may act as the plastic component.

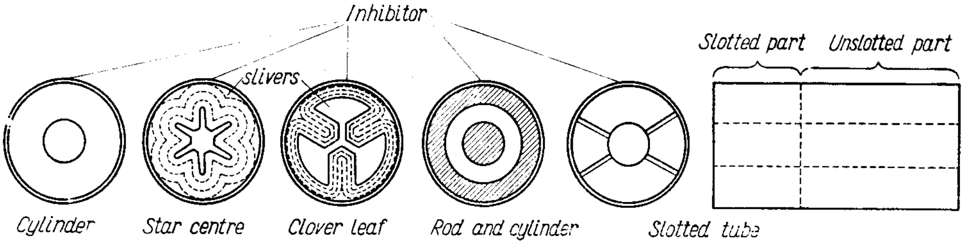


FIG. 107. Charge shapes (cross sections).

Other compositions are similar to pyrotechnic mixtures containing explosive substances, e.g. salts of picric acid.

To increase the heat energy emitted during the reaction metallic powders may be added, e.g. aluminium. Charcoal or soot are added sometimes to make the mixture burn smoothly.

The advantage of the majority of the mixtures concerned lies in the cheapness and stability of their ingredients, which do not decompose during storage and the uncomplicated and relatively safe method of manufacture. Periodic chemical stability testing for smokeless powders, which necessitates a suitable organization and entails a high expenditure, is unnecessary.

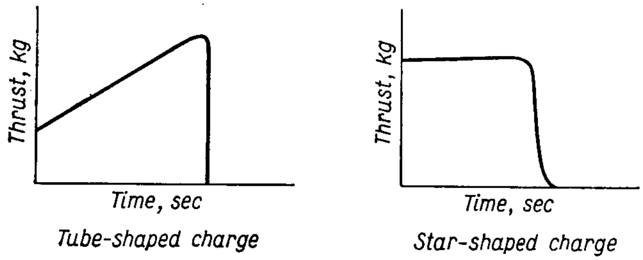
A general requirement is that the average molecular weight of exhaust gas should be low. This restricts the choice of solid propellant components to those containing elements of low atomic weight. Low atomic weight elements often release a greater heat of reaction.

Very little is known about the burning mechanism of these mixtures. There is a "two-temperature" theory of propellant combustion [2, 3].

According to this theory the rate-controlling reactions are associated with the gasification (pyrolysis) of the solid oxidant and the solid binder which in a composite propellant are essentially independent of each other.

The modern grains have their outer surface protected by an inhibiting layer and they burn from the inner surface created by differently shaped cores. Cross sections of some typical charge are shown in Fig. 107. The purpose of the different shapes is to permit the rocket to operate at constant pressure by keeping the burning surface constant. The most commonly used charge design has a star-shaped core or some similar shape (e.g. clover leaf) [4, 5]. The thrust–burning time curves of cylindrical and star-shape charges are given in Fig. 108.

The star-shaped charge leaves slivers which burn out at low pressure and this leads to impulse losses. The slivers may remain unburnt and their weight is then added to the payload. Rods and cylinders do not leave slivers, but supporting the central cylinder may present some difficulty and a tube slotted at the nozzle end seems to be a more practical design [4].



Tube-shaped charge

Star-shaped charge

FIG. 108. Thrust–burning time curves of cylinder- and star-shaped charges.

MIXTURES WITH THE SALTS OF PERCHLORIC ACID

Mixtures composed of the salts of perchloric acid and an elastomer or plastic polymer are now the most popular of the composite propellants.

Mixtures containing potassium perchlorate are characterized by a relatively high rate of burning, high exponent n in the equation $V=kp^n$ and a high flame temperature. When burning they produce a dense smoke. Mixtures containing ammonium perchlorate have a lower rate of burning, low exponent n and flame temperature and yield less smoke. The rate of burning of these mixtures is however higher than that of similar mixtures with ammonium nitrate. Andersen *et al.* [3] found that a composite propellant with 75% ammonium perchlorate and 25% copolymer of polyester and styrene burns under a pressure of 6 kg/cm^2 at 15°C with a rate of 0.64 cm/sec, i.e. 2–3 times faster than corresponding mixtures with ammonium nitrate.

The forerunner of the rocket propellant containing perchlorates as oxidants was the American product, Galcit, developed in the Jet Propulsion Laboratory (JPL) of the Guggenheim Aeronautical Laboratory, at the California Institute of Technology. It consisted of asphalt as a fuel and potassium perchlorate as an oxidant, mixed hot. Originally the material was hot-pressed into rockets. However, at high pressures the flame penetrated between the charge and the walls of the rocket, causing an abrupt increase of the burning surface and consequently of the pressure, so the modification was introduced of pressing the material into blocks, which were not in contact with the walls of the rocket.

This composition was useless outside certain temperature limits, i.e. outside the range 4–38°C (40–100°F), the mixture becoming brittle and breakable at lower temperatures, and soft and shapeless at higher ones.

Zaehringer [6] gives the following composition for Galcit Alt 161:

Potassium perchlorate	75%
Asphalt with mineral oil or resin	25%

Resin was added to the asphalt to raise its softening temperature.

Specific impulse I_s was 186 sec at 1350–3700 lb/in^2 pressure range.

MIXTURES OF PERCHLORATES WITH ELASTOMERS. THIOKOL PROPELLANTS

Some of these propellants are apparently very popular. They are probably the cheapest composite propellants now in use.

T. L. Smith [7] discusses the properties required in elastomeric binders and the mechanical properties of solid cast-in-place case-bonded propellants. He considers that the most important mechanical property required in composite propellants containing an elastomer and intended for case-bonded grains is a relatively large ultimate elongation over a range of temperature and strain rate of experimental time scale. Moreover, the propellant grain must not creep excessively during rocket storage, and the grain must not crack or deform excessively under flight acceleration forces.

According to T. L. Smith an ideal elastomeric binder should have low "glass" temperature, should exhibit high elongation over a wide temperature range, should be cross-linked preferably through stable covalent bonds, and should not crystallize spontaneously during storage at any temperature.

The uncured binder material should be a liquid which cures with minimum heat release and shrinkage and without evolution of gases.

The binder should not be a solvent of the oxidant and should be chemically stable for long periods in close contact with the oxidant.

A more detailed discussion of the visco-elastic properties of rubber-like elastomers for composite propellants was recently given in a paper by Landel and T. L. Smith [8].

Among the composite propellants containing elastomers, those containing polyethylene sulphide "rubber", so called Thiokol, are widely used. Since 1950 they have been developed by the Thiokol Chemical Corporation in the U.S.A. under the general name of "Thiokol Propellants".

These compositions consist of thiokol and perchlorate, most probably in proportions:

Thiokol	20–40%
Perchlorate	80–60%

As there is no certainty that common solid thiokol produced in the form of latex should give a sufficiently homogeneous mass, Thiokol Corporation have worked out a method of starting with liquid thiokol which is then "cured".

As a rule, the liquid thiokol, mixed with an oxidant and an accelerator is poured into a prepared rocket chamber and cured *in situ* when the charge is solidified.

Liquid thiokol

The basic ingredient of the mixtures is liquid thiokol.

According to descriptions published by the Thiokol Chemical Corporation [9] and Göbel [10] liquid thiokol is obtained in the following way: ethylene chlorohydrin is condensed into dichlorodiethylformal (I) which is then treated with sodium polysulphide to form the polymer (II):

$$2ClCH_2CH_2OH + CH_2O \rightarrow \underset{\mathrm{I}}{ClCH_2CH_2OCH_2OCH_2CH_2Cl} \xrightarrow[x=\text{from 1 to 5}]{Na_2S_x}$$

$$\underset{\mathrm{II}}{HS\text{—}[C_2H_4OCH_2OC_2H_4SS]_n\text{—}C_2H_4OCH_2OC_2SH}$$

Other dichloro compounds may be used instead of dichlorodiethylformal, e.g.: 1,2-dichloroethylene, 1,3-dichloropropylene, dichlorodiethyl ether, dichlorotriethyl ether which, however, have never yet been put to practical application.

There are now six types of Thiokol Liquid Polymer (LP for short) in commerce: LP-2, LP-3, LP-31, LP-32, LP-33, LP-8 (see Table 83).

TABLE 83

	LP-31	LP-2 and LP-32	LP-3 and LP-33	LP-8
Physical state	Mobile liquid	Viscous liquid	Mobile liquid	Mobile liquid
Colour	Amber	Amber	Amber	Amber
Specific gravity at 20°C	1.31	1.27	1.27	1.27
Viscosity at 25°C (cP)	80,000–140,000	35,000–45,000	750–1500	250–350
Average molecular weight	7500	4000	1000	500–700
n (in the formula II)	42	23		
pH (water extract)	6.0–8.0	6.0–8.0	6.0–8.0	6.0–8.0
Stability (years)	over 3	over 3	over 3	over 3
Moisture content (%)	max. 0.2	max. 0.2	max. 0.2	max. 0.2

The difference between these polymers lies in the degree of polymerization or cross-linking. Thus LP-2 and LP-32 are cross-linked polymers. Of these two types the cross-linking of polymer LP-32 is weaker, therefore the modulus of elasticity of LP-32 (after curing) is smaller. The bursting stress of cured LP-32 is twice that of cured LP-2.

A similar difference exists between LP-3 and LP-33. Polymer LP-33 differs from LP-3 in having a weaker cross-linking.

The viscosity of polymers LP depends to a high degree on temperature.

Thus for a sample of Thiokol LP-31:

at 26.7°C (80°F) the viscosity was *ca.* 120,000 cP
at 48.9°C (120°F) the viscosity was *ca.* 28,000 cP
at 71.1°C (160°F) the viscosity was *ca.* 10,000 cP

At 25°C Thiokol LP-2 had a viscosity of 35,000–45,000 cP, but at 80°C the viscosity was only 5000 cP.

The curing of liquid thiokol is based on the reaction of the liquid polymer with lead dioxide or peroxides. Dehydrogenation of the terminal groups of the mercaptan chains of the polymer then takes place followed by elongation of the chains. This reaction may be depicted as:

$$2RSH + PbO_2 \rightarrow \underset{\text{III}}{—R—S—S—R—} + H_2O + PbO$$

The lead oxide so produced and the lead oxide present as an impurity of lead dioxide may continue to react:

$$2\,—R—S—S—R— + PbO \rightarrow \underset{\text{IV}}{—R—SPb—S—R} + H_2O$$

The lead mercaptide thus obtained may undergo oxidation during heat curing or on heating with a small amount of sulphur to form chain (III):

$$\underset{\text{IV}}{—R—S—Pb—S—R} + S \rightarrow \underset{\text{III}}{—R—S—S—R—} + PbS$$

Three to five parts by weight of PbO_2 are usually used per hundred parts of LP.

Up to 0.5% of sulphur may also initiate the curing effect of lead dioxide. Conversely, the addition of fatty acids and their salts may exert an inhibitory influence upon the curing process of polymer LP. Thus the addition of one part by weight of stearic acid to polymer LP approximately doubles the curing time.

Peroxides (e.g. cumene hydroperoxide) are alternative curing agents. The reaction then proceeds according to the equation:

$$2\,—R—SH + O \rightarrow \underset{\text{III}}{—R—S—S—R—} + H_2O$$

Approximately five parts by weight of hydroperoxide are used per hundred parts of polymer LP. The reaction may be accelerated by an alkaline medium, so that a small (e.g. 0.2 part) amount of weak bases may be added e.g. benzyl-dimethylamine or tri(dimethylamino)-methylphenol (DMP-30).

Also noteworthy is the addition of an agent to increase mechanical strength (e.g. carbon black, titanium dioxide, zinc sulphide, lithopone) and plasticizers which usually serve to disperse the PbO_2 within the polymer.

Thiokol Chemical Corporation suggests the following compositions for B (Base compounds) (in weight units):

TABLE 84

Composition of B compounds	LP-31	LP-2	LP-32
Thiokol LP	100	100	100
Carbon black	–	30	30
Soot or zinc sulphide or lithopone	30–50	–	–
Stearic acid	1	1	1
Sulphur	0.15	–	0.1

The composition of C (Curing compound) is:

PbO_2	50%
Stearic acid	5%
Dibutyl phthalate	45%

B compound is mixed with C compound in the proportions of hundred parts of Thiokol LP to ten to fifteen parts of C compound.

Thiokol Chemical Corporation gives the following characteristics of polymers LP-2 and LP-32 cured in 24 hr at 26.7°C (80°F) and then pressed for 10 min at 175–190°C (287–310°F):

TABLE 85

	LP-2	LP-32
Tensile strength lb/in^2	500	550
300% modulus lb/in^2	350	250
Crescent tear index	125	145
Shore A hardness	50	45
Low temperature flexibility (°F)	−65	−65
High temperature resistance (°F)	275	275
Ozone resistance	excellent	excellent
Sunlight resistance	excellent	excellent
Ageing resistance	excellent	excellent

Cured polymers obtained in this way show very high resistance to such solvents as petrol, water and ethanol. On the other hand they swell and absorb ketones, esters (ethyl acetate) and carbon tetrachloride.

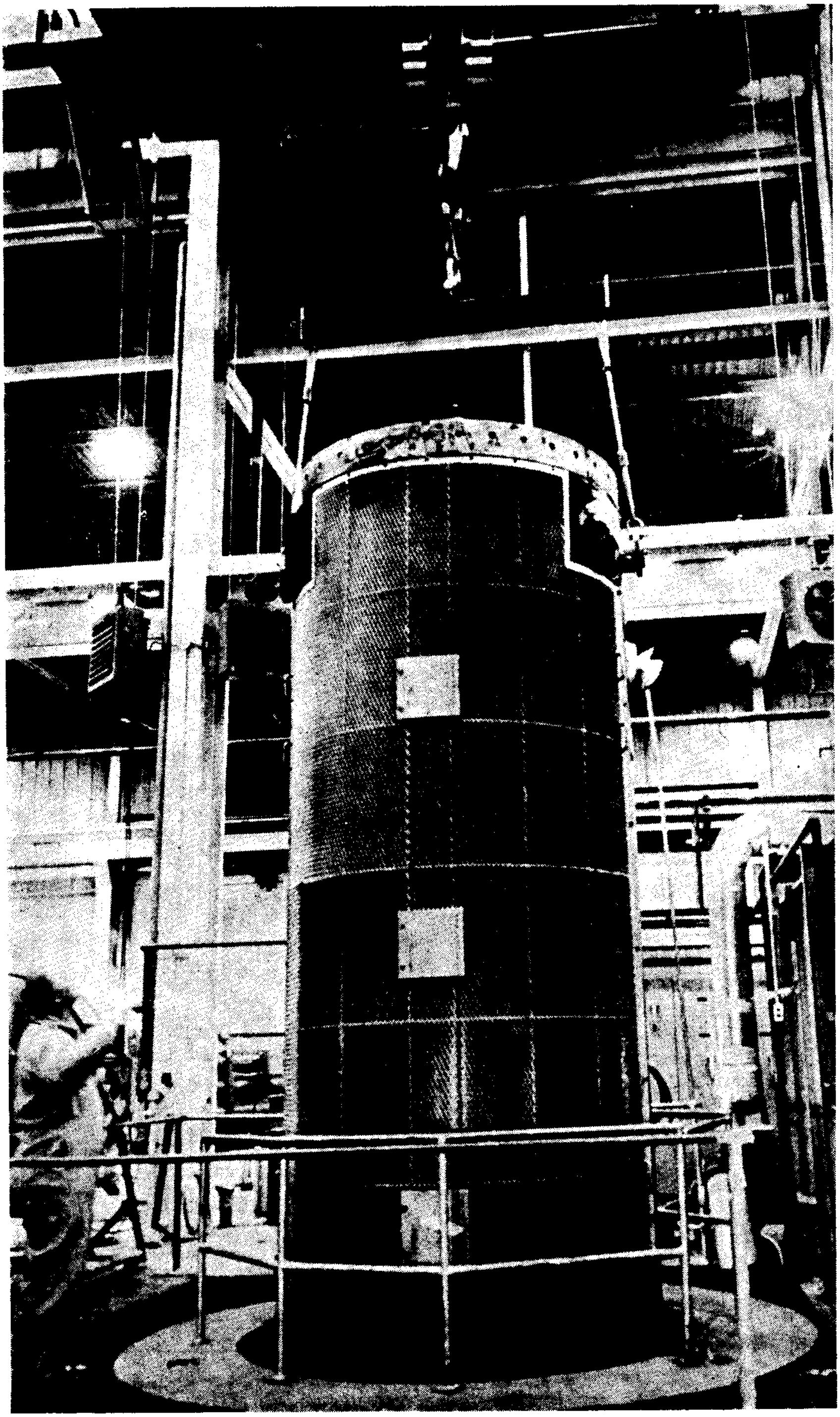


FIG. 109. Rocket chamber being lowered into a vapour degreasing pit to remove all traces of grease and oil (according to Dykstra [11]).

THE TECHNOLOGY OF THE MANUFACTURE OF ROCKET CHARGES CONTAINIG COMPOSITE PROPELLANTS WITH THIOKOL

It is characteristic of the technology of the manufacture of rocket charges containing composite propellants with thiokol that the semi-liquid mixture is poured directly into the rocket chamber lined from within with an insulating layer to which the charge adheres tightly ("case-bonded" charge). This is a very cheap and rapid method of manufacture.

Warren [5] describes the following stages of manufacture as used at the Thiokol Chemical Corporation's Redstone Arsenal, Huntsville, Alabama:

(a) chamber preparation,
(b) oxidant preparation,
(c) mixing,
(d) casting,
(e) curing,
(f) finishing and inspection.

Chamber preparation (Case-bonded propellants)

The rocket chamber itself is used as the mould. The inner surface of this chamber must be very carfully cleaned so that the propellant will be well bonded to it. Any rust or foreign material should be removed by wire brushing or sand blasting. After that, particles loosened by this operation, together with any grease or oil which may be present, are removed by a vapour-degreasing, trichlorethylene being the most popular degreasing agent. With large units the solvent is poured directly into the chamber which is then rotated and brushed at the same time (Fig. 109).

Most propellant manufactures apply an insulating lining to the chamber surfaces to protect the metal wall. The propellant itself is an insulator during most of the burning, so presumably the lining acts as an insulator only during the final burnout. Another important function of the lining is to inhibit burning on the outside of the charge where there is a poor bond to the metal case. The same binder that is used in the propellant, but without the oxidant, makes an effective lining. It is generally sprayed on and polymerized in place by a short curing treatment at an elevated temperature. The thin layer provides an excellent surface to which the propellant can be bonded.

While chamber preparation is going on the cores or "risers" are prepared to act as moulds for the perforation of the charge. The cores can be placed in the rocket chamber prior to casting and held in place by special supports, but usually they are added after the propellant has been cast. Precise alignment of these cores is of the utmost importance. A star-shaped core is given in Fig. 110.

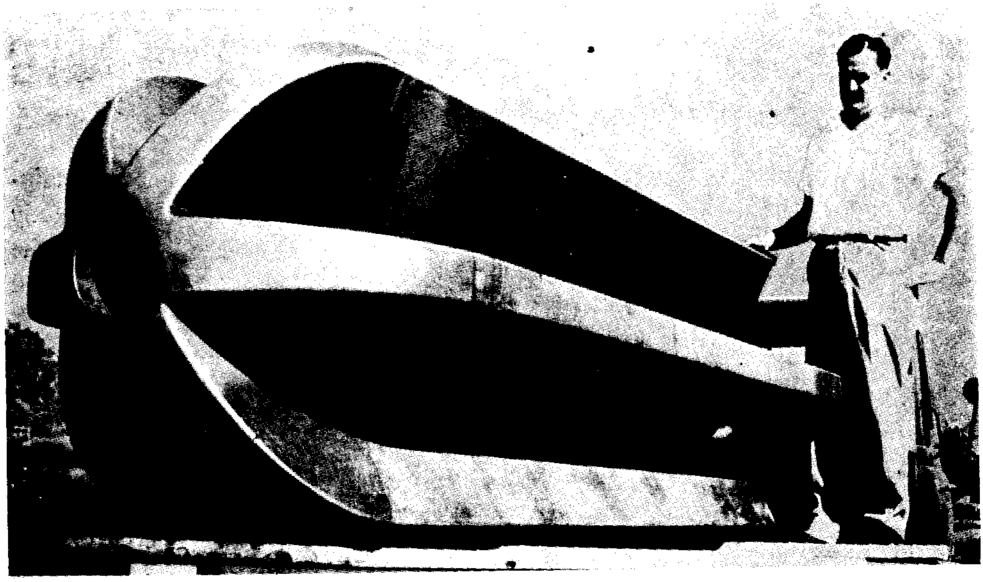


FIG. 110. Charge with a star-shaped core (Thiokol Chemical Corporation, according to Chapman [12]).

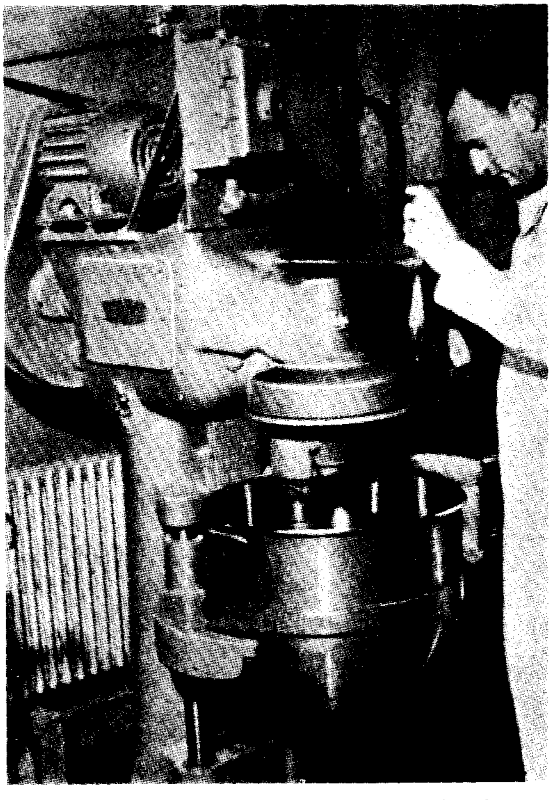


FIG. 111. A double-motion paddle mixer for premixing Thiokol propellant (Thiokol Chemical Corporation, Redstone Arsenal, according to Warren [5]).

Preparation of the oxidant

Inorganic oxidants are used exclusively in composite propellants; their properties have already been discussed. Huggett [13] draws attention to the importance of the particle size of the finely ground potassium perchlorate in compositions. They should be ground with extreme care.

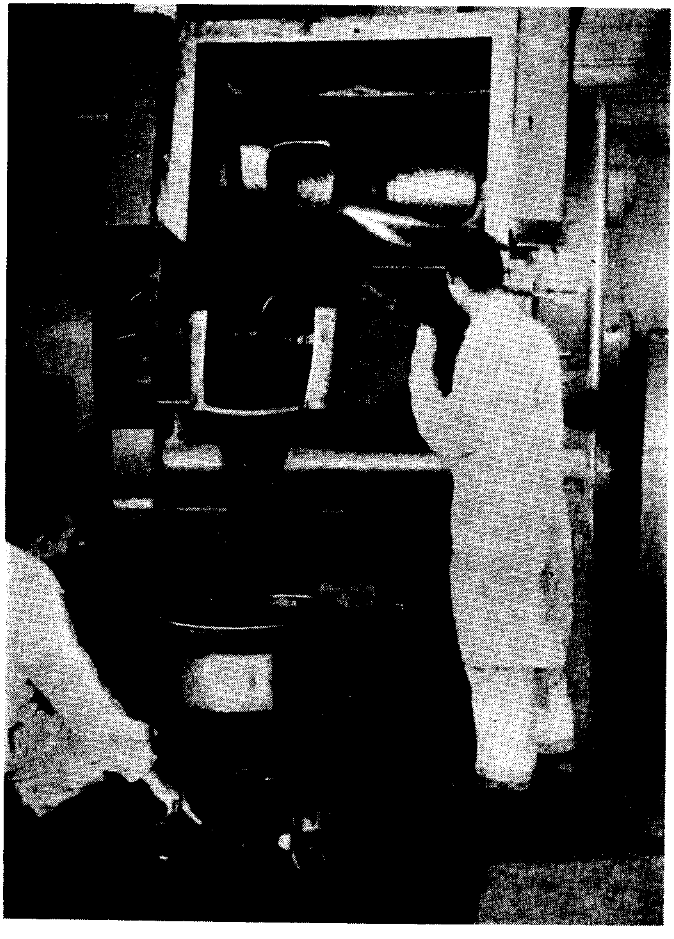


FIG. 112. Removal of propellant from mixer to transport vessel (Thiokol Chemical Corporation, Redstone Arsenal, according to Warren [5]).

By using a suction mill and operating under conditions of controlled humidity, uniform particles of 2–10 μ can be obtained. The oxidant is ground only in the quantities needed for each batch and is never stored in a finely-ground state as the fine particles have a tendency of "caking" and agglomerating into larger ones. The grinding operation is not without its hazards and extreme care must be exercised, especially with the perchlorates.

Mixing

A "premix" is prepared by mixing the fuel binder (i.e. a polysulphide rubber in the case of the Thiokol propellant) with the necessary curing agents, inert additives, and ballistic modifiers in a double-acting paddle mixer. This mixer is equipped with a paddle rotating on a shaft located off center in the mixing vessel. As the shaft rotates it also revolves about the central axis of the vessel, so that it operates in all parts of the vessel in turn. Figure 111 shows the paddle mixer in operation. (Different fuels may require different mixing systems.) When the premix has been thoroughly blended it is transferred to a larger mixer.

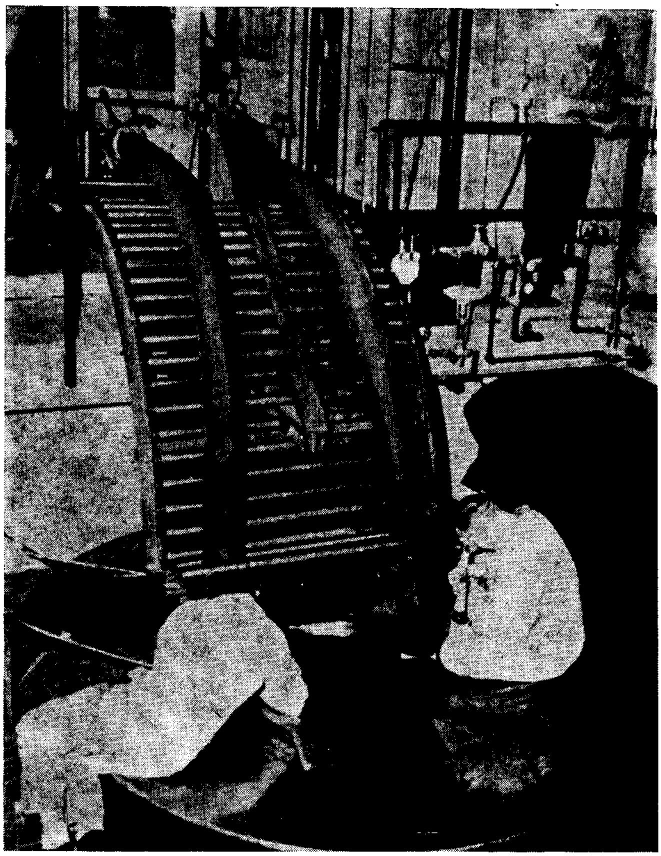


FIG. 113. Casting propellant around a star-shaped core, according to Dykstra [11].

The final mixing takes place in a large Werner–Pfleiderer (or Baker–Perkins) type sealed mixer of the type extensively used in smokeless powder manufacture (Fig. 206). A capacity up to 2000 lb is used in the case of thiokol propellants. After the premix has been added to the mixer, the finally ground oxidant is added. This material is conveyed to the mixer in a closed container and is added so that the container and mixer remain cut off from the outside air. Mixing is continued at a controlled temperature until the mixture becomes uniform. The duration of the mixing depends on the material used. The blended material is very viscous, but still pourable and is poured into a transfer vessel for transportation to the casting room (Fig. 112). Here, it should be de-aerated under vacuum prior to casting to ensure uniform burning characteristics.

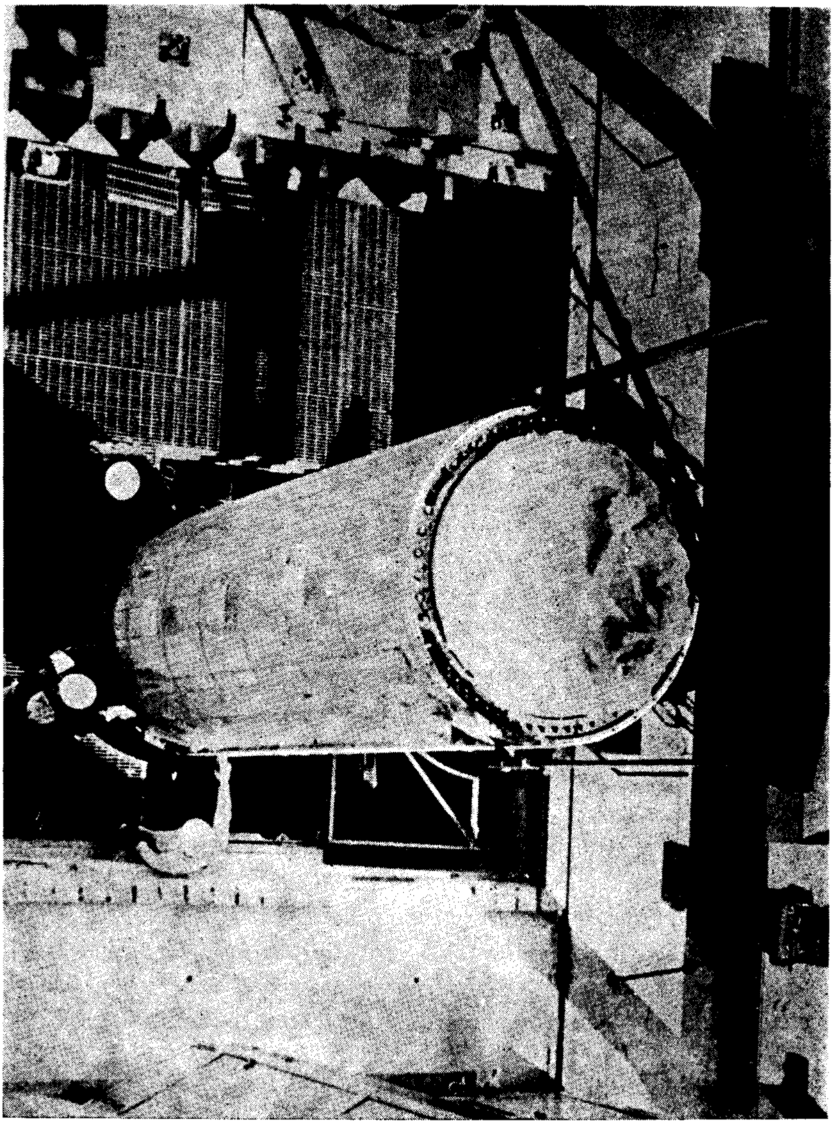


FIG. 114. The rocket chamber with the cured propellant is removed from the curing oven, according to Dykstra [11].

Casting

There are several ways of filling the rocket chamber with the propellant. It can be introduced through a long tube ("bayonet") which is lowered into the chamber or it can be added through the bottom of the tank. The material is cast into the chamber around the core (Fig. 113) or the core is lowered into the chamber after the propellant has been cast in the rocket chamber. The loaded motor chamber is then sent to the curing ovens.

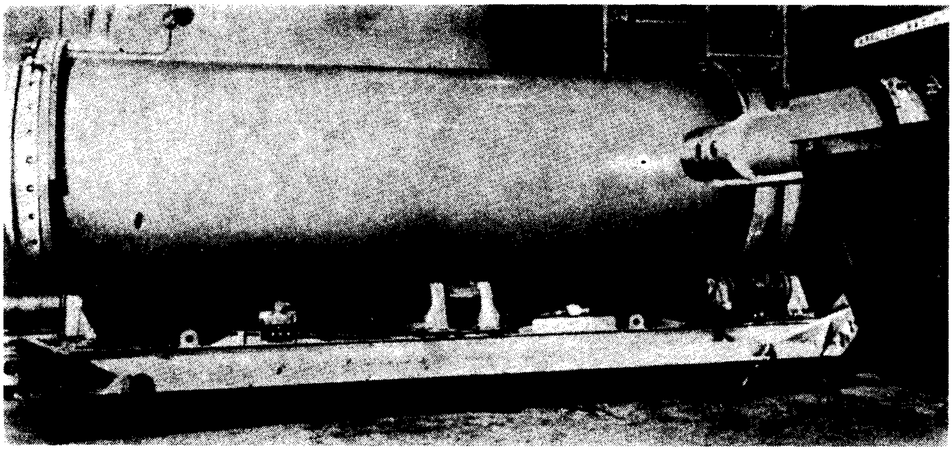


FIG. 115. X-Ray inspection of the 65.5 in. dia. cast propellant, according to Dykstra [11].

Curing

The filled chamber is placed in an oven where the temperature is gradually raised at a given rate to a definite temperature (sometimes up to 150°C). At this temperature it is held for a determined time, the oven is then cooled to ambient temperature and the chamber removed from the oven (Fig. 114). Curing rate and curing time must be carefully controlled to obtain the desired physical and ballistic characteristics. After curing is complete, the cores are removed and excess propellant cut away. The "grain" is now ready for final inspection.

Inspection

Inspection during the course of the manufacture is extremely important. By chemical analysis the quality of most of the ingredients is maintained within specified limits. Visual inspection is made of chamber surface and lining condition before casting. Sieve analysis should be used to check the particle size of the oxidant. As with most plastic materials, control of the quality of the product can be assured only by careful control of the variables affecting the polymerization of the material.

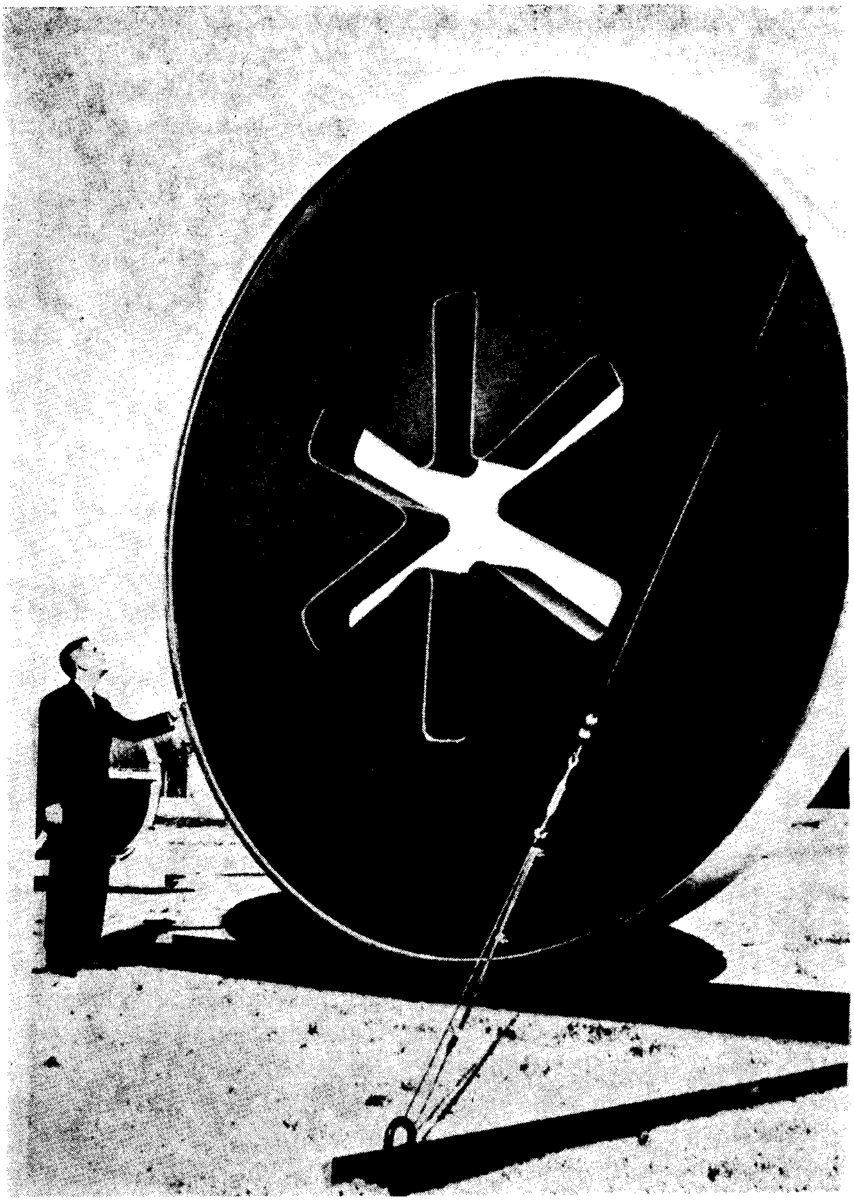


FIG. 116. Cross-section of a Thiokol propellant for 14 ft dia. rocket 63 ft in length [14].

Temperature, time, rate of mixing and quantity of ingredients are important variables.

Once the materials have been mixed, it becomes very difficult to analyse quan itatively for individual ingredients. This is especially true when curing is complete. After curing, the propellant grain and chamber pass through a series of inspections including weighing, radiography, X-ray (Fig. 115), fluoroscopic examination, gauge measurements, and checking with optical comparators. Small rockets can be given a final check by the static or flight testing of a random sample. With large rockets, such testing becomes too expensive and must therefore be kept to a minimum.

Inspection for storage stability, a most important factor in the case of the nitric esters, is a different matter with composite propellants. These compositions unlike nitrocellulose do not undergo spontaneous decomposition. However, composite systems do undergo a change in character during storage. Burning properties and physical characteristics (e.g. tensile strength) may change continually with time. By improving the composition and curing techniques these changes can be reduced considerably. Figures 116 gives a cross-section of a thiokol propellant "grain" of a 14 ft dia. rocket.

MIXTURES OF PERCHLORATES WITH OTHER ELASTOMERS

Among the possible alternatives synthetic rubber may be mentioned. In particular the mixtures of potassium or ammonium perchlorates with butadiene–styrene copolymer are recommended.

There is, however, limited information on the method of manufacture and on the properties of these compositions.

Among various elastomers recently recommended as combustible ingredients of composite propellants polyurethanes are particularly important and promising [15]. Three basic building blocks are used for polyurethane-rubber fuel-binder: di-isocyanates, low-molecular weight triols and long-chain diols—linear organic compounds terminated at each end by hydroxyl groups with molecular weights from 1000–2000.

New copolymer diols derived from ethylene oxide and tetrahydrofuran yield linear polyurethanes of superior physical properties [16].

The chief problem in the manufacture of polyurethane propellants lies in determining the point where the liquid, uncured propellant is reduced to the uniform consistency necessary to obtain reproducible ballistic performance.

MIXTURES OF PERCHLORATES WITH PLASTICS

Among the plastics which in addition to being combustible ingredients of these mixtures serve also as binders imparting mechanical strength to the charges, the following substances have recently become of considerable interest: methyl methacrylate, polystyrene.

The use of polyethene has also been mentioned. So far the best-described mixtures are those with methyl methacrylate. Mixtures with ammonium perchlorate go by the name of Aeroplex N, those with potassium perchlorate are known as Aeroplex K.

Among the few papers on the physico-chemical properties of these mixtures that of Alterman and Katchalsky [17] is noteworthy as it contains data on a number of solid physico-chemical mixtures of methyl polymethacrylate with potassium perchlorate.

The figures obtained by the authors are given in Table 86.

TABLE 86

Composition (% by weight)		Density g/cm³	Specific heat cal/g	Heat of decomposition kcal/kg	Flame temperature °K	Ignition temperature with 20 sec delay °K	Rate of burning (cm/sec) at pressures of:		
Methyl polymethacrylate	$KClO_4$						30 atm	50 atm	100 atm
20	80	1.88	0.241	800	3750	925	1.41	–	–
22.5	77.5	1.88	0.247	832	3770	927	1.43	2.34	5.48
25	75	1.86	0.254	859	3778	930	1.38	2.33	–
30	70	1.82	0.267	828	3518	936	1.17	2.12	–

The very high flame temperature of the above mentioned mixtures is noteworthy. In the majority of smokeless nitrocellulose or nitroglycerine powders it is considerably lower: 2000–3000°K.

Attention has recently been paid to the possible use of alkyd type polyester resins as combustible binders of composite propellants. The use of polyester resins from maleic, adipic or phthalic acid has been suggested. Their main advantage is that they can be cured in the cold by the addition of styrene or diallyl phthalate. Curing the charges can thus be performed at a relatively low temperature.

These binders possess properties which are very important for ease of manufacture and for obtaining a uniform product. Thus they have low viscosity on casting without sedimentation of solids, have sufficient reactivity for complete low-temperature cure and evolve little heat on polymerization (e.g. much lower than heat of polymerization of methyl acrylate).

Noteworthy among the few reports in the literature on this subject is the work of Andersen, Bills, Mishuck, Moe and Schultz [3] on the mechanism of combustion of a mixture of 75% NH_4ClO_4 and 25% polyester with styrene. The work of Grodzinski [18] who investigated the thermal decomposition of the mixtures of various combustible substances with potassium perchlorate in a ratio of 20/80 by weight, is also of great interest. The combustible ingredients include asphalt and polyester resin from unsaturated (maleic) or saturated acids.

The following figures characterize the temperature at which explosion occurred after the lapse of a certain induction period or "time lag" (see Table 87).

The ignition temperature of a sample of the mixture of $KClO_4$ with unsaturated polyester resin introduced into a thermostat heated to 296°C, in relation to time, is shown in Fig. 117 (curve *I*). The curve resembles that given by Roginskii for nitroglycerine heated at 41°C in the presence of nitric acid as a catalyst (Vol. II, Fig. 11, p. 48). Here the temperature of the sample just before the explosion was 298°C,

TABLE 87

Combustible ingredient	Temperature °C	Induction period min
Asphalt	320	75
Saturated polyester resin	340	10
Unsaturated polyester resin	290	32
Polyethylene	440	15
Paraffin oil	440	56
Starch	265	4
Cotton linters	245	5
Graphite	305	2
Active carbon	315	3
Carbon black	440	3

i.e. only 2°C higher than the ambient temperature. Curve *II* represents the result of a similar experiment with a mixture of potassium perchlorate and ethylene glycol.

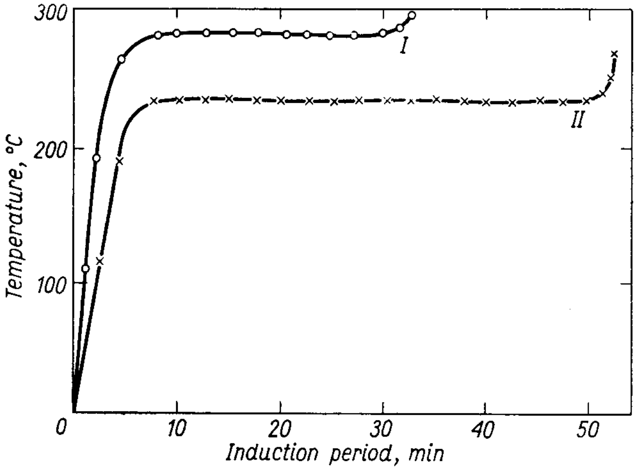


FIG. 117. Low-temperature explosions of mixtures of potassium perchlorate with some combustible substances: *I*—with polyester resin (temperature of the thermostat 296°C), *II*—with ethylene glycol (temperature of the thermostat 241°C), (according to Grodzinski [18]).

Grodzinski ascertained that the addition of potassium or lithium chlorate to these mixtures does not change the ignition temperature but reduces the induction period.

The exothermic decomposition of the mixtures of potassium perchlorate with charcoal at 300–360°C was studied by Gordon and Campbell [19].

Some technological information on the Aerojet General Corporation's composite propellants technology was published recently [20]. Ammonium perchlorate is ground to the particle sizes ranging from 1 to 200 μ and then mixed to form a blend of the various particle sizes which gives the best mechanical and ballistic properties. Ammonium perchlorate is mixed with liquid polybutadiene–acrylonitrile fuel, liquid plasticizer and aluminium powder (Fig. 118). The motor casing is coated internally with an antirust compound, insulated with silica-filled nitrile rubber and finally lined with polybutadiene-rubber polymer similar to the propellant fuel and binder (Fig. 119). The polymer is cured in the usual way. Casting the propellant is done through the "bayonets" from the casting pot to the case (Fig. 120).

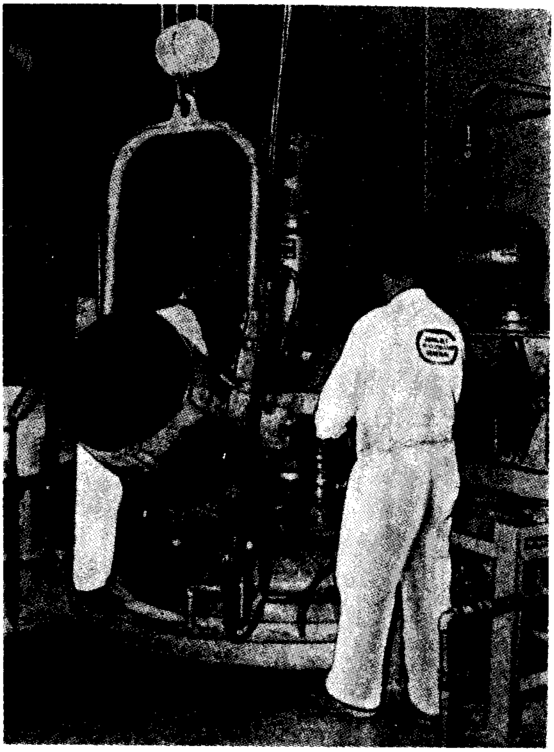


FIG. 118. Pre-mixing ammonium perchlorate with liquid polymer, plasticizer or aluminium (Aerojet General Corp. [20]).

MIXTURES WITH AMMONIUM NITRATE

Mixtures containing ammonium nitrate have recently been suggested as materials for rocket propulsion.

According to J. Taylor [21] potassium dichromate is an efficient catalyst of the decomposition of ammonium nitrate. J. Taylor and Sillitto [22] found that mixtures for rocket propulsion, with ammonium nitrate as a chief component, should contain ammonium dichromate which facilitates the onset of the decomposition of ammonium nitrate and subsequently supports this decomposition.

These authors suggest the use of fusible mixtures containing ammonium nitrate (of the type described above—p. 253) from which the propellant "grains" are cast. The grains in the form of tubes have a high density and are suitable for rockets of small calibre.

FIG. 119. Preparation of the case (Aerojet General Corp. [20]).

The composition of two mixtures of this kind is given in Table 88.

These mixtures have a density of about 1.7. During decomposition they evolve 1150–1350 ml of gas per kg.

Other mixtures consist of ammonium nitrate activated with ammonium dichromate, for instance, plus a combustible ingredient also acting as a binder.

Little is known about the composition of these mixtures.

Phillips Petroleum in the United States [23] developed a propellant composed of ammonium nitrate as oxidant and rubber as a combustible and binding agent. The rubber consists of synthetic rubber and such typical rubber ingredients as carbon black (to improve the mechanical properties of rubber), an accelerator and an inhibitor (to prevent oxidation). To endow the rubber with sufficient plasticity to yield a fairly homogeneous composition on mixing, a certain amount of plasticizer is added.

TABLE 88

	Oxidizing mixture	Mixtures giving complete combustion
NH_4NO_3	72	58
$NaNO_3$	16	–
NH_4Cl	4	–
Nitroguanidine	–	11.6
Dicyandiamide	–	7.2
$(NH_4)_2Cr_2O_7$	8	8
Melting point (°C)	115–120	105

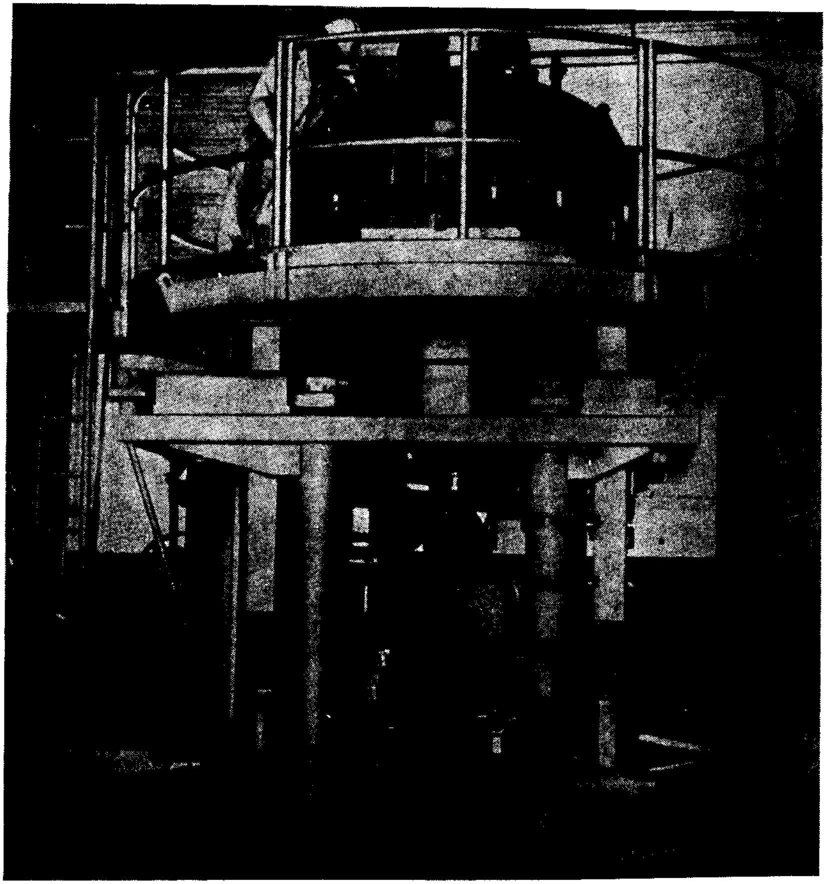


FIG. 120. Casting from the casting pot (on the top) down to the case through the "bayonets" (Aerojet General Corp. [20]).

As ammonium nitrate is a rather slow oxidant small quantities of a catalyst, presumably of potassium dichromate, are added to it.

The composition of the powder is:

Ammonium nitrate	83%
Combustion catalyst	2.3%
Synthetic rubber	10%
Carbon black	2%
Curing substance	0.4%
Plasticizer	2.0%
Inhibitor	0.3%

The manufacture of this powder consists of the following operations.

Milling

Ammonium nitrate is milled until granules with a particle size ranging from 5 to 500 μ are obtained. Fineness of grinding governs the rate of burning of the mixture.

Synthetic rubber is mixed with such ingredients as carbon black, plasticizer, accelerator and inhibitor. Mixing is carried out on the rollers commonly used in the rubber industry.

Final mixing

The milled ammonium nitrate and combustion catalyst are added to the fuel so formed, which at the same time acts as a binder. This final stage of mixing is carried out between rollers heated to 50–60°C. The temperature should not exceed 60°C. The final mixing last for $\frac{1}{2}-2$ hr.

Pressing

The hot, homogeneous mass is shaped in a hydraulically-operated extrusion press of the type used for smokeless powder (Fig. 121). It is usually cruciform. A guillotine cuts the extruded material to the required length. The outer surfaces of the limbs of the cross are covered by a substance which does not burn readily (e.g. strips of plasticized cellulose acetate or polystyrene 1.5–5 mm thick), and cemented in place, to prevent uneven burning at the surface.

Curing

The final operation in propellant manufacture is the curing of the binder. The shaped material is placed in a curing oven for 16–48 hr at 80–110°C. The temperature and duration of this operation depend on the composition of the mixture, the dimensions of the charge and the physical properties desired.

After curing, the charges are given their final dimensions. In some rockets a high dimensional tolerance is admissible, and the final dimensions may be imparted before curing.

Dekker and Zimmerman [24] described a cast ammonium nitrate propellant containing polyester styrene–methyl acrylate binder.

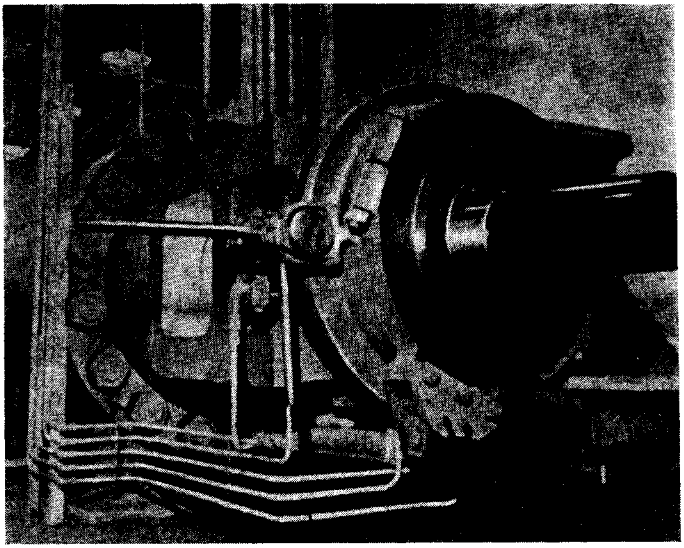


FIG. 121. Extrusion press for extruding ammonium nitrate composite propellants, Astrodyne, Inc. (according to Warren [5]).

A typical composition of AMT-2011 propellant was:

Ammonium nitrate	72.79%
Genpol A-20 polyester resin	9.79%
Methyl acrylate	12.22%
Styrene	2.22%
Methyl ethyl ketone	0.49%
Cobalt octoate (1% in styrene)	0.25%
Lecithin (10% in styrene)	0.25%
Ammonium dichromate	1.99%

The binder itself (Genpol A-20 polyester resin, styrene and methyl acrylate) was combined with the necessary polymerization catalyst (methyl ethyl ketone peroxide) and an accelerator (cobalt octoate or naphthenate).

The viscosity of the binder was adjusted by varying the ratio of polyester to monomer so as to achieve a castable composition (Fig. 122). Lecithin was used to reduce the viscosity.

The proportion of the oxidant could be as high as 82%. This gave a limit of pourability of the mixture. This high content of solid oxidant could be achieved by

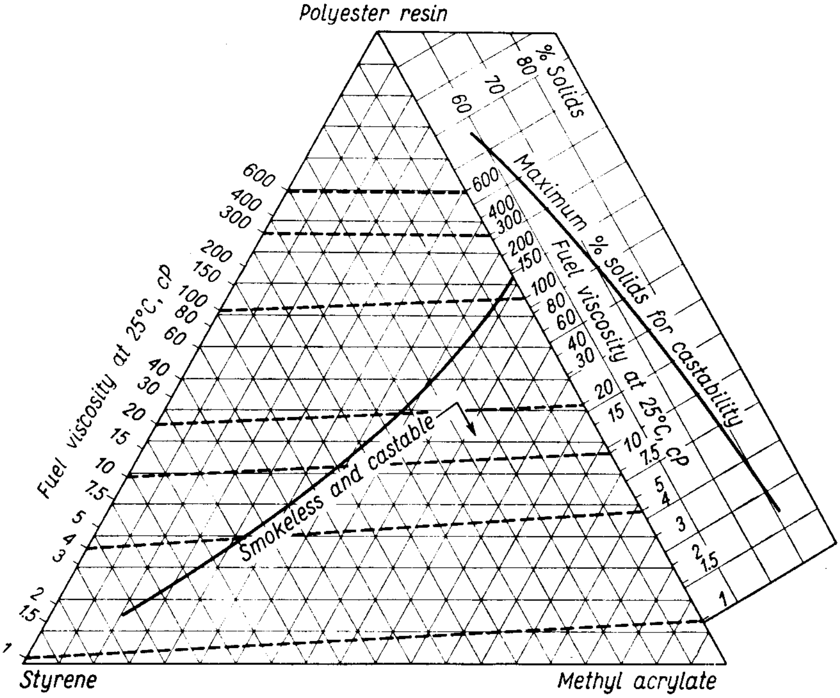


FIG. 122. Binder composition and viscosity. Smokeless and castable compositions are indicated with an arrow (according to Dekker and Zimmerman [24]).

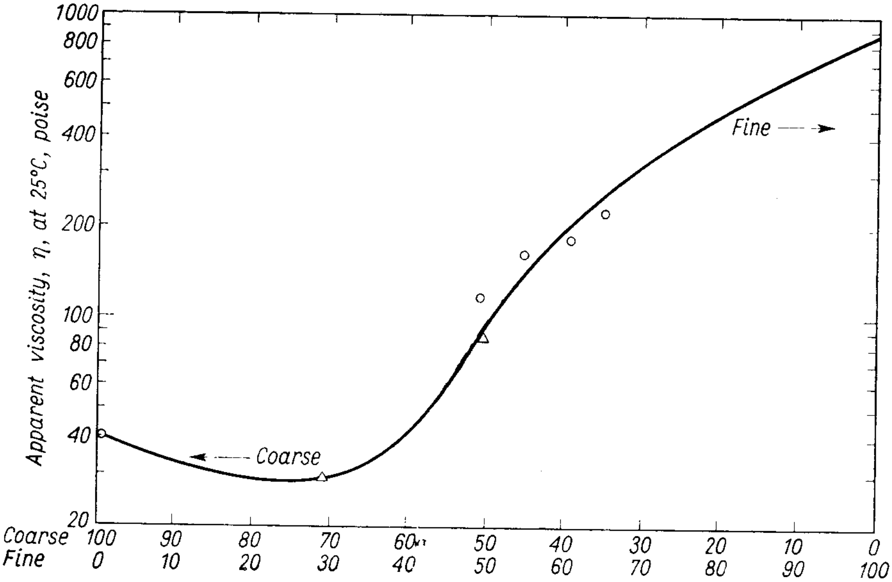


FIG. 123. Effect of blends of fine and coarse ammonium nitrate on viscosity of a propellant containing 64% by volume solids and 0.025% by weight lecithin. Binder vicosity was 20 cP (according to Dekker and Zimmerman [24]).

selecting ammonium nitrate of a specific particle size. By using two particle size ranges in which 70% was coarse and 30% fine (the size of fine crystals was approximately $\frac{1}{6}$ that of the coarse material) it was possible to obtain an oxidant with a high bulk density. Only a small quantity (18%) of uncured binder was sufficient to obtain a castable propellant.

Further increase of the proportion of the binder could be obtained by introducing a third distinctly different particle size.

The stoichiometric mixture was composed of 92% of ammonium nitrate and 8% of the fuel.

The specific impulse was relatively low (*ca.* 190 sec at 1000 lb/in^2).

The propellants have found an application in auxiliary or emergency power units (JATO—jet assisted take off) for use in aircraft, with good performance in the range of −75 to 180°F (i.e. −59 to 82°C).

Greek, Dougherty and Mundy [25] give two typical formulations for castable and extrudable ammonium nitrate propellants (Table 89).

TABLE 89

TYPICAL PROPELLANTS WITH AMMONIUM NITRATE AS OXIDIZER

	Castable %	Extrudable %
Liquid polymer	10.8	–
Rubber polymer	–	12.0
Filler	–	2.5
Plasticizer	3.0	2.5
Curing agent	1.0	0.5
Anti-oxidant	0.2	0.4
Metal powder	16.0	–
Oxidizer	68.0	80.0
Catalyst	1.0	2.1

A general lay-out of the plant was given by the same authors (Fig. 124).

These propellants possess several advantages: they give smokeless exhausts, are non-corrosive and non-erosive, and have a low rate of burning and low flame temperature.

NEW METHOD OF MIXING INGREDIENTS OF COMPOSITE PROPELLANTS

A process for continuous pneumatic mixing of ingredients of solid composite propellants has recently been developed by the U.S. Naval Propellant Plant, Indian Head, Md., according to A. J. Colli [26]. The solid and liquid ingredients (oxidizers and prepolymer respectively) are conveyed pneumatically through a porous tube. Air flowing into the tube through the pores provides turbulent mixing. The process is shown diagrammatically in Fig. 125.

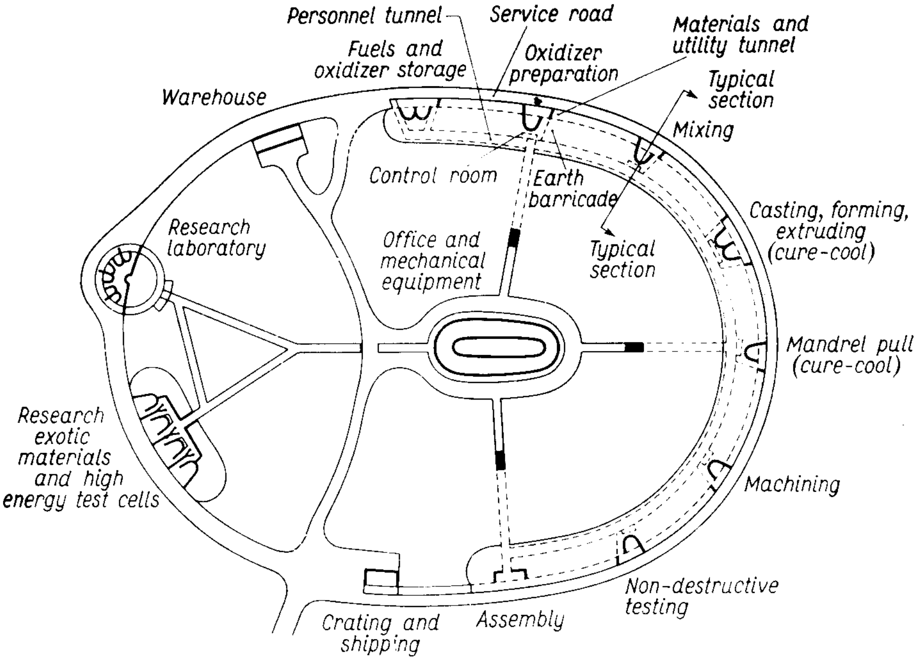


FIG. 124. Lay-out of the plant for ammonium nitrate composite propellants [25].

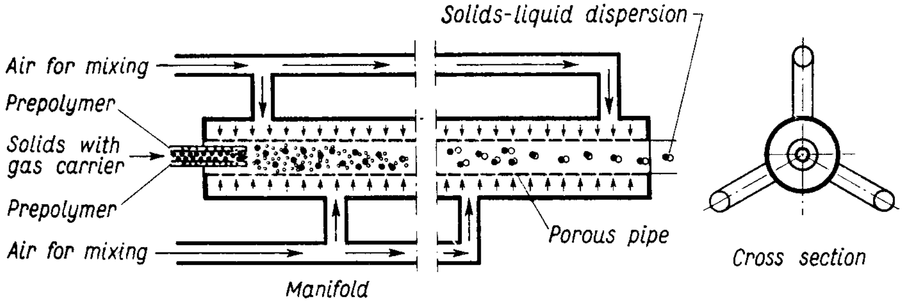


FIG. 125. Continuous mixer of composite propellants' components [26].

The mixture leaving the apparatus must be de-aerated. The air is removed from the solids–liquid dispersion by a centrifugal separator before the propellant is vacuum cast and cured.

The main purpose of utilizing a continuous process is to achieve a high degree of safety with a high output: only a very small quantity of material is present in the mixer at any given time, and the ingredients are in contact only for a fraction of a second. While handling only 1 lb in the mixer an output of 5000 lb per hour is achieved.

The carrier gas moves solids and droplets at random, providing intimate mixing. The gas also prevents the material from sticking to the wall of tube. As the solid particles and associated liquid droplets move through the tube, uneven radial distribution between two phases disappears.

Extensive research on the burning mechanism of a mixture containing ammonium nitrate has been reported by Chaiken [2] and Andersen, Bills, Mishuck, Moe and Schultz [3].

These studies were based on the "two temperature" theory of propellant burning.

According to this theory it is assumed that in a composite propellant containing ammonium nitrate the oxidant starts to gasify at a temperature of about 600°K due to the endothermic reaction resulting in the formation of ammonia and nitric acid. These gaseous products then undergo exothermic redox reactions giving a flame of about 1250°K in the vicinity of burning substance. This temperature brings about the pyrolysis of the organic binder. The gaseous products of this reaction react in turn with the gaseous products of pyrolysis of the oxidant to create a hot flame of about 2400°K at a certain distance from the surface of the charge.

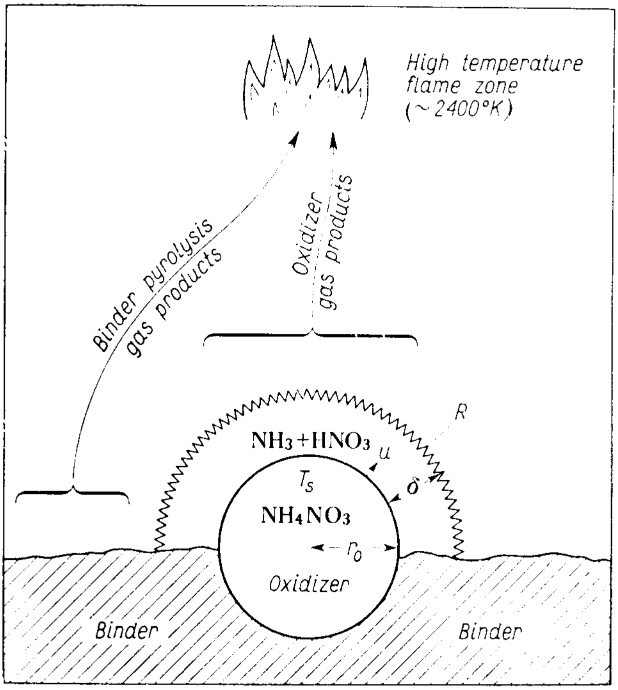


FIG. 126. Thermal layer model of combustion of solid composite propellant with ammonium nitrate, according to Chaiken [2]; R—redox reaction flame zone (temperature T_f), u—gas velocity, δ—thickness of the thermal layer, T_s—surface temperature of oxidizer particle, r_0—radius of oxidizer particle.

The diagram (Fig. 126) given by Chaiken represents a simplified picture of this mechanism.

Andersen *et al.* [3] have examined a number of the mixtures of ammonium nitrate and polystyrene with various molecular weights and determined experimentally the average temperature of the surface of the oxidant (573–599°K) and that of the binder (from 796°K for low-molecular polystyrene MW=142,000 to 979°K for high-molecular polystyrene MW=500,000).

In mixtures with methyl methacrylate the corresponding figures are: 562 and 950°K.

In mixtures with copolymer polyester–styrene the temperature of the oxidant is 582°K and that of copolymer 1020°K.

Andersen *et al.* obtained a similar result for mixtures of ammonium nitrate with copolymer polyester–styrene–acrylate and with copolymer butadiene–styrene.

They also suggest that the same mechanism applies to a mixture of ammonium perchlorate with copolymer butadiene–styrene.

The rate of burning of mixtures of ammonium nitrate with polymers at a pressure of 1000 lb/in^2 (*ca.* 67 kg/cm^2) at 60°F (*ca.* 15°C) ranges within 0.21–0.36 cm/sec.

VARIOUS COMPOSITE PROPELLANTS AND THEIR CHARACTERISTICS

Napoly [27] collected the information on various composite propellants. They are given in Table 90.

TABLE 90

CHARACTERISTIC OF SOME COMPOSITE PROPELLANTS [27]

Oxidizer Combustible binder	NH_4ClO_4 Polybutadiene	NH_4NO_3 Cellulose acetate	NH_4ClO_4 Polyurethane	NH_4ClO_4 Polyurethane	NH_4ClO_4 Polyester	NH_4ClO_4 Polyvinyl chloride
Burning under pressure (kg/cm^2)	1–140	1–140	1–140	14–125	30–140	1–120
Specific impulse I_s at $p=70$ kg/cm^2	250	171	238	236	178	225
Rate of burning (mm/sec) under pressure $p=70$ kg/cm^2	11.9	2.2	5.8	12.2	17.5	6.5–13.5
Exponent n in the equation $V=kp^n$	0.236	0.50	0.5	0.479	0.69	0.4
Density	1.74	1.55	1.72	1.74	1.88	1.64

The same author [27] gives some data on a propellant which is intermediate between composite and double base propellants. It is composed of ammonium perchlorate and a nitroglycerine–nitrocellulose powder (double base powder).

It gives a very high specific impulse $I_s=250$–255 (at 70 kg/cm^2), and has a high rate of burning: 17.3 mm/sec (at the same pressure), exponent $n=0.45$ and density 1.75.

MIXTURES WITH AMMONIUM PICRATE

During World War II mixtures were developed in Great Britain with ammonium picrate as the chief component for rocket propulsion, on the suggestion of the author of the present book. These mixtures also contained sodium or potassium nitrate and a combustible binder.

Similar mixtures were adopted in the United States. Zaehringer [6] quotes the following two compositions (Table 91).

TABLE 91

COMPOSTION OF AMMONIUM PICRATE PROPELLANTS

Ingredients	Name	
	NDRC Type EJA 218 B	NDRC Type EJA 480
Ammonium picrate	46.6	46.4
Sodium nitrate	46.6	46.4
Buramine resin*	5.2	—
Ethyl cellulose-arochlor**	—	7.2
Santicizer 8***	1.6	—

* Thermosetting urea or melamine resin.
** Arochlor—chlorinated diphenyl.
*** A plasticizer.

Rühl [28] has recently reviewed the patent literature on solid rocket propellants.

EXPLOSIVE PROPERTIES OF COMPOSITE PROPELLANTS

Composite propellants with elastomers (thiokol, polyurethane) do not detonate readily and this is due to their non-porous texture [29].

Most of the cast propellants' charges also possess very high density and thanks to this they are difficult to detonate (e.g. Price and Jaffe [30]). They are prone to detonation when they are shredded and put into vessels of high degree of confinement [31].

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CHAPTER V

MINING EXPLOSIVES

BLACKPOWDER is a weak explosive, too slow in action to be an effective blasting agent. Attempts have therefore been made to replace it by a more powerful explosive (e.g. to substitute potassium chlorate for potassium nitrate). At first, however, this produced nothing of value. It was not until the second half of the nineteenth century when nitroglycerine had been produced that new prospects of improvement emerged. The fact that nitroglycerine is a more powerful explosive than blackpowder was perceived at once, although how this property could be exploited fully was not immediately clear. Both blackpowder and nitroglycerine were fired with a fuse. A blackpowder primer was used with nitroglycerine. In both cases the explosives were ignited and then, since they were burning in a confined space explosion, but not detonation, occurred. Yet nitroglycerine is a typical explosive capable of detonation. Thus the potential energy released by the detonation of nitroglycerine was not utilized. The proper exploitation of nitroglycerine as an explosive became possible only when detonators filled with mercury fulminate were introduced (1867).

Nobel's use of kieselguhr to produce dynamite [1] (Vol. II, p. 33) was a milestone since nitroglycerine thus acquired a solid form easy to handle. Guhr dynamite, however, failed to utilize fully the explosive power of nitroglycerine due to the presence of a large proportion (25%) of the inert material kieselguhr. The discovery of blasting gelatine [2] and of dynamites containing blasting gelatine as a chief ingredient was a step forward in improving mining explosives.

Another advance in this field was the use of ammonium nitrate as a chief component. In 1867 Ohlsson and Norrbin [3] patented a mining explosive—Ammoniakkrut (ammonium powder, cf. p. 331) consisting of ammonium nitrate mixed with 5–10% charcoal. Ohlsson and Norrbin added to this mixture 10–30% nitroglycerine to make detonation easier and to increase the power of the explosive. Similarly Nobel began to add ammonium nitrate to his dynamites.

The largest application of explosives is now in coal mines. They are also widely used in mining ores, in quarrying, for many civil engineering works such as road building, tunnel driving, land reclaimation, canal construction, and changing the course of rivers—even for extinguishing fires (e.g. conflagrations of oil wells). In recent years large quantities of explosives have also been employed in seismographic prospecting for new oil fields.

When shotfiring in mines, quarries, rock blasting, the demolition of old buildings etc. the first step is to bore a cylindrical shothole. The hole is loaded with one or more blasting cartridges (usually a cartridge is 100 g in weight and 30 mm dia.). The first cartridge is fitted with a detonating cap or an electric detonator (in coal mines charges are fired only by electric detonators), and the shothole sealed with stemming material, commonly moist clay.

An explosive intended for use in coal mines must be safe to handle and to operate in the presence of material as ignitable as coal. Moreover to produce good lump coal slow-acting explosives should be employed which displace rather than fragment the coal. Conversely, in rock blasting greater explosive power is needed; the safety factor is less important.

RESEARCH ON THE SAFETY OF MINING EXPLOSIVES

The increasing use of explosives in mining greatly increased coal output but numerous gas explosions occurred in mines where blackpowder was used. The development of nitroglycerine and more modern explosive compositions did not eliminate this hazard. As the industry developed and the demand for coal increased the safety of explosives used in mines become so urgent and important a problem that in the nineteenth century many countries set up special commissions charged with its detailed analysis.

Although firedamp explosions in mines were notified as early as the seventeenth century in the oldest scientific establishments—the Academy of Paris and the Royal Society of London—the scientific and technical world in general was little concerned with them. But in 1812 an explosion at Branding Main near Gateshead-on-Tyne in England in which ninety-two miners were killed was given great publicity. The disaster led to the formation in 1813 of "The Sunderland Society" for preventing accidents in coal mines. The Society succeeded in persuading Sir Humphrey Davy to interest himself in the problem and in 1815 he devised the well known safety lamp. In 1849 a further step was taken in Great Britain with the passing of an Act for the Inspection of Coal Mines in Great Britain from which the modern era in coal mining really began (cited by J. Taylor and Gay [4]). In 1877 the Commission de Grisou was formed in France. Work began on the elucidation of the conditions under which mixtures of air and methane explode (Mallard and Le Chatelier [5]). It turned out that these mixtures explode at 650°C after a certain induction period which, at this temperature, is 10 sec. At a higher temperature it is shorter (e.g. at 1000°C it is approximately 1 sec). Although the temperature of explosion of any explosive is considerably above 650°C, the gaseous products of explosion cool rapidly due to expansion, and furthermore a large amount of the heat of explosion is converted into mechanical work on bursting the walls of the shothole. Thus, the explosion of a high explosive does not necessarily produce a temperature at which a mixture of air and methane will explode.

The duration of the flame produced by the explosion is another important factor. The flame of a high explosive is of extremely short duration and may not be sufficient to ignite firedamp. Conversely the flame produced by burning blackpowder lasts much longer and is therefore more dangerous. Clearly, the duration and temperature of the flame of explosion are the factors which determine the safety of an explosive used in mines.

On the basis of many experiments the Commission de Grisou and later, the Commission de Substances Explosives headed by M. Berthelot and Le Chatelier introduced, in 1890, the following safety rules for the use of explosives in coal mines [6]:

1. On explosion the explosive must not leave any combustible products such as CO, H_2, carbon.

2. The detonation temperature computed from the heat of explosion and from the average specific heat of the products must not exceed 1900°C for explosives intended for penetrating rock and 1500°C for those to be used in coal mines.

On these grounds blackpowder was excluded from coal-mining works, for it is an explosive that leaves a combustible residue and has a very high explosion temperature (approximately 2400°C).

The theoretical calculation of the detonation temperature as a safety criterion was adopted only in France. In all other countries (and more recently also in France) a practical criterion has been introduced based on an experimental evaluation of the effect of explosion of a sample of the explosive on a mixture of air and methane, or on a suspension of coal-dust in air, under conditions similar to those existing in mines. For this purpose testing galleries were devised, simulating the conditions of mine galleries.

A typical one (Fig. 149, p. 441) consists of a cylindrical or elliptical tube made of wrought iron. At one end the tube is closed with a thick plate simulating the coal face. It is provided with a steel mortar, which imitates the shothole. A section of the gallery containing the mortar loaded with an explosive charge is separated by a paper diaphragm from the remainder to form an explosion chamber which is then filled with a defined amount of methane. The explosive charge is fired electrically with a No. 8 detonator. The course of the explosion is watched through the observation holes along the gallery.

The first testing gallery was built in Germany, at Gelsenkirchen in 1880. It was a tube of elliptic cross section of 2 m^2, 35 m long. Next, about 1890 another testing gallery was built in Great Britain, at Hebburn-upon-Tyne, by The North of England Institute of Mining and Mechanical Engineers. It consisted of a wrought-iron tube, 101 ft long and 3 ft dia., with a paper diaphragm 22½ ft from the closed end forming an explosion chamber. The 1½ in. dia. mortar was 42 in. long, the explosive being fired both stemmed and unstemmed (according to J. Taylor and Gay [4]).

The important conclusion drawn from investigations with this gallery was that high explosives were less liable than blackpowder to ignite an inflammable mixture of air–methane and coal-dust.

Another testing gallery was built in Great Britain at the beginning of this century at Althofts by the Mining Association of Great Britain [7]. It was over 200 m long, 2.30 m dia. and served mainly for testing the explosibility of coal-dust and methods of preventing it (such as stone-dust, stemming with sodium hydrogen carbonate, etc.).

A Home Office Testing Gallery Committee was appointed in 1896. The Committee's aim was to establish the best test for determining the safety of explosives in coal mines. On its recommendation a testing station was erected at Woolwich and the testing of explosives for inclusion in the "Permitted List" began in 1897. The testing gallery was 27½ ft long and 2½ ft dia. and was filled with an inflammable medium: (15% coal gas +85% air). The steel mortar had a bore of 1¾ in. dia.

The charges were stemmed with dry clay.

The Home Office testing station was transferred to Rotherham in 1911 and a new gallery was erected. It was 5 ft dia., with an explosion chamber 18 ft long. The steel mortar was 120 cm long with a 55 mm bore.

In 1921, difficulties with the supply of coal-gas at Rotherham led to the temporary transfer of testing to Ardeer and eventually a new Research Station was established at Buxton in 1922.

In Belgium the official testing gallery was erected at Frameries under direction of Watteyne and Stassart in 1902. It was of elliptical cross section (1.85 m/1.40 m), 85 m long.

In France two testing galleries were built at Liévin in 1907. Both were cylindrical. One of 2 m^2 cross section and 15 m long was used for testing explosives. Another one of 2.80 m^2 section was 300 m long and was used for examining coal-dust explosion and methods of preventing it. In Austria–Hungary two galleries came into use in 1908.

In the U.S.A. a cylindrical gallery of 6 ft 4 in. dia. and 100 ft long was built 1909 in Pittsburgh.

Modern testing galleries are described later (p. 439 and Table 108).

In addition to the experiments in testing galleries laboratory research has also been conducted, including a study of the flames produced by explosives when exploded. These flames have been studied photographically to determine their dimensions, intensity and duration. The following papers are noteworthy: Siersch [8], Bichel and Mettengang [9], Wilkoszewski [10], Will [11], Taffanel and Dautriche [12].

When observing the flame projected from the mortar of a testing gallery Lemaire [13], Payman [14] and Audibert [15] came to the conclusion that the ignition of air–methane mixtures may also be caused by glowing particles formed on explosion and thrown out of the shothole.

On the basis of flame studies, explosives may be divided into two principal groups:

(1) Explosives with a secondary flame which have not enough oxygen for complete combustion. On the detonation of these materials combustible products are formed such as CO, H_2, CH_4 etc. These products become mixed * with air, producing

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* Oxygen-positive explosives may also produce combustible products, although in negligible quantity. The amount of such products is greater on detonation in the open.

combustible gaseous mixtures which explode in turn giving rise to a bright secondary flame (Fig. 127). Trinitrotoluene, picric acid and guncotton belong to this group. Blackpowder which does not detonate but only explodes also gives a secondary flame.

FIG. 127. Flame from picric acid. The primary flame (relatively small) is visible with the secondary flame above it. The duration of both flames is shown on the scale: the primary flame of short duration, the secondary of long duration. The material was fired in a mortar (according to Will [11]).

(2) Explosives with a primary flame only. This group comprises all mixtures containing more than enough oxidizing agents to provide a positive oxygen balance. They differ from each other in flame intensity. Rock explosives (e.g. dynamites, i.e. explosives with nitroglycerine) give a glaring flame of high-temperature and relatively long duration (Figs. 128 and 129). Permitted Explosives* give a faint, low-temperature flame of short duration (Fig. 130).

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* English term for coal-mining explosives which have passed special tests as explosives assuring a sufficient safety for use in coal mines where inflammable mixtures of methane and air occur. In the U.S.A. they are called permissible explosives.

As a result of these investigations, group (1) explosives were withdrawn from use in coal-mines. The duration of the secondary flame is rather long so that the gaseous mixture ignites easily.

Rock-blasting explosives of group (2) have a very high temperature of explosion. Among these dynamites have been permitted exclusively for work in rock and in non-fiery mines.

FIG. 128. Flame from Dynamite I (61–63% nitroglycerine). Duration 7.66 millisec. The material was fired in a mortar (according to Bichel [16]).

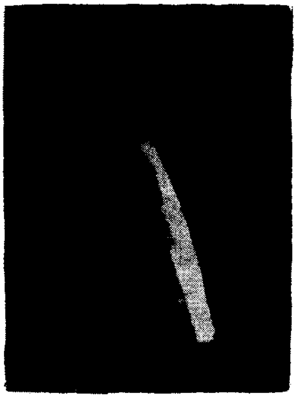

FIG. 129. Flame from dynamite having a low nitroglycerine content (Gelatine-Dynamite). Duration 1.25 millisec (according to Bichel [16]).

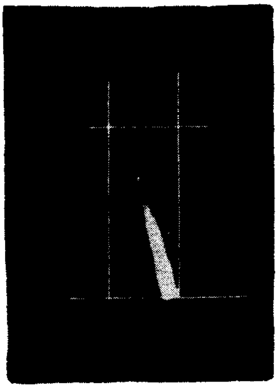

FIG. 130. Flame from ammonium nitrate explosive (Ammoncarbonit). Duration 0.33 millisec (according to Bichel [16]).

The ammonium nitrate explosives of the same group may be fired without igniting a methane–air mixture even when relatively large charges are used whereas other explosives ignite the gas mixture unless used in small amounts. Thus arose the concept of the maximum charge that can be fired without causing the ignition of a definite methane–air mixture in a testing gallery. This is called the "charge limit". This made clear that apart from the temperature of the flame of explosion (calculated from the heat of reaction and the mean specific heat of the products) there are other agents which may provoke an explosion. One factor that increases the danger is a very high rate of detonation and "specific pressure" *f* or lead block expansion. The shock-wave produced by the detonation may involve a rapid, almost adiabatic compression of the methane–air mixture. The higher the rate of detonation, the greater is such compression and, in consequence, the probability of explosion of the gas mixture. In addition, when the energy of the explosion of a charge is transformed into work only to a small extent, it may happen that the shock-wave thus produced involves the adiabatic compression of the gas mixture referred to. This means that it is dangerous to load shotholes with a larger amount of explosive than is necessary for the work in hand. The unused surplus of energy may cause an accident since a large quantity of heat is not transformed into work and the products of detonation then have a higher temperature. This proves the necessity of strict observance of the maximum safety charge (charge limit). However, the concept of charge limit was recently subjected to revision (see p. 413).

Superficially, this seems to contradict the rule that the use of explosives which do not detonate but only explode (or burn) like blackpowder, as mentioned above, is unsafe, but in fact this is not so. The point is that both non-detonating explosives with a flame of long duration (like blackpowder) and those marked by high rate of detonation producing a violent shock-wave are unsafe. The safest explosives are those with intermediate properties, i.e., which give a not very high rate of detonation and lead block expansion, but in which the reaction of explosive decomposition proceeds much more quickly than in blackpowder, which burns or explodes relatively slowly.

These investigations showed that no modification of blackpowder by the addition of "cooling salts", i.e., those that reduce the flame temperature (e.g. oxalates) will improve its safety. On the other hand, the presence in dynamites of 35–63% of inert (non-explosive) salts, such as sodium hydrogen carbonate, ammonium oxalate, or salts containing crystallization water, increases their safety not only by lowering the temperature of the flame of explosion but also by reducing their explosive power. Chlorides of alkali metals, such as potassium and sodium, are particularly efficient in this respect.

It was also found that mixtures containing a large amount of ammonium nitrate (ammonium nitrate explosives) ensure much greater safety than dynamites or chlorate and perchlorate explosives.

Early in the present century attention was drawn to the danger created in mines by coal-dust. Until 1906 it was believed in France that this hazard could be entirely explained by the presence of firedamp, but even in the early nineteenth century it was supposed that a suspension of coal-dust in the air may also explode. Thus, as early as 1803, it was suggested in the U.S.A. that coal-dust might be involved in mine explosions [17]. In 1844, Faraday drew attention to this (according to J. Taylor and Gay [4]), and later Galloway [18] discussed the coal-dust danger. By the end of the last century the possibility of explosion was proved experimentally, but it was believed that an explosion of methane–air mixture is necessary to initiate a coal-dust explosion and that conditions were safe if there was no methane in the atmosphere.

At the turn of the nineteenth century, explosions occurred in Great Britain, in non-fiery mines, proving the possibility of an explosion of coal-dust without methane as an initiating agent. It was however insufficient to rouse the experts to action.

Meanwhile, in 1906, a terrible coal-dust explosion occurred at Courrière in France, in which about 1100 men lost their lives. The mine at Courrière had no methane at all and was considered to be safe, but as it turned out, it contained coal which in dust form produced a very dangerous suspension. The vast extent of this disaster aroused public indignation. It became obvious that the explosion of coal-dust may extend over a large area under ground and that this is much more dangerous than the explosion of methane which is usually localized within a small area.

It was also obvious that the immediate cause of explosion of both methane and coal-dust may be the use of explosives in mines. Particular attention was paid to the hazard involved in the use of blackpowder in mines (e.g. in Great Britain H.M. Commissioners [19]; Royal Commission on Explosions [20]).

Attempts were made to reduce the danger in the use of blackpowder by surrounding the charge with a water sheath (Abel [21]), but this method was abandoned as it was very troublesome in practice. Recently it has been revived in an improved form (p. 489).

Another method was to dip blackpowder pellets in paraffin wax. This rendered them waterproof, and also surrounded them with a "cooling sheath". A blasting powder made in this form called "Bobbinite" was introduced in Great Britain. It will be discussed later. These half-measures brought little improvement and attention was centred on the use of ammonium nitrate explosives.

After the explosion at Courrière experiments were carried out in testing galleries on blasting explosives and on suspensions of coal-dust in air. As the coal-dust from various mines showed different inflammability, the most inflammable kind, i.e., that with a high content of volatile matter, was commonly used for testing.

The explosion of coal-dust is usually of a thermal character. It undergoes degasification under the influence of a high temperature to form coke grains. If such grains are found after an underground explosion it is proof that the explosion was due to coal-dust.

It should however be pointed out that the principal source of colliery accidents is not explosion but roof falls. Rogers [22] gives the following annual figures for 1923–59 in Great Britain (Table 92):

TABLE 92

	1923–32	1933–42	1943–52	1953–59
Roof falls	500	450	250	166
Haulage	250	170	110	95
Explosions and fires	50	90	50	30
Shafts	40	20	20	15

SAFETY EXPLOSIVES BEFORE WORLD WAR I

Certain types of safety explosives were designed on the basis of a number of tests, although until recently there were considerable differences in the composition of these explosives in different countries. This was due to different working conditions in mines, different methods for testing the safety of explosives etc.

After World War II some standardization in composition was achieved largely as the result of international cooperation. The annual International Conferences of Directors of Safety in Mines Research greatly contributed to this.

The first safety explosives produced in **France** are tabulated below:

TABLE 93

COMPOSITION OF EARLIEST FRENCH SAFETY EXPLOSIVES

Name	Ingredients (%)			
	Nitroglycerine	Nitrocellulose	Ammonium nitrate	Potassium nitrate
For coal work				
Grisoutine Couche	12	0.5	87.5	–
Grisoutine Couche au Salpêtre	12	0.5	82.5	5.0
For rock work				
Grisoutine Roche	29.0	1.0	70.0	–
Grisoutine Roche au Salpêtre	29.0	1.0	65.0	5.0

These explosives are characterized by an absence of "cooling substances" even when intended for use in coal mining. In a number of countries they were considered dangerous.

The same explosives were formerly employed in **Russia**, where the mining explosives industry was financed by French capital. In both countries Favier Powders (Poudres Favier) or Favier explosives (Explosifs Favier) were also employed. Their composition is tabulated below.

TABLE 94

COMPOSITION OF FAVIER EXPLOSIVES

Favier Explosive	Ingredients (%)			
	Ammonium nitrate	Sodium nitrate	Nitronaphthalene	Dinitronaphthalene
1A	88	–	–	12
1B	67	18	15	–
2	44	37.5	18.5	–
B	–	75	25	–

Chlorate explosives were also used in both countries, in mines, viz.: Miedziankit type in Russia (p. 278) and Cheddite type in France (p. 277).

In **Belgium**, at first explosives modelled on the French ones were used, but later they were replaced by others containing "cooling" ingredients, such as ammonium chloride, sulphate, or oxalate or sodium chloride. The safety explosives used initially in Belgium included mixtures with ammonium perchlorate, of the Yonckite type. Examples of these explosives for rock and coal work are given in Table 95.

TABLE 95

COMPOSITION OF SOME BELGIAN SAFETY PERCHLORATE EXPLOSIVES

Ingredients (%)	Yonckite type, brisant No. 13 (roche)	Yonckite type antigrisouteuse No. 10 bis (couche)
Ammonium perchlorate	20	25
Ammonium nitrate	27	30
Sodium nitrate	27	15
Barium nitrate	6	—
TNT	20	10
Sodium chloride	—	20

In **Great Britain** the first explosives which passed the test in the testing gallery at Woolwich were approved for use in mines under the name of *Permitted Explosives.* At Woolwich the charge of explosive in the test mortar was stemmed with dry clay, a practice that differed from that followed in other countries.

On the basis of these tests the following substances were considered safe and were used in mines.

(1) Bobbinite—an explosive having virtually the composition of blackpowder but with the flame temperature of explosion reduced by the addition of salts or a mixture of paraffin with starch.

(2) Saxonite—dynamite, made safe by the addition of about 13% ammonium oxalate.

(3) Monobel—an ammonium nitrate explosive containing about 80% ammonium nitrate and 10% nitroglycerine, plus 10% wood meal which adsorbed the nitroglycerine.

(4) Faversham Powder—another type of ammonium nitrate explosive, without nitroglycerine, containing, for instance, 90% ammonium nitrate and 10% TNT.

(5) Cambrite—an ammonium nitrate explosive modelled on the German "Carbonits" (see Table 124). It contained a small quantity of nitroglycerine, potassium or sodium nitrate and a considerable amount of carbonaceous material (e.g. wood meal, charcoal etc.). This material was added to prevent the complete combustion of the carbon included in the explosive (to carbon monoxide only), to reduce the heat of explosion and, in consequence, the temperature of the explosion.

Bobbinite and some of the other explosives permitted for use in mines caused, however, a number of explosions of firedamp and coal-dust, and it was decided therefore to adopt a more exacting form of test. In 1912, the Rotherham test was introduced. In this the explosive charge was fired unstemmed, as in the Continental test. At the same time the charge limit was determined. These tests led to the exclusion of Bobbinite from the Permitted List (except in some experimental mines) and to a considerable reduction of power of all the permitted explosives, by the addition of cooling substances such as sodium chloride, ammonium oxalate etc. In this way mining explosives having the composition presented in Table 96 were evolved.

TABLE 96

EARLIEST BRITISH PERMITTED EXPLOSIVES

Ingredients	Ammonite	No. 1 Bellite	No. 3 Dynobel	No. 2 Cambrite	No. 3 Samsonite	No. 2 Viking Powder	Tees Powder
Nitroglycerine	–	–	14–16	22–24	50.5–52.5	7.5–9.5	9–11
Nitrocellulose	–	–	0.25–0.75	–	2–4	–	–
Dinitronaphthalene	4.5–6.5	–	–	–	–	–	–
Dinitrobenzene	–	–	–	–	0–0.5	–	–
DNT	–	–	0.5–2.5	–	–	–	–
TNT	–	14–16		–	–	–	–
Ammonium nitrate	71–75	62–65	51–54	–	–	65–69	58.5–61.5
Sodium nitrate	–	–	–	–	9–11	–	–
Potassium nitrate	–	–	–	26–29	–	–	–
Barium nitrate	–	–	–	3–4.5	–	–	–
Woodmeal	–	–	4–6	32–35	–	7–9	8–10
Starch	–	3.5–5.5	–	–	–	–	–
Potassium chloride	–	–	–	7–9	–	–	–
Sodium chloride	20–22	15.5–17.5	24–26	–	9–11	14–16	19–21
Borax	–	–	–	–	24–26	–	–
Magnesium carbonate	–	–	1.0	–	–	0.5–1.0	–
Moisture	0–1	0–2	0–2	3.5–6	0–1.5	0–2	0–2

Chlorate explosives, such as Colliery Steelite, which were used for a short time in coal mines, had the following composition:

72.5–75.5% of potassium chlorate
23.5–26.5% of nitrated resin
0.5–1.5% of castor oil

They were also removed from the Permitted List.

In **Austria** explosives similar to those of the French Favier type were permitted for use in mines.

In **Germany**, slow-action (non detonating) explosives of the blackpowder type (blasting powder, black blasting powder—see Table 78) were used even in dusty mines up to 1923 and typical high explosives (1910) with the composition given in Table 97, were also employed.

The explosives which did not contain cooling salts belonged to the carbonite or donarit groups and were intended for work in rock or in non-dusty and non-gassy coal mines. Those containing cooling salts (Wettersprengstoffe) were used for work in more dangerous coal mines. The composition of the Gelatine Wetter-Astralit explosive in which dinitrochlorohydrin was added to nitroglycerine to form an antifreezing mixture is particularly noteworthy.

TABLE 97

EARLY GERMAN SAFETY EXPLOSIVES

Ingredients	Donarit	Wetter-Astralit	Chrome Ammonit	Ammon Carbonit	Gelatine Wetter-Astralit
Nitroglycerine	4	4	–	3.9	4
Dinitrochlorohydrin	–	–	–	–	16
Nitrocellulose	–	–	–	0.1	0.5
Nitrotoluene	–	–	–	–	1
DNT	–	–	–	–	4
TNT	12	7	12.5	–	–
Ammonium nitrate	80	74.5	70	82	40
Potassium nitrate	–	–	10	10	–
Sodium nitrate	–	–	–	–	7.5
Flour	–	–	–	4	8
Woodmeal	4	1	–	–	–
Charcoal	–	1	–	–	0.5
Vaseline or paraffin	–	2.5	0.5	–	–
Castor oil	–	–	–	–	2
Chromium-potassium alum	–	–	7	–	–
Ammonium oxalate	–	–	–	–	2.5
Sodium chloride	–	10	–	–	14

CONDITIONS OF SHOTFIRING IN MINES

As knowledge of the danger created by the use of explosives in coal mines grew, attempts were made to obtain new, more suitable explosives and to work out the safest possible methods for their use, including shotfiring methods. Strict regulations were laid down for charging shotholes, stemming (governing the type of stemming materials, length of stemming etc.), firing charges etc. Wherever danger existed, due to the presence of methane or coal-dust, electric detonators replaced fuses which, if defective, might spark through the sheaths. Detailed instructions were also evolved for firing procedure. Simultaneous firing of the charges in several shotholes (shotfiring in rounds) was found to be safer than firing in sequence, when one shot might raise a "cloud" of coal-dust which then might be exploded by the following shot. On the other hand the use of electric detonators with a delay-fuse increases output since the early shots can create free faces facilitating the work of the following shots. It is, therefore, not surprising that short-delay detonators are now in wide use, very often in combination with shotfiring in rounds of 2–6 shots. Research is still under way to ascertain whether when using short-delay detonators there is in danger of ignition from the possibility that one shot might cause conditions dangerous for another. The risk may arise due to the opening of fissures that release firedamp and, as previously described, due to raising a cloud of coal-dust before the last shot in the round is fired. Some authors concluded that under experimental conditions ignition only occurs when the interval between successive shots exceeds 70 millisec and it was therefore concluded that the usual short delay of 25 millisec should be considered safe (Fripiat [23]).

Entirely new safeguards were also introduced to avert danger. When it was found that coal-dust may explode it was suggested that the cartridges would be stemmed by filling them with water (MacNab [24]) or with a porous mass mixed with water. The water, dispersed by the detonation, forms a cloud that may reduce the probability of explosion. Stemming with incombustible substances in powder form was also tried. On detonation, such stemming was intended to form an air suspension that would prevent explosion of the coal-dust. Cybulski [25], however, proved the inefficiency of this method by showing that stemming with dust does not produce a cloud capable of providing protection against explosion. In addition, a powder stemming is ejected more quickly from the shothole than one made of clay.

Watteyne and Lemaire [26] recommended that outside the shothole, or strictly speaking outside the stemming, a paper bag should be placed, containing an incombustible material, such as ground sand, salts containing water of crystallization (e.g. sodium sulphate), salts volatile at a high temperature (e.g. sodium chloride), or salts decomposing at a high temperature (e.g. ammonium sulphate). This was later developed by Lemaire into the use of a sheath of inert substance around the cartridges (see p. 429).

Numerous tests indicated the factors that influence the results of shotfiring and showed, in particular, that variations in results are caused by changes in the composition of the methane–air mixture (e.g. when gas produced by coal carbonization, which is liable to variations in composition, or natural gas which varies in composition depending on its origin, was used for testing instead of pure methane). This emphasized the need to use a test gas of constant composition.

It was also found that the coal-dust in the presence of which explosives were tested, varied in ignitability; to achieve comparable results therefore coal-dust from the same seam of the same mine must be used. If the same explosive is always used, the ignitability of coal-dust in a given mine may be tested to determine to what extent work in the mine is dangerous. It is obvious that changes of atmospheric humidity also affect the results.

Numerous tests were also carried out to examine other, less tangible factors which affect the accuracy and reproducibility of the results obtained in a testing gallery. The following factors were found to be of importance:

(1) The density of loading of the shothole (greater density facilitates ignition of methane or dust);

(2) The diameter of the explosive charge (larger diameter favours easier ignition);

(3) The shape and surface area of the testing gallery (elliptical shape and smaller surface favour easier ignition);

(4) The wrapping of the explosive charge, e.g. paraffined paper, parchment paper, tinfoil etc. (this factor was tested over a long period and some of the results are discussed further on p. 424).

MINING EXPLOSIVES USED DURING WORLD WAR I

In World War I the belligerents reserved nitric acid and its salts for military purposes. The mining industry could obtain only small amounts of ammonium nitrate and other salts of nitric acid, and therefore had to employ other oxidizing agents.

For blasting rock and for work in non-gassy and non-dusty coal mines, chlorate explosives were widely used, e.g. Miedziankit in Russia and Germany, Cheddites in France. In Belgium and Germany perchlorate rock explosives were also in general use: in Belgium, ammonium perchlorate (Yonckites), in Germany, potassium perchlorate (the composition of these explosives differs slightly from those included in Table 121, which were introduced immediately after World War I). During the war an explosive "Blastin" was used in Great Britain for rock work. It consisted of:

Ammonium perchlorate	60%
Sodium nitrate	22%
TNT	11%
Paraffin	7%

For coal work, especially in gassy and dusty mines a safety perchlorate explosive with the composition tabulated below (Table 98) was manufactured in Germany.

TABLE 98

GERMAN SAFETY PERCHLORATE EXPLOSIVES

Ingredients	Wetter Permonit	Wetter Persalit	Wetter Perchlorit 4	Neuleonit II
Potassium perchlorate	32.5	35	30	35
Ammonium nitrate	34.5	—	34	10
Sodium nitrate	—	31	—	3
DNT	—	25	10	11
TNT	7	—	—	—
Nitroglycerine	3	6	—	4
Flour	4	—	—	5
Woodmeal	3	3	3	2
Glue solution in glycerine (1 : 7)	1	—	—	—
Charcoal	—	—	1	—
Sodium chloride	15	—	22	30

These mixtures, however, brought no new advantages and did not fully meet requirements with regard to safety in gassy and dusty mines, sensitiveness to impact and friction and mining efficiency. In addition, perchlorate explosives, like chlorate ones, have the defect that under certain conditions they do not detonate, but burn out in the shothole, which may lead to a catastrophic fire or explosion. Perchlorate explosives were then withdrawn from coal work after World War I and restricted exclusively to rock work. Japan seems to be the only country where some perchlorate explosives are accepted as "permitted explosives" (see p. 474).

RESEARCH AFTER WORLD WAR I

After 1918 research started before the war was continued intensively, by erecting further testing stations and extending the sphere of their activity. Table 108 shows the characteristics of the most important testing galleries in use between and after the wars as official testing stations. Here the new explosives are studied to determine their suitability for use of mines; safe methods of shotfiring are sought; and ways of preventing explosions of methane and coal-dust investigated. The classification of mines from the view point of coal-dust safety is also carried out at these testing stations. Testing galleries are also in operation at explosive factories. These are used to control the manufacture of explosives, and to test new safety explosives. Diagrams and descriptions of some galleries will be found in a later section (Table 108, p. 440).

The intensive, many-sided work of these testing stations contributed greatly towards overcoming the hazards of using explosives in mines. They led to the production of explosives possessing a high degree of safety and to the formulation of safety regulations laid down on the basis of long experience so that coal mining is little more hazardous than work in other branches of industry. The problem of the safe use of explosives in coal mines was developed into a new branch of applied science, which exceeds the scope of this book. Here only a few fundamentals will be given.

The flame of explosion. Experiments by Hiscock [27] and T. Urbański [28] showed that the flame of safety explosives in firedamp and coal-dust is very small and its intensity insignificant. These explosives, differed little in the dimensions and intensity of flame produced in these tests.

Audibert [29], Payman [30] and Beyling [31] studied the flame of explosives detonating in a steel mortar with or without stemming, and showed that a stemming 12 cm or so long is sufficient to quench a flame perceptible in a photograph. On shots fired without stemming the authors made a number of important observations:

(1) In a shothole of definite depth with the detonator placed at the end of the charge facing the opening, the flame decreases with increasing charge.

(2) With a constant explosive charge the flame increases with the depth of the shothole i.e. as the space between the charge and the opening increases.

(3) With a constant free space between the charge and the opening, the dimensions of the flame are independent of the size of the charge.

(4) The flame is increased by moving the detonator from the open end of the shothole to the bottom of the shothole.

No definite relationship has been found between the dimensions of the flame and the ability of the explosive to ignite the methane–air mixture. According to Beyling, for instance, if the detonator is situated at the open end of the shothole, as is usual in shotfiring, no charges within the range 50–100 g ignites the gas provided that the free space between the charge and the opening lies within the limits 0–200 cm. It has also been found that a decrease in the free space decreases safety, creating a greater probability of explosion in spite of the decrease of flame (case 1).

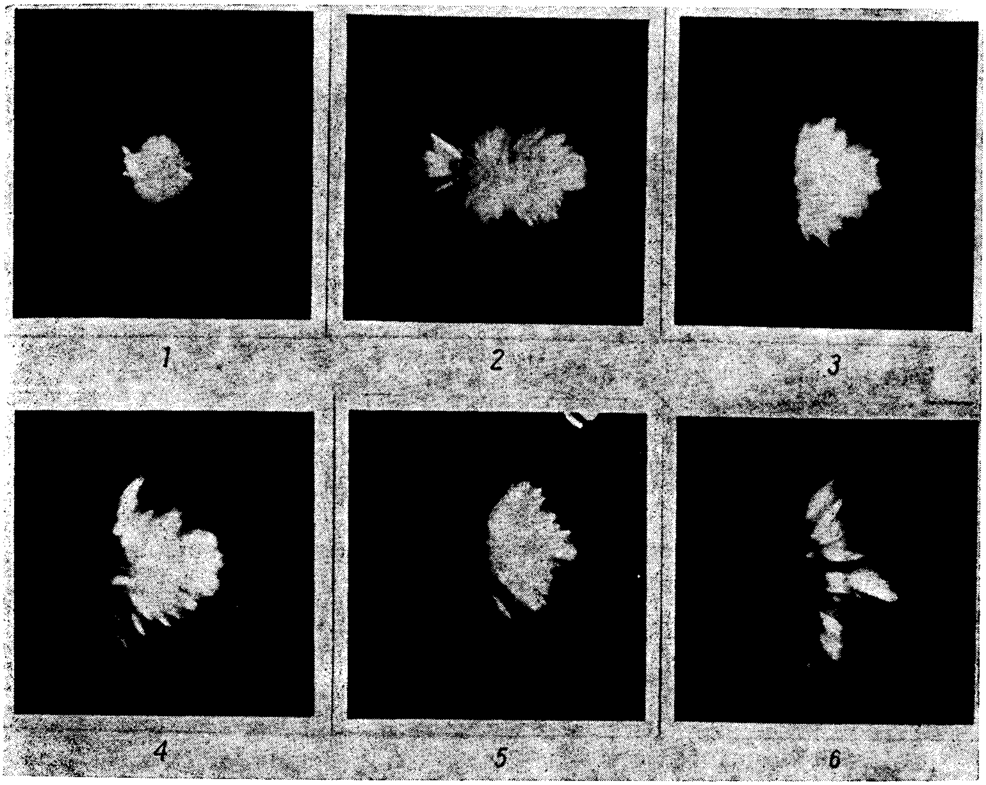

FIG. 131. Detonation flame of Metanit B, according to Cybulski [25]. Diameter 32 mm, charge 300 g, suspended in air. Time interval between the photographs 0.051 millisec. Total duration of the flame 0.306 millisec.

Thus, Payman found that a smaller charge of ammonium nitrate explosive (No. 2 Viking Powder, see Table 96) is more likely to explode the gas mixture than a larger one. This would be compatible with observation 1; on the other hand, on moving the charge nearer to the mouth of the shothole the flame is removed almost completely, although, as Payman reports, this increases the chance of explosion, contrary to observation 1.

A detonator placed in the lower section of the charge is more likely to explode a methane–air mixture. This is attributable to the increase of flame, in accordance with observation 4.

Such contradictory test results show that the safety of explosive cannot be assessed solely in terms of the dimension of the explosion flame.

It is the opinion of many authors that high speed photographs of the flame should be supplemented by information about its position at a given moment in relation to the shock wave and the hot products of explosion.

Nevertheless examination of the flame on high-speed film makes an important contribution to the understanding of the properties of explosives and is often employed as an auxiliary test for the determination of the safety of explosives intended for use in mines.

The two sets of photographs illustrated were taken by Cybulski. Both refer to safety explosives used in Poland, viz., ammonium nitrate type Metanit B (Fig. 131) and nitroglycerine (dynamite) type, Barbaryt AGI (Fig. 132).

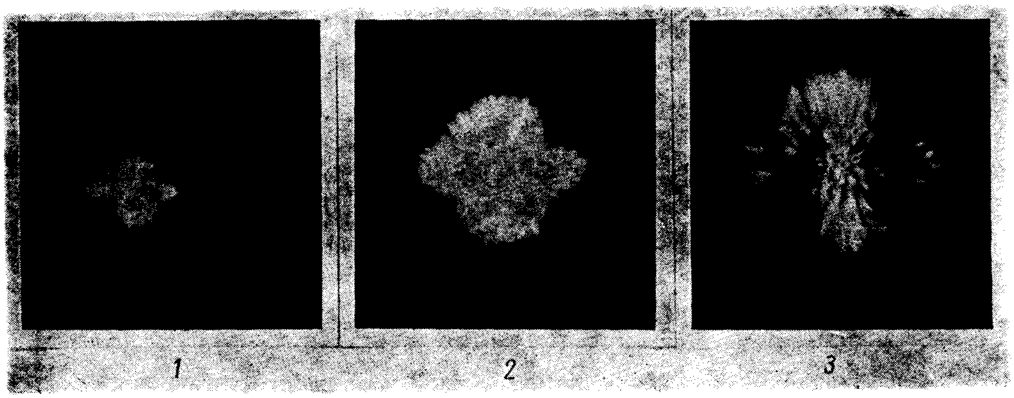

FIG. 132. Detonation flame of Barbaryt AGI, according to Cybulski [25]. Diameter 32 mm, charge 100 g, suspended in air. Time interval between the photographs 0.051 millisec. Total duration of the flame 0.153 millisec.

The effect of solid particles. In his studies of the detonation products of explosives stemmed in different ways, Audibert [29, 32] paid attention to the fact that in charges insufficiently stemmed a certain amount of the explosive remains in the form of small particles which may undergo further explosive decomposition according to conditions, i.e., temperature and ambient pressure. If these particles are ejected into a space filled with a methane–air mixture they may lead to the explosion of this mixture. The possibility of the existence of particles of undecomposed explosive in ejected detonation products has been disputed by some authors (Segay [33]), but many others have proved that it can occur. T. Urbański [34] found that a thin layer on the periphery of a cylindrical charge of ammonium nitrate explosive is scattered by the explosion of the charge and does not explode. Beyling [31] showed that undetonated particles of ammonium nitrate explosive may cause ignition of the methane–air mixture in a testing gallery.

There is also a certain probability that fragments of the walls of a shothole ejected by detonation may join these unexploded particles. Further, it has been suggested that the remnants of a metallic detonator case cause ignition of methane–air mixtures. Payman's [14] photographic studies proved that the particles of a copper detonator case cannot provoke ignition. Being always surrounded by detonation products they cannot penetrate the shock wave created by the explosion products and come into contact with the methane–air mixture. Conversely, the particles of an aluminium detonator case may penetrate into the methane–air mixture through the shock wave. Hence the hazard in the use of aluminium cases, which has been confirmed frequently in practice. In addition, the very high heat of combustion of aluminium, giving high temperatures, must be taken into consideration as a factor liable to increase the probability of a methane explosion.

Shock wave. An early assumption, originally unsupported by direct experience, that the detonation of an explosive may involve the explosion of a methane–air mixture even when the detonation is not accompanied by a large, hot flame, has been confirmed experimentally. It was found that a mixture of 6.5% methane with air, for instance, may ignite under rapid compression by mechanical means up to 54 atm.

Perrott [35] ascertained photographically that on the detonation of an explosive in a methane–air mixture, the ignition of the latter starts at a spot not yet reached by the flame of detonation of the explosive. Thus, in all probability the ignition is caused by a shock wave travelling ahead of the flame.

Payman *et al.* [36, 37] showed the substantial validity of this observation. By a schlieren photographic method Payman found that the detonation wave has the same direction as the gaseous products when the detonator is situated at the bottom of the shothole. With this arrangement, the ejection of gases from the shothole is more intense, the velocity of the shock wave is higher and the probability that the methane–air mixture will ignite is also greater. If, on the other hand, the detonator is placed in the normal way, i.e. near to the stemming, the direction of the detonation wave is opposite to that of the gaseous products. The latter then form a sort of "gaseous stemming" around the detonator which holds back the shock wave and thus reduces the probability of explosion of the gas mixture.

Investigations into the shock wave arising on the detonation of an explosive as part of the problem of safety in the use of explosives attracted attention to the rate of detonation of mining explosives as a factor directly influencing the velocity of the shock wave. The earlier observation that a mining explosive, to be safe with methane, should be relatively weak, was thus confirmed. The reason why explosive charges with a large diameter are more dangerous than those with a small diameter also became clear. This is due to the higher rate of detonation of charges with a larger diameter.

GENERAL CONSIDERATION ON SAFETY OF EXPLOSIVES

From many tests carried out in testing galleries and from mining practice it has been shown that an explosive which is safe against methane, should have a rate of detonation of approximately 2000 m/sec at the given density and should give a lead block expansion not exceeding 200 cm^3. In 1924 a special commission in Germany established a lead block figure of 235 cm^3 at 15°C as the maximum value admissible for the explosives used for coal mining. This is now considered too high.

Dubnov [38] postulated the causes of the explosibility of methane by the detonation of an explosive. On being ejected from the shothole the products of detonation of an explosive charge are mixed with the air and the methane present in the atmosphere. The probability that the mixture will explode depends on the following factors:

(1) Time t, which elapses before the combustible ingredients achieve a concentration capable of being exploded.

(2) Induction period τ, which is necessary to bring about the explosion of this gaseous mixture at a given temperature.

Since after time t has been surpassed, the composition of the gaseous mixture tends towards a decreasing concentration of combustible ingredients while the temperature of the mixture falls, the safety condition is fulfilled when $\tau > t$.

Until recently the concept of a safe "charge limit" was regarded as one of the fundamentals in the use of explosives in coal mines. However, Cybulski's [39] investigations have shown that the thickness of the clay layer used as stemming is critical for the safety of the explosive, which is relatively little affected by the type of explosive. Also the charge weight seems to be unimportant according to these experiments. Therefore doubt arises as to whether the concept of charge limit, as a measure of safety of the explosives, is of real value. It appears that proper stemming is of greater significance.

Figure 133 shows the relationship between the safety of an explosive (expressed by a charge limit for the non-ignition of the methane–air mixture) and its power (expressed in per cent of the power of blasting gelatine), according to British investigations [4, 40]. Since the usual initiation near the mouth of the mortar does not give a sufficiently clear picture (the majority of safety explosives then fail to ignite methane), detonation was initiated at the back of the mortar. As the two curves show, there is a greater probability of the ignition of methane in a drift with a smaller diameter. It is obvious that the relationship between charge limit and power is comparable only for explosives of the same type (e.g. ammonium nitrate, gelatinous, semi-gelatinous etc.). The power of an explosive must not therefore be considered in the abstract, apart from its composition, and the above-mentioned view, that limitation of the rate of detonation is recommended, may be right only within definite limits governing the composition of the explosive and under definite experimental conditions. J. Taylor [41] reports the following experimental results:

Polar Ajax, a gelatinous explosive was fired as usual in the mortar of a testing

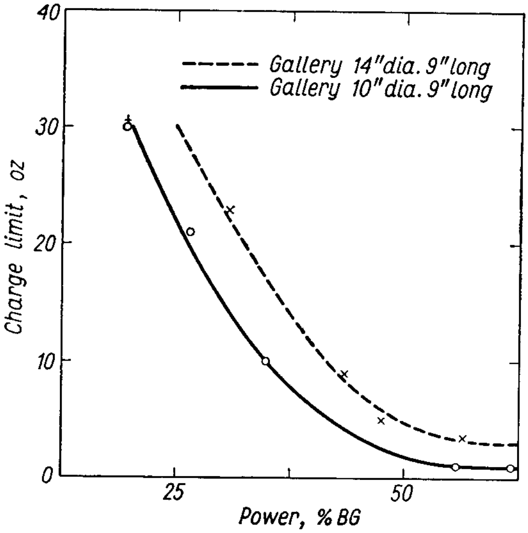

FIG. 133. Relationship between charge limit and power of explosives (J. Taylor and Gay [4]; Titman and Wilde [40]).

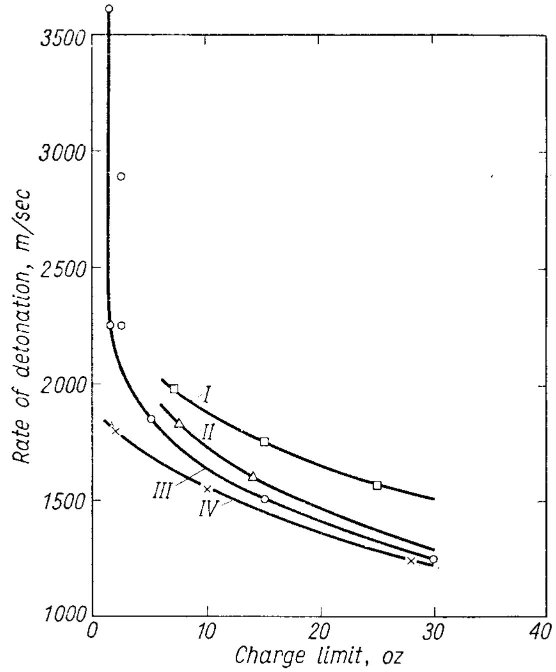

FIG. 134. Relationship between charge limit and rate of detonation of explosives suspended in methane–air mixture, according to J. Taylor [41]; *I*—explosive containing no cooling salt; *II*—explosive containing 10% sodium chloride; *III*—explosive containing 50% sodium chloride; *IV*—explosive based on sodium nitrate.

gallery at two different rates of detonation: 2400 m/sec by initiation with an ordinary detonator and 4800 m/sec by priming with a tetryl pellet. Initiation was from the bottom of the bore. The charge limits were respectively 14–16 oz and 10–12 oz, a difference which is almost negligible. Finely ground TNT, with a rate of detonation of 4100 m/sec, and coarse grained TNT, with a rate of detonation of 1680 m/sec behave similarly: their charge limit is the same: 2–4 oz.

However, J. Taylor found that the converse may also hold good: on the detonation of an explosive freely suspended in a chamber filled with a mixture of 9% methane in air (i.e. not fired in a mortar), the relationship between the charge limit and the rate of detonation (Fig. 134) is clearly marked in explosives of similar composition. Murata [42] came to the same conclusion. Likewise, if detonation is initiated near the mouth of the test mortar, i.e. conditions similar to those of firing an explosive suspended in a methane–air mixture, the rate of detonation has a pronounced effect on the charge limit, i.e. the higher the rate, the smaller the charge.

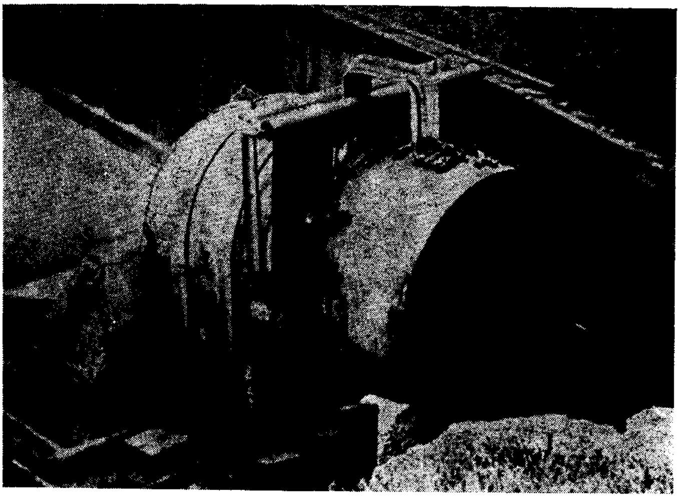

FIG. 135. Free suspension test gallery, according to J. Taylor and Gay [4].

The procedure for testing with the explosive charges suspended in the methane–air mixture, as carried out at Ardeer, Great Britain, and described by J. Taylor and Gay [4] is shown in the photograph (Fig. 135). The diagram (Fig. 136) shows the test lay-out.

This kind of situation usually does not occur in coal mining practice, but in fact there have been instances when an explosive charge has been fired across gaps filled with methane inside the shothole. The conditions characteristic of the firing of explosive charges suspended in a methane–air mixture are then very similar to those met in practice.

Experiments have shown that the ejection of detonation products perpendicular to the axis of the charge (angle detonation) is more dangerous than ejection from an ordinary mortar, i.e., in the direction of the mortar's axis (Payman and

Wheeler [43]; J. Taylor and Hancock [44]). A special mortar, the "angleshot mortar" is used for determining the effect of this phenomenon. It is shown diagrammatically in Fig. 137. This is a diagram of equipment used at the German testing station at Dortmund-Derne (J. Taylor and Gay [4]). A steel ricochet plate from which the detonation products are reflected is situated alongside the mortar. The angle of reflection of these products depends on the angle of the mortar with respect to the ricochet plate.

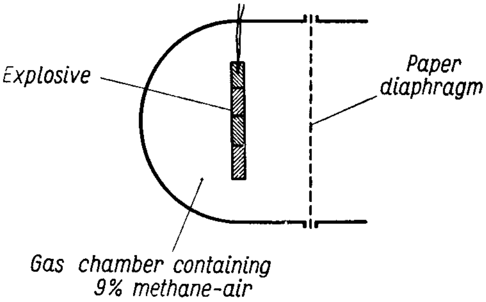

FIG. 136. Diagram of free suspension test gallery, according to J. Taylor and Gay [4].

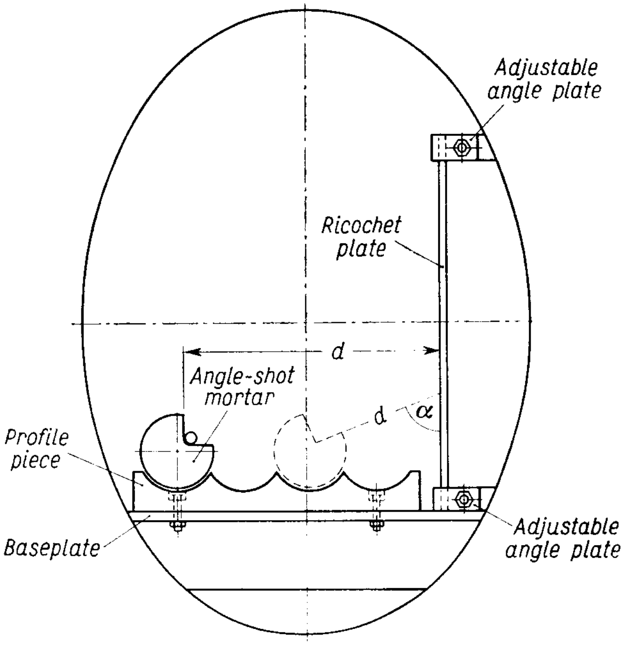

FIG. 137. Diagram of angle-shot mortar test at Dortmund-Derne, according to J. Taylor and Gay [4].

The latter may be 90° or less, as is shown in Fig. 137. The reflection of the detonation products from a barrier such as the ricochet plate involves a violent rise in temperature at this spot, due to the adiabatic compression of gases. A general view of angle shot mortar at Derne is given on Fig. 138.

In Poland another system is also known that works on the same principle as the angle-shot mortar. This is a mortar with a horizontal slit. Figure 139 shows diagrammatically the arrangement in a rectangular section gallery at Mikołów.

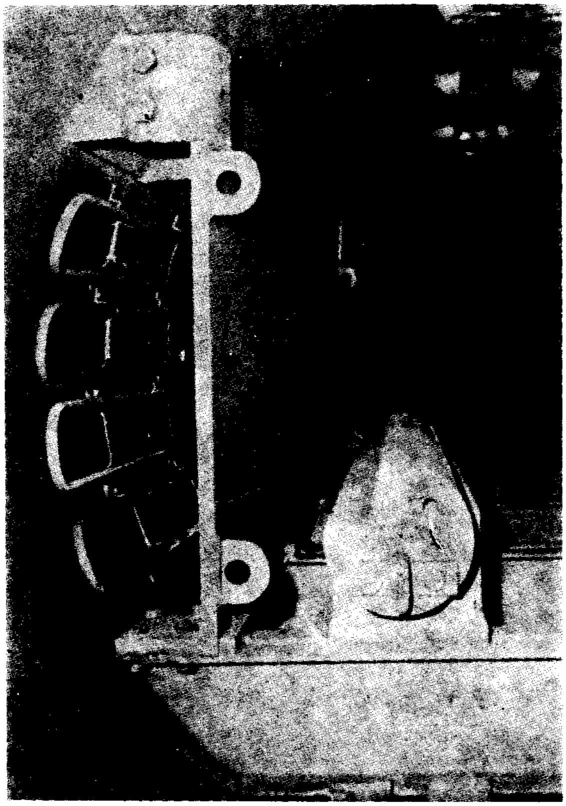

FIG. 138. General view of angle-shot mortar at Dortmund-Derne [45].

According to Cybulski's studies [46, 47] the severity of this test is increased by the prolonged effect of high temperature on the cloud of coal-dust: in the first stage volatile matter is released from the coal-dust, and only afterwards does the ignition of the explosive system occur. Ignition of coal-dust may be achieved more easily by the simultaneous detonation of several shots. Firing in the angle-shot mortar gives results which approach the natural condition of working in coal mines to a much greater degree than firing in the classical mortar. According to Cybulski [39] the classical test gives less reliable results than the angle-shot method.

Deflagration of mining explosives. Long experience in the use of explosives in mining shows that some high explosives undergo deflagration instead of detonation in a shothole. Delayed shots then occur, commonly called "blown-out shots" (gekochte Schüsse).

Such shots are characterized by the fact that immediately after firing the detonator there is no report which is the normal acoustic effect. Instead, after a certain delay, the gas pressure in the shothole increases due to combustion of the explosive, and the stemming is ejected with a report similar to that of a normal shot. The course of deflagration may differ with the conditions. Deflagration, however, always creates a great danger of ignition of methane since the deflagrating explosive gives a flame of long duration and of very large dimensions. Moreover, the explosive does not carry out the normal work of blasting, but only achieves the insignificant result of ejecting the stemming. Since, therefore, the heat of the explosive decomposition is not converted into work, the temperature of the deflagration flame is very high and hence more dangerous.

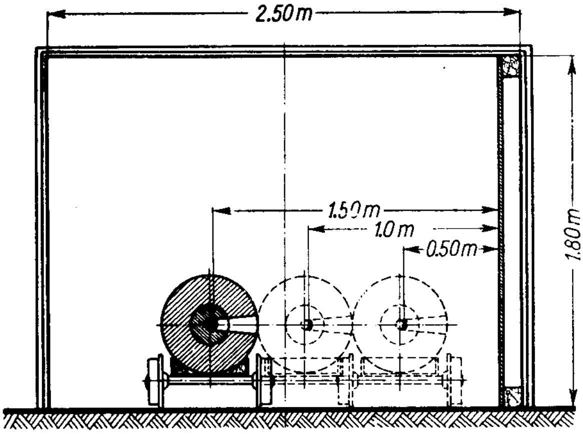

FIG. 139. Diagram of a mortar with slit in a gallery at Mikołów (Poland).

It has long been known that inflammable explosives, such as dynamites, and especially chlorate and perchlorate explosives are particularly prone to deflagration. This is one of the reasons why chlorate and perchlorate explosives have either been withdrawn from use in mines in a majority of countries or restricted to use in rock, where there are no inflammable gases.

The amonium nitrate explosives are much harder to deflagrate and are therefore generally recognized as the safest, although they may deflagrate under certain conditions.

The first systematic studies which elucidated the conditions under which explosives and especially ammonium nitrate ones undergo deflagration, were carried out by Cybulski [48]. This work indicated that deflagration of explosives, including ammonium nitrate ones, may occur in mining practice, if they happen to be mixed with coal-dust in the vicinity of the detonator. The sensitiveness of an explosive to detonation is then reduced, but its ignitability is increased, hence the explosive takes fire instead of being detonated. Ammonium nitrate explosives are readily detonated, but are ignited with difficulty. Clearly, this is their great advantage, but nevertheless, under the conditions described above (admixture with coal-dust) they may be subject to deflagration. Mixing with coal-dust may result from incorrect loading of the shothole and from negligence over freeing the shothole from coal-dust. Careful loading of the shothole and the use of ammonium nitrate explosives is a sufficient guarantee for the prevention of delayed shots.

Cybulski established that penetration of coal-dust into the explosive near the detonator is most dangerous, creating conditions particularly favourable to deflagration.

Explosives containing nitroglycerine and also chlorate explosives are more liable to deflagration than those containing ammonium nitrate without nitroglycerine.

When a partial misfire occurs in the shothole, there is great danger that the charge will deflagrate. The hot detonation products act on the undetonated remnant of the charge and may initiate it. It may happen that detonation of a part of the charge opens the shothole by ejecting the stemming or by shattering some coal. The deflagration of the remaining part of the charge may then be prevented.

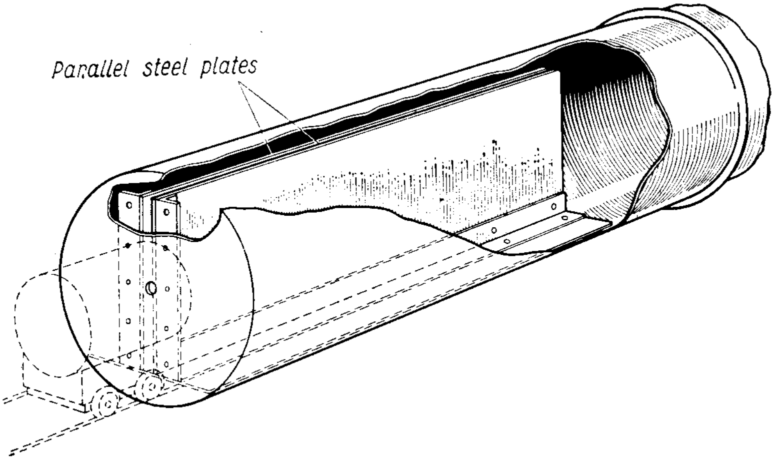

FIG. 140. Diagram of break gallery, according to J. Taylor and Gay [4]. (By permission of Controller H.M. Stationery Office.)

A partial misfire may have various causes. For instance, the charge may be contaminated by coal-dust, as described above. The incomplete detonation of hardened cartridges of ammonium nitrate explosive occurs widely. It is obvious that the incomplete detonation of damp explosives is also possible.

Cybulski's [48] extensive investigations in coal and rock have also solved the problem of the double detonation. It is now known that the deflagration of an explosive in the shothole may pass into detonation after a certain time. This occurs with particular ease in nitroglycerine explosives. The results of Cybulski's studies [48] are now taken into consideration in Poland in defining which explosives may be used in mining.

In Great Britain a test was devised for simulating the effect of blown-out shots in a shothole. Small charges of explosive were fired, from a suspended position or from a gun, in a methane–air mixture between two steel plates 2–4 in. apart in a "break gallery" (Fig. 140) developed by Shepherd and Grimshaw [49].

Explosibility of coal-dust. It is of great importance to know the conditions governing the explosion of coal-dust in order to develop methods of preventing it. Extensive, fundamental studies have been carried out in leading coal producing countries [50]. In Poland they have been carried out by Cybulski since 1925, mainly on a great scale in an underground testing gallery 200 m long and also in smaller galleries 44 and 100 m long.

Cybulski [51] found that there is a straight line relationship between the explosibility of coal-dust and the specific surface area of the dust. This may be expressed by the formula:

$Z = 0.0010119\,F + 0.7836578$, where

Z—degree of explosibility of the dust,

F—the specific surface area of dust.

Cybulski has shown that very fine coal-dust contains a higher proportion of volatile matter than the average sample. This increases the danger created by fine coal-dust.

Cybulski [52] has also shown that very fine coal-dust may explode even when it contains less than 12% combustible volatile matter. The presence of a significant amount of water in coal-dust may lead to its explosion even if free from volatile matter. This indicates the particularly hazardous nature of fine coal-dust. Cybulski has also shown that under particularly unfavourable conditions the coal-dust must contain as much as 95% incombustible matter (e.g. by admixture with non-inflammable stone dust) if explosion is to be avoided.

More recently attention has been paid to the problem of the explosive properties of sulphur dust suspended in air. This is of great importance to work with explosives in sulphur mines.

Sulphur dust is more dangerous than coal-dust, because of the low ignition temperature of sulphur suspensions in air. According to Dubnov [53] 100 g charges of the U.S.S.R. explosives Ammonit No. 1 and 8 ignited sulphur dust. The same explosives did not ignite a methane–air mixture when the quantities were 400 and 500–650 g respectively. In sulphur mines explosives of very low detonation temperature should be used.

FUNDAMENTAL COMPONENTS OF MINING EXPLOSIVES

The ample theoretical and practical material derived from investigations of mining explosives in testing stations and from mining practice led to the conclusion that the composition of mining explosives should be subject to certain rules aimed at the highest possible safety in the use of the explosives together with the conservation of maximum working efficiency. These rules are stated below.

OXYGEN CARRIERS

Nitrates. The chief oxygen carrier, employed in all modern explosives, is ammonium nitrate (it is discussed more fully in Vol. II, p. 450).

In some countries (Great Britain) ammonium nitrate is used with an admixture of triphenylmethane dye, Acid Magenta which inhibits the transformation of one crystalline form into the other at 32°C (Vol. II, p. 454).

Substances that reduce hygroscopicity are also frequently added. This is discussed more fully in Vol. II (p. 453). The substances used are: carboxymethylcellulose and calcium stearate (J. Taylor and Sillitto [54]). Silicone resins are used in France.

In mixtures in which sodium chloride occurs together with ammonium nitrate, there is a possibility of molecular exchange and of the formation of the more stable system: sodium nitrate–ammonium chloride:

$$NH_4NO_3 + NaCl \longrightarrow NaNO_3 + NH_4Cl$$

Kreyenbuhl and Sartorius [55] found that this exchange proceeds slowly if the moisture content is less than 1%. If it is 1% or more so, the exchange is complete after 3–6 months and is accompanied by decreased explosive power. The addition of a moisture absorbent (e.g. urea resin foam) inhibits this exchange (French explosive Noburex, p. 552).

Alternatively, the use of mixtures with sodium nitrate and ammonium chloride have been proposed in place of those containing ammonium nitrate and sodium chloride (see below). Other nitrates—sodium, potassium, barium—are of minor importance. They are generally used in insignificant amounts in admixture with ammonium nitrate. The use of potassium nitrate has been prohibited in Germany since 1925, when it was thought that the presence of potassium nitrate in some ammonium nitrate explosives may cause the ignition of methane–air mixtures. It was believed that the decomposition of potassium nitrate during detonation proceeds too slowly and may cause a long duration of flame. Although this was not proved experimentally, the prohibition has remained in force and potassium nitrate has been replaced by barium nitrate.

Sodium nitrate is often employed as an oxygen carrier in dynamites.

For some time mixtures of safety explosives containing sodium nitrate with ammonium chloride were recommended instead of ammonium nitrate with sodium chloride since the system $NaNO_3 + NH_4Cl$ is more stable than $NH_4NO_3 + NaCl$ (see above). According to the investigations of Hackspill, Rollet and Lauffenburgier [56] the system sodium nitrate–ammonium chloride is stable at room temperature. These observations led to studies of explosive mixtures with sodium nitrate and ammonium chloride. At first, the results were encouraging. Thus Ahrens [57] established that the safety of these explosives seems to be greater than that of explosives with ammonium nitrate and sodium chloride. It was believed that this is due to formation of free sodium ions at high temperature. This can be represented diagrammatically:

$$NH_4Cl + NaNO_3 \longrightarrow \overset{\oplus}{Na} + \overset{\ominus}{Cl} + \underset{\substack{\downarrow \\ \text{detonation}}}{[NH_4NO_3]}$$

The power of explosives containing sodium nitrate and ammonium chloride was found to be the same as that for equivalent compositions containing ammonium nitrate and sodium chloride [58]. The compositions with ammonium chloride--sodium nitrate are now very popular in France, Germany, Belgium and Great Britain.

However with poor ventilation they seem to give more persistent smoke than compositions based on ammonium nitrate and sodium chloride. Analysis of the smoke showed it to be due to finely divided ammonium chloride suspended in moist air, and although not harmful it may be objectionable to the miners. In addition, calcium sulphate was included to suppress the smoke (J. Taylor and Gay [4]). Calcium nitrate found only a limited use as a substance for lowering the temperature of detonation flame.

Murata [42] showed that the addition of a few per cent of potassium and sodium nitrates somewhat increases the safety of an explosive with respect to methane but in larger quantities their effect is almost negligible.

Perchlorates

Perchlorates are not used now as oxygen carriers in safety explosives. Perchlorate explosives were used temporarily during World War I, and later a small admixture of potassium perchlorate was introduced into ammonium nitrate safety explosives such as Bradyt F (p. 475), used for a certain time in Poland. Potassium perchlorate was added on the assumption that during explosive decomposition it may promote the formation of an additional amount of potassium chloride, a substance inhibiting the explosion of methane–air mixtures. Bradyt F did in fact prove to be highly safe on examination in a testing gallery. Moreover, an admixture of perchlorates increases the sensitiveness to detonation in ammonium nitrate explosives. At present, perchlorates are used as ingredients of ammonium nitrate explosives only in Belgium, France and Japan.

Chlorates

Chlorates have been little used. Only potassium chlorate has been employed as a non-hygroscopic ingredient in the simplest rock explosives, including Miedziankit (p. 278). Experience of many years proves that such explosives often burn out in the shothole, creating a great risk of fire. As was pointed out earlier (Vol. II) chlorates should never be mixed with ammonium salts (such as ammonium nitrate), because of the formation of highly unstable ammonium chlorate. At present, chlorate explosives are banned in underground mines in the majority of countries and their use in coal mines is prohibited everywhere.

ACTIVE INGREDIENTS AND COMBUSTIBLES

All ammonium nitrate explosives containing non-explosive salts (e.g. sodium or potassium chloride) should include at least 4% nitroglycerine to increase their sensitiveness to detonation. Small amounts of nitroglycerine (up to 6–8%) do not require gelatinization with nitrocellulose; it is enough to introduce a certain quantity (up to 2%) of woodmeal into the mixture to absorb nitroglycerine and to prevent its exudation. In addition, the woodmeal stabilizes nitroglycerine explosives by absorbing impurities and the product of decomposition of the ingredients. Explosives containing woodmeal therefore possess enhanced chemical stability.

If the content of nitroglycerine exceeds 10%, the explosives are called dynamites. It is then necessary to bind the nitroglycerine with highly viscous "dynamite collodion cotton" (Vol. II). Dynamites thus acquire a plastic consistency which is a very convenient form of mining explosive, facilitating the introduction of a detonator with a fuse. In countries where the explosive may be exposed to frost, a mixture of nitroglycerine with nitroglycol or nitrodiglycol should be used, since the explosive then retains its plasticity even at low temperatures. In the U.S.S.R. another type of plastic explosive with nitroglycerine was recently introduced containing a 3–5% solution of methyl polymethacrylate in nitroglycerine.

Woodmeal is of particular importance among combustible ingredients since apart from its stabilizing effect, discussed above, it enables the mixture to be retained in a loose state with a low density. Charcoal is another ingredient sometimes added.

The addition of aluminium to increase the heat of the explosion and, in consequence, the power of the explosive, as practised for some time, is now believed to be too dangerous. Ammonium nitrate explosives with aluminium are permitted only for rock work in opencast mining (e.g. quarries) or underground, where there is no methane.

Ammonium nitrate explosives usually contain a certain amount of nitro compounds from mononitro (e.g. nitronaphthalene) to trinitro compounds (e.g. trinitrotoluene).

Some ammonium nitrate explosives used in the U.S.S.R. contain a small amount of paraffin (0.5–1%) to reduce the hygroscopicity of the ammonium nitrate.

Recently Hino and Yokogawa [59] found that by adding less than 1% surface active agents, an improvement of transmission of detonation of ammonium nitrate explosives can be achieved.

OXYGEN BALANCE

The maintenance of an adequate oxygen balance in a mixture is a problem of high importance. Former German explosives of the Carbonit type *, with incomplete combustion, have been banned. Modern mining explosives are required to have an oxygen balance equal to or higher than zero. Investigations in the U.S.S.R. have

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* Carbonits had a negative oxygen balance on the wrong assumption that incomplete combustion gives greater safety for use in mines, by lowering the heat and temperature of explosion.

shown that a highly positive balance is disadvantageous since it favours the formation of nitric oxides in the products of an explosion. For earth moving, farming, and opencast mining the use of explosives with a negative oxygen balance (e.g. picric acid, TNT etc.) is permitted.

According to Soviet findings a concentration of carbon monoxide of less than 0.00025% is admissible in the atmosphere of a coal mine, after ventilation of the shotfiring position. Before ventilation, immediately after shotfiring, the content of CO should not exceed 0.02%.

A positive oxygen balance markedly reduces the quantity of carbon monoxide formed. Assonov and Rossi [60] report the following results of experiments on the effect of the oxygen balance of explosives on the composition of the gaseous products of explosion (Table 99).

Other agents also examined in the U.S.S.R. exert an influence on the combustion of the products of an explosion. According to Assonov and Rossi [60] increase in the moisture content of an explosive involves the increase in the content of gaseous products.

TABLE 99

COMPOSITION OF GASEOUS PRODUCTS OF EXPLOSION IN EXPLOSIVES WITH A DIFFERENT OXYGEN BALANCE

Explosive	Oxygen balance %	Content of toxic gaseous products (l. per kg of explosive)	
		carbon monoxide	nitric oxides
2 T Ammonit	+9.0	15.0	25.1
No. 1 Dinaftalit	+0.6	7.0	7.3
T Ammonit	−1.0	7.5	6.2
Dynamon	−9.8	95.6	6.5

Other factors include the density of loading (with a larger density a smaller quantity of nitric oxides is obtained), the diameter of the cartridge (a larger diameter favours the reduction of the amounts of carbon monoxide and nitric oxides); e.g. after the explosion of 62% dynamite* 8.5 l./kg of carbon monoxide and 4.2 l./kg of nitric oxides were found in the gaseous products, with cartridges 30 mm dia. With cartridges 20 mm dia. the figures were 9.0 l./kg and 12.5 l./kg respectively.

Cybulski [61] and Assonov and Rossi also found that if made of paper saturated with paraffin, the cartridge case affects the composition of the gaseous products, considerably increasing the quantity of carbon monoxide.

Assonov and Rossi report that with a proportion of 2 g of paper per 100 g of explosive, the content of paraffin should be less than 2.5 g. With this paraffin content the amount of toxic gases formed is 26.4 l./kg of carbon monoxide and 37.7 l./kg of nitric oxides.

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* 62% dynamite means a "straight" dynamite containing 62% nitroglycerine or a dynamite of the same power as one with 62% nitroglycerine, according to U.S.A. nomenclature.

If the content of paraffin is 4.0 g, 29.5 l./kg of carbon monoxide and 59.7 l./kg of nitric oxides are formed.

According to Taffanel [62] paraffin paper also reduces the safety of an explosive towards methane. He established this for explosives with a high oxygen balance (Grisounaphthalite and Grisoudynamite, with oxygen balance +13 and +18% respectively). As shown by Murata [42] this phenomenon occurs only in explosives with a highly positive oxygen balance. If an explosive has only a slightly positive oxygen balance, the presence of paraffin paper tends to enhance its safety (Fig. 141).

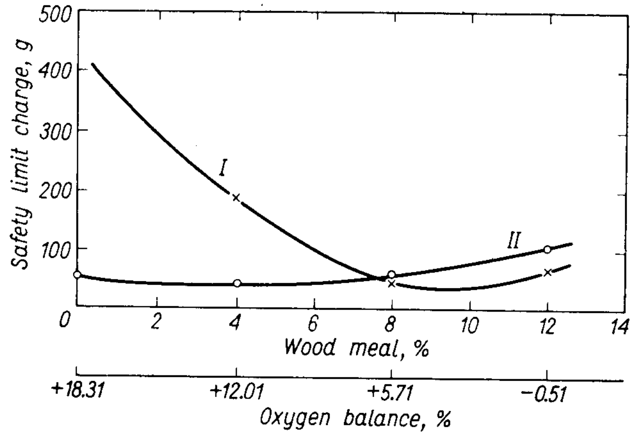

FIG. 141. Effects of paraffined paper cartridges upon the safety of explosives of various oxygen balances: *I*—cartridge of paper only; *II*—paraffined paper cartridge (according to Murata [42]).

Good stemming, occupying at least ⅓ of the shothole, prevents the formation of large amounts of toxic gases.

Experiments carried out in the U.S.S.R. have shown that the content of carbon monoxide and nitric oxides in the products of an explosion is influenced by the medium in which the explosion takes place. The quantity of carbon monoxide and nitric oxides is higher with shotfiring in coal and lower in copper and iron ore seams. The figures given by Assonov and Rossi are summarized in Table 100.

TABLE 100

QUANTITY OF TOXIC OXIDES FORMING IN THE PRODUCTS OF EXPLOSIONS OCCURRING IN VARIOUS SEAMS

Explosive	Shotfiring			
	in coal		in iron ore	
	carbon monoxide l./kg	nitric oxides l./kg	carbon monoxide l./kg	nitric oxides l./kg
2 Ammonit	40.7	29.8	4.7	7.9
62% Dynamit	54.3	4.8	3.3	8.0

Calculation of the oxygen balance is carried out by taking into consideration the quantity of oxygen supplied by the oxygen carrier and that required by the combustible ingredients of the explosive mixture. The figures for the most frequently used ingredients are tabulated below.

TABLE 101

QUANTITY OF OXYGEN GIVEN OR REQUIRED BY INGREDIENTS OF MINING EXPLOSIVES

Oxygen carrier	Quantity of oxygen (kg) given by 1 kg of the substance
Inorganic salts	
Ammonium nitrate	+0.200
Ammonium perchlorate	0.340
Barium chlorate [$Ba(ClO_3)_2 \cdot H_2O$]	0.298
Barium nitrate	0.306
Calcium nitrate [$Ca(NO_3)_2 \cdot 4H_2O$]	0.339
Potassium chlorate	0.396
Potassium nitrate	0.396
Potassium perchlorate	0.462
Sodium chlorate	0.450
Sodium nitrate	0.470
Organic substances	
Nitroglycerine	0.035
Tetranitromethane	0.490
Substances requiring oxygen	**Quantity of oxygen (kg) required for total combustion of 1 kg of the substance**
Aluminium	−0.890
Cellulose ($C_6H_{10}O_5$)	1.185
Charcoal	2.667
Cyclonite (RDX)	0.216
Diglycoldinitrate (DGDN)	0.408
Dinitronaphthalene	1.394
Dinitrotoluene (DNT)	1.144
Nitrocellulose (11.95% N)	0.387
Nitroglycol	0.000
Nitroguanidine	0.308
Nitronaphthalene	1.988
Penthrite	0.100
Sulphur	1.000
Trinitrotoluene (TNT)	0.740
Trinitroxylene	0.896
Woodmeal ($C_6H_{10}O_5$)	1.185

INERT INGREDIENTS INCREASING SAFETY

Long experience has shown that the most efficient non-explosive ingredients for increasing the safety of explosives towards methane and coal-dust are sodium and potassium chlorides. The latter is more efficient due, no doubt, to the action of the potassium ion which inhibits explosive reactions in the gaseous phase. This will be considered further when discussing the problem of securing flashless discharge from guns (p. 544). An explosion of a methane–air mixture is a phenomenon of the same type as the explosion of a mixture of muzzle gases with air. It is also beyond question that as in the latter case, the inhibition of an explosion of a methane–air mixture is to a less degree a thermal phenomenon which results from the temperature fall of the igniting flame. To a much higher degree it is based on the spraying in gas of a substance containing potassium ions. A number of authors have shown that this is not only a thermal phenomenon. For instance Dubnov [38] proved this by experiments in which he added sand instead of sodium chloride to the explosives. He matched the quantity of sand so that the heat capacity was the same, and found that the presence of sand cannot prevent explosion of a methane–air mixture.

Dubnov [53] also reports the results of experiments in a testing gallery. The charge consisted of 90% of 80/20 ammonit (80% ammonium nitrate and 20% TNT) and 10% of various salts. A steel mortar was loaded with a 200 g charge, without stemming, and fired in an atmosphere containing 8–10% methane. The percentage number of ignitions of methane was then determined (Table 102).

TABLE 102

Salt	Specific heat	Percentage ignition of methane
KF	0.200	0
KH_2PO_4	0.208	20
KCl	0.162	40
K_2SO_4	0.178	40
KNO_3	0.221	60
NaCl	0.206	60
Na_2CO_3	0.273	70
CaF_2	0.215	80
$CaCO_3$	0.189	100
NH_4Cl	0.363	100
$Pb(OOCCH_3)_2$	0.134	100

These figures show that a high specific heat is not correlated with inhibition of explosion of methane. E.g. the high specific heat of ammonium chloride does not help this salt to inhibit methane explosions.

As mentioned previously (p. 421) ammonium chloride and sodium nitrate in stoichiometric proportion has also been suggested, as an effective source of sodium ions which possess marked ability to inhibit methane explosions.

Dubnov examined the effect of various salts on the ignition temperature and on the explosion lag of methane–air mixtures (Table 103).

TABLE 103

EFFECT OF THE ADDITION OF VARIOUS SALTS ON EXPLOSIVE PROPERTIES

Salt	Minimum ignition temperature °C	Explosion lag (sec) at different temperatures							
		750°C	760°C	770°C	780°C	790°C	800°C	810°C	820°C
No salt added	710	1.8	1.0	1.0	0.8	—	—	—	—
$CaCO_3$	710	1.4	1.1	0.9	0.7	—	—	—	—
NaCl	730	3.2	1.9	1.4	1.0	0.8	0.6	—	—
LiCl	790	—	—	—	—	—	4.2	2.2	1.95
KCl	800	—	—	—	—	—	5.6	3.9	1.85
$CaCl_2$	810	—	—	—	—	—	—	4.0	3.0

These experiments confirm that the efficiency of potassium chloride is higher than that of sodium chloride in inhibiting explosion. (On inhibition of other gaseous explosive mixtures by potassium chloride see papers by Prettre [63]).

Highly interesting results were obtained by Murata [42], showing very high efficiency of potassium chloride and somewhat lower efficiency of sodium chloride. Investigations on the effect of potassium and sodium nitrate are also noteworthy. They were found to have a beneficial influence only when a few per cent were used; in greater quantity they have practically no effect.

According to Dubnov [53] ammonium chloride seems to be particularly suitable as a cooling agent in explosives for sulphur mines.

Dubnov [53] also describes experiments which prove that the activity of an inert salt increases with its fineness (Table 104). The figures in the Table refer to sodium chloride. An explosive charge containing 35 or 40% sodium chloride was detonated in a methane–air mixture.

TABLE 104

ACTIVITY OF INERT SALT AS A FUNCTION OF ITS FINENESS

Average size of the particles of sodium chloride mm	Content of sodium chloride %	Percentage ignitions	Power of explosive according to lead block test
1.38	35	100	221
1.16	35	100	219
0.70	35	70	210
0.38	35	85	216
below 0.14	35	10	192
1.38	40	100	197
0.70	40	45	187
0.38	40	5	181

Recently "ultra-safe" explosives were introduced in Great Britain. They contain cooling salts ground to a finer size than it is customary (p. 467).

Dubnov [53] reports figures depicting the relationship of charge limit, power, heat of detonation and temperature and sodium or potassium chloride content for an explosive containing ammonium nitrate and TNT in the proportion 80 : 20 (Table 105).

TABLE 105

CHARGE LIMIT AND POWER OF EXPLOSIVES AS A FUNCTION OF SODIUM OR POTASSIUM CHLORIDE CONTENT

Content of inert salt %	Charge limit g		Lead block expansion cm³		Heat of detonation kcal/kg		Calculated temperature °C	
	NaCl	KCl	NaCl	KCl	NaCl	KCl	NaCl	KCl
10	100	150	340	342	817	845	2100	2120
15	200	250	296	298	745	774	2040	2070
20	350	450	272	279	673	703	1980	2023
25	450	550	245	254	600	632	1920	1975
30	550	650	214	226	525	560	1860	1926

It is interesting to note that the compositions containing potassium chloride gave higher calculated values of the heat and temperature of explosion. In spite of this, the efficiency of potassium chloride as an agent increasing the safety of the use of the explosive in presence of fire-damp is higher. It confirms the former observation that potassium ions are efficient inhibitors of gas explosions.

Murata [42] reported similar results for explosives containing ammonium nitrate, 8% of nitroglycerine, 0.3% of nitrocellulose and 8% of woodmeal. Sodium or potassium chloride in proportion 1–15% and 1–10% respectively replaced the corresponding part of ammonium nitrate.

In 1914 Lemaire [64] proposed the use of a sheath made of incombustible and inexplosive substances in explosive charges. As an inert material he recommended: milled sand, salts containing water of crystallization (e.g. sodium sulphate), salts volatilizing at high temperatures (e.g. sodium chloride, sodium fluoride, cryolite), salts decomposing at high temperatures (e.g. ammonium chloride). Sheaths were made by placing the substance between the dual walls of a paper tube.

The preliminary experiments indicated the importance of this discovery. It was found, for instance, than even 800 g of blasting gelatine fitted with a sheath of sodium chloride or sodium fluoride weighing as much as the explosive itself failed to ignite methane or coal-dust. On the other hand 100 g of blasting gelatine, without an inert sheath, was enough to cause explosion of methane or coal-dust.

After investigations carried out in Belgium at the Institut National des Mines de Pâturages in 1930, an inert sheath with the following specification was introduced:

thickness of mantle: 3 mm
composition: 25% of binder (usually calcium sulphate or clay)
75% of salts: sodium or calcium fluoride or sodium chloride with an admixture of at least 35% of sodium fluoride.

The total weight of material forming the sheath was 65 g per 100 g of explosive.

Later, the thickness of the mantle was increased to 5 mm in safety explosives (S.G.P.—p. 447) and to 6.5 mm in rock explosives.

In 1947, sodium hydrogen carbonate was introduced as the most efficient salt.

About 1933 work on the use of sheaths of this kind was also started in other countries. In the U.S.S.R. sheaths of 9 mm thickness composed of powdered salts in paper tubes were adopted.

In the Home Office Gallery at Buxton (Great Britain) the effect of the following groups of substances used for filling the sheaths was tested:

(1) Substances preventing explosion of methane–air mixture, e.g. potassium chloride;

(2) Cooling substances with high thermal conductivity, e.g. iron chips;

(3) Substances evolving incombustible gases, assumed to form a gaseous sheath around the explosion, e.g. sodium hydrogen carbonate;

(4) Reducing substances which may combine with atmospheric oxygen, thus removing the ingredient necessary for the explosion of methane, e.g. sodium hydrosulphite.

Experiments in a testing gallery showed that addition of the majority of these substances increases the charge limit to such an extent that it cannot fit into the mortar. For this reason, a very strict test was carried out on the basis of the detonation of an explosive directly suspended in a methane–air mixture. Under such conditions the charge limit was diminished nearly four times as compared with that determined for a mortar.

TABLE 106

Substance in a sheath	Charge limit g
No sheath	56
Kieselguhr	113
Lead sulphate	170
Sodium thiosulphate	170
Sodium hydrogen sulphite	170
Sodium formate	226
Manganese dioxide	226
Ferrous oxalate	226
Hydrated sodium carbonate	226
Sodium hydrosulphite	283
Sodium hydrogen carbonate	283
Iron chips	340
_a_ and _b_ Belgian mixtures	170
_c_ Belgian mixture	226

Table 106 presents the results of some experiments on the Tees Powder explosive (p. 405) provided with a sheath 4 mm thick.

On the basis of these experiments a sheath was introduced in England filled with sodium hydrogen sulphite, a cheap substance and fairly efficient when in the form of a mantle about 2.5 mm thick, protected from the outside by non-impregnated watertight paper. The explosives which may be used with a sheath of this kind are designated by the symbol "S" (sheathed).

The use of sheaths very slightly weakens the strength of an explosive but does not reduce its sensitiveness to detonation. On the other hand it considerably increases its safety for use in mines with methane and sensitive coal-dust.

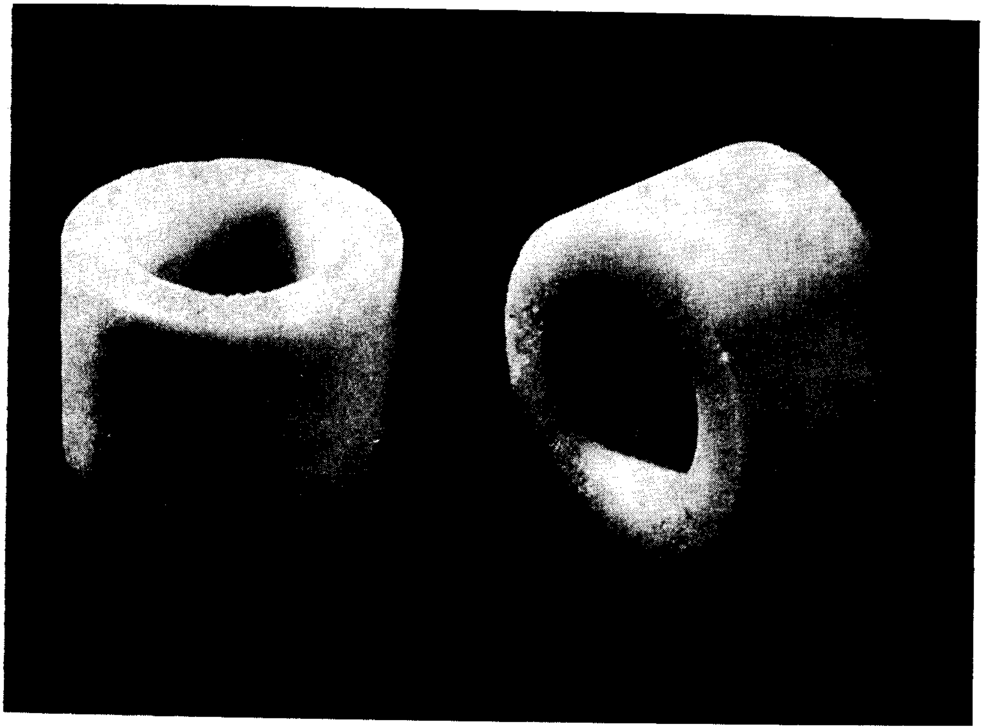

FIG. 142. Rings of sodium chloride or sodium hydrogen carbonate for making rigid sheaths (Courtesy Dr. L. Deffet, Sterrebeck, Belgium).

The production of sheaths has led, however, to some new and unexpected difficulties. Thus, the explosive core was sometimes not sufficiently well centered, or the substance filling the sheath moved to one end and formed a barrier to the transmission of detonation from one cartridge to another.

It is also evident that the increased safety produced by using sheathed explosives is lost if the sheath is removed deliberately. The latter may happen, for instance, if the hole into which the charge is being loaded is too narrow.

To avoid this danger various solutions were suggested and introduced, for instance, the use of rigid sheaths. In Belgium these were made by the compression of rings of sodium chloride or sodium hydrogen carbonate (Fig. 142) or by the extrusion of mixtures of sodium chloride with wet clay which was then dried.

This arrangement has the additional advantage that it facilitates detonation. In the U.S.S.R. Seleznev suggested [60] a rigid sheath composed of china clay, sodium chloride and calcium sulphate.

Another method of increasing the mechanical strengths of sheaths was suggested by Fleming [65]: it consisted of making them from "bicarbonate felt"—90% sodium hydrogen carbonate and 10% paper pulp.

In Great Britain an alternative solution was found. The inert material was directly and uniformly incorporated into the explosive itself, instead of forming a separate sheath (J. Taylor [66]). These explosives were marked "Eq. S.", i.e. equivalent in safety to sheathed explosives of the same class.

In addition to the ordinary inert sheath, an active sheath in Germany and the U.S.S.R. consisting of "cooling" salts admixed with nitroglycerine has been developed, for the following reasons:

(1) The substance of a sheath is better sprayed after the detonation owing to the presence of nitroglycerine taking part in the detonation and since it is then better mixed with the detonation products of the explosive;

(2) Being an explosive, the sheath does not weaken the charge and does not inhibit the transmission of detonation from one cartridge to another.

In Germany sheaths consisting of 12 or 15% nitroglycerine, 33 or 35% sodium chloride and 50 or 55% sodium hydrogen carbonate are used. Each cartridge comprises 70 g of explosive and 50 g of sheath.

In the U.S.S.R. a sheath composed of nitroglycerine, sodium chloride, potassium chloride, sodium nitrate and woodmeal is employed.

In Belgium "Bicarbite" special charges have been introduced, consisting of 85% sodium hydrogen carbonate and 15% gelatinized nitrocellulose. Cartridges of this composition are placed in the shothole alternately with explosive cartridges. By altering the proportion of explosive cartridges to Bicarbite ones the degree of safety towards methane and coal-dust can be modified.

Recently Boucard and Deffet [67] examined the action of organic compounds containing halogens, such as: carbon tetrachloride, hexachloroethane, γ-hexachlorocyclohexane, chlordane ($C_{10}H_6Cl_8$), iodoform and also iodine.

It was found that the organic compounds in question could inhibit the explosion of methane–air mixture particularly if they were first subjected to a thermal decomposition. It seems advisable to add these compounds to explosives so that they undergo some decomposition in the course of the detonation. They do not seem to form substances increasing the safety by themselves.

INERT NEUTRALIZING AGENTS

Since ammonium nitrate always contains a small amount of free nitric acid a certain amount of substances to neutralize the acid should also be added to ammonium nitrate explosives containing nitroglycerine. Since soluble bases (e.g. sodium hydrogen carbonate) exert a negative influence on ammonium nitrate and other ingredients of explosive mixtures such as TNT, insoluble bases, e.g. calcium or magnesium carbonates, should be employed. Ferric oxide may also be used, e.g. in the form of pyrites ash.

In explosives which contain a small amount of nitroglycerine (4–8%) the addition of woodmeal (p. 423) provides adequate stability.

To reduce the density, a larger amount (6–12%) of light woodmeal, peat meal or vegetable fibre (e.g. cellulose) is sometimes added. This brings about a considerable reduction in density (to 0.70) and increases the sensitiveness of the explosive to detonation.

Powdered plastic foam may also be used for this purpose.

In the U.S.S.R. a cartridge of a basic substance was added to charges of explosives to neutralize the acid and harmful products which might result from incomplete detonation (e.g. nitrogen dioxide). This was a cartridge comprising calcium hydroxide in an amount equal to 25% weight of the whole stemming. This reduced the quantity of acid gaseous products (CO_2 and NO_2) by 10–20%.

The addition of water to the stemming has a similar effect.

An important ingredient for improving the composition of the products of explosion used in Great Britain is calcium sulphate.

The effect of the addition of barium sulphate has also been tested in Great Britain. This substance has the exceptional property of sensitizing a nitroglycerine gel immersed in water, so that the explosive is capable of propagating an explosion with a detonation rate of 6000 m/sec, under water at depths as great as 2750 ft. According to J. Taylor and Gay [4] this phenomenon may be due to the reflection of the shock wave at the interface between the explosive and the sensitizing powder, an effect which occurs only when the latter is compressed above a certain minimum density. This has been exploited in the design of explosives for deep seismic explosions.

TESTS FOR MINING EXPLOSIVES

Any explosive which is intended for use in mines has to satisfy certain requirements and to ensure overall safety. All mining explosives, both for coal and rock must be subjected to the tests before being licensed for use. The tests vary from one country to another. Those described below are based mainly on methods applied in Poland.

TRANSMISSION OF DETONATION

To examine this property of explosives, it is necessary to determine the maximum distance between two cartridges (weighing 100 g each, 30 mm dia.) at which detonation will propagate from the cartridge fitted with a No. 8 detonator to the second cartridge which has no detonator. This distance should not be less than 3 cm, and for special permitted explosives 4 cm; for ammonium nitrate explosives it is usually 4–8 cm and for dynamites it is more. Sometimes the transmission of detonation is expressed in terms of units, based on the calibre of the cartridge (e.g. 32 mm).

SENSITIVENESS TO DETONATION

To determine the sensitiveness to detonation 3 cartridges of explosive each weighing 75 g and 25 mm dia., or 4 cartridges each weighing 100 g and 30 mm dia. may be used. The cartridges are set out in a row so that they touch each other. One of the end cartridges is then detonated by the weakest possible detonator. The explosives tested should be detonated completely under these conditions by a weak detonator*. The weakest detonator producing the detonation of the above mentioned cartridges is characteristic to the sensitiveness to detonation of a given explosive.

Testing transmission of detonation and sensitiveness to detonation is intended to establish whether or not a given explosive ensures complete detonation in a shothole. An incomplete detonation is always undesirable since it involves a considerable waste of time and effort and may cause an accident during subsequent shots. Both tests are always employed as inspection tests during production. Freshly manufactured explosive should not be used in these tests, since much better results are obtained after a few days' storage. Thus, according to T. Urbański's experiments [68], the permitted explosive Bradyt F (p. 475) initially gives a transmission of detonation value of 14–15 cm. The next day, the same cartridges give values not exceeding 7 cm. This occurs because the freshly-mixed explosive contains a considerable quantity of air which greatly facilitates the transmission of detonation. After a few days or even a few hours, when the excess of air has escaped, the transmission of detonation deteriorates. These changes in the explosive, however, are not so great as to affect the rate of detonation and expansion in the lead block.

In dynamites and in blasting gelatine, containing a large amount of nitroglycerine gelatinized with collodion cotton, the changes in properties caused by the presence of air persist for a very long period of time (often about a year) since the air dispersed in the viscous colloid of blasting gelatine remains there much longer than in explosives with a powdery consistency. E.g. blasting gelatine, containing 91% nitroglycerine and 9% collodion cotton gives a lead block expansion of 580 cm^3 immediately after mixing and 545 cm^3 two days later. After longer storage (more than a month) this figure may fall to 500 cm^3 or to even less.

The rate of detonation undergoes similar variations. E.g. dynamite consisting of 62.5% nitroglycerine, 3.5% collodion cotton, 28% potassium perchlorate and 6% woodmeal detonates with a rate of 7000 m/sec immediately after mixing. In

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* To determine the sensitiveness to detonation of mining explosive in some countries (including Poland) special standard detonators have recently been introduced, containing 0.05, 0.1, 0.15, 0.20 g etc. of silver azide. The stronger contains 0.60 g of silver azide or an equivalent quantity of lead azide.

six months the rate of detonation may decrease to 2750 m/sec. If the explosive is kept in warm premises the rate may decrease still more—up to 1800 m/sec. If the cartridges harden due to the setting of ammonium nitrate or potassium chlorate, transmission of detonation becomes worse and detonations may be impaired.

An explosive intented for tests on the transmission and rate of detonation must therefore be seasoned for at least 24 hr.

With dynamites the tests should be repeated after a few days and then after a few weeks.

The detonators employed for these tests should be reliable and their initiation strength must be checked.

It should be pointed out that the transmission of detonation depends not only on the composition of the explosive and the previously mentioned factors but also on the diameter of the cartridges, their confinement and their density.

The transmission increases with the diameter up to a certain diameter at which it becomes constant.

An investigation of the probability of transmission of detonation as a function of the diameter of the cartridge was carried out by Hino [69]. This is depicted by the diagram in Fig. 143.

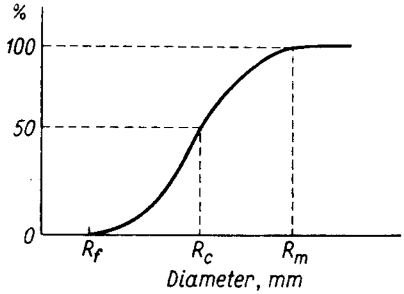

FIG. 143. Probability of detonation (in %) as a function of cartridge diameter, according to Hino and Yokogawa [59]. R_f—diameter which does not give any transmission of detonation; R_c—"critical" diameter (50% probability of transmission of detonation); R_m—minimum diameter which gives 100% probability of transmission of detonation.

The transmission of detonation in a confined space (in a tube or shothole) is higher than in the open air. E.g. an ammonium nitrate explosive with 4% nitroglycerine which ordinarily has a transmission value of 10–15 cm, in a mortar gives the value 19–23 cm, according to T. Urbański [70]. This author studied change of transmission as a function of density. The results for ammonium nitrate explosives are given in the diagram in Fig. 144.

The decrease in transmission values with density beyond a certain value (density higher than 1.1) seems to be of particular significance. T. Urbański showed as early as 1926 [70] that the shock wave produced by detonation of an explosive can move along a shothole, or a mortar, at a rate higher than the rate of detonation (e.g.

for the rate of detonation of 3220 m/sec in a tube 35/42 mm, the rate of the shock wave was 3830 m/sec). The shock wave may "dead" press the cartridges to a degree which renders their transmission of detonation difficult.

According to Hino and Yokogava [59] an addition of surface active agents (0.5–1%) to mixtures of ammonium nitrate with liquid coal-tar improves the transmission of detonation and increases the rate of detonation. These authors assume that the surface active agents increase the rate of reaction between the ammonium nitrate solid phase and the coal-tar liquid phase.

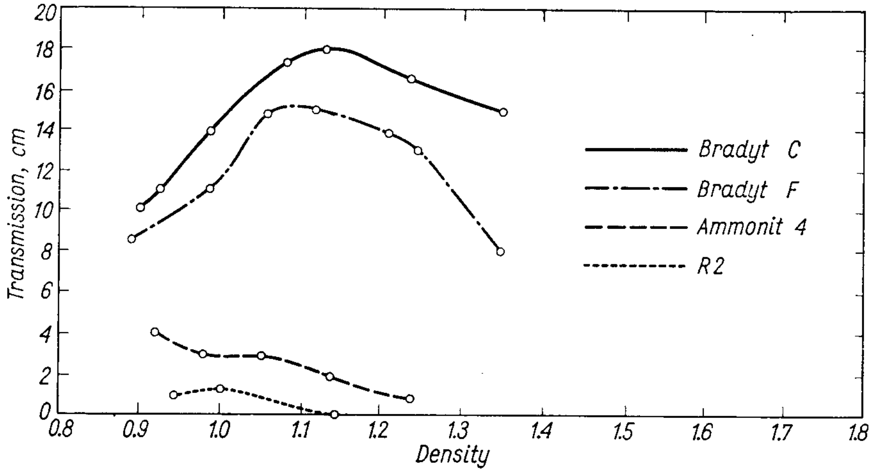

FIG. 144. Transmission of detonation as a function of density, according to T. Urbański [70].

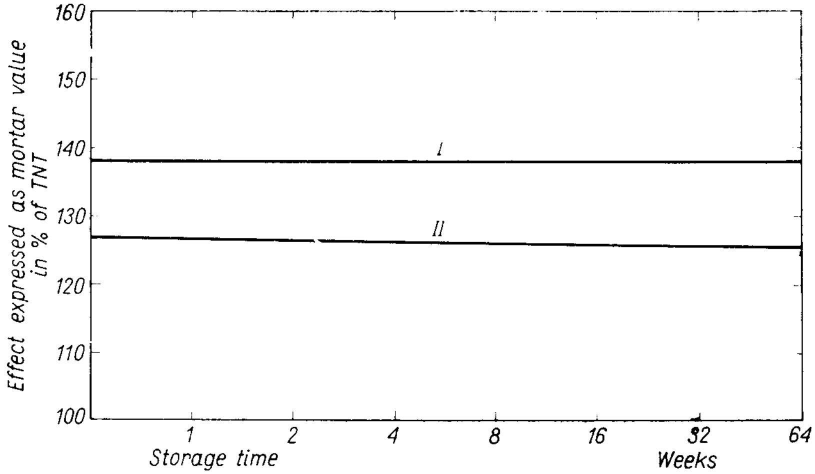

FIG. 145. Change in the power of explosives on storage [71]; *I*—ammonia gelatin, type B with 35% NG; *II*—ammonium nitrate explosive, type II with 6% NG and 76% NH_4NO_3.

Wetterholm [71] gave a number of diagrams illustrating the change of explosive properties of mining explosives during storage.

Figure 145 suggests a very small reduction in the power of dynamite and ammonium nitrate explosives on storage, measured in a ballistic mortar. Figure 146 indicates the change in the transmission of detonation during storage. The decline in transmission of a gelatine explosive (35% nitroglycerine) can be halted and restored by re-kneading the explosive. The change in transmission of detonation with temperature is depicted on another diagram (Fig. 147). The change of the rate of detonation of these explosives on storage is given in Fig. 148. Wetterholm also gives the value of the rate of detonation at various temperatures (Table 107).

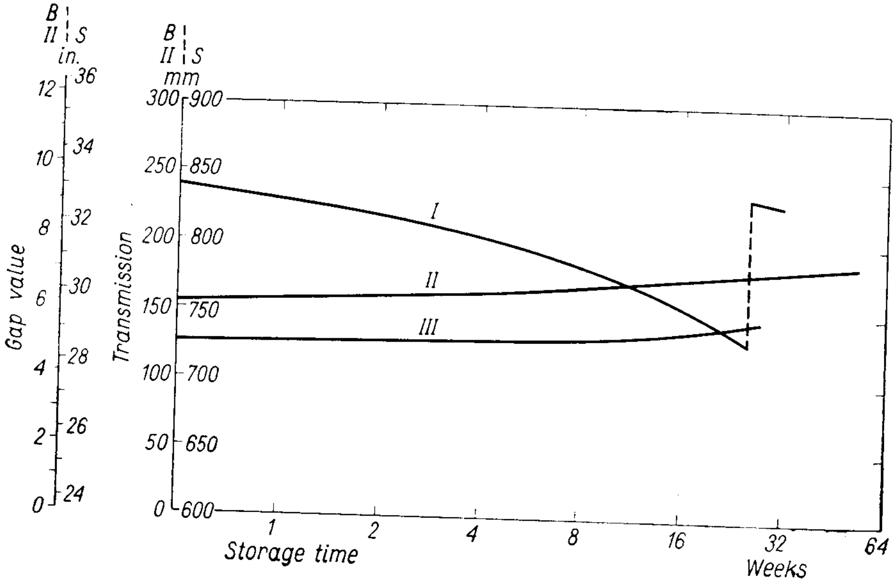

FIG. 146. Change in the transmission of detonation of explosives on storage [71]; *I*—ammonia gelatin, 1 in. (25 mm) dia., type B with 35% NG; *II*—ammonium nitrate explosive, 1 in. (25 mm) dia., type II with 6% NG and 76% NH_4NO_3; *III*—semi-plastic explosive, $1\frac{3}{16}$ in. (30 mm) dia., type S with 54% NG.

TABLE 107

Temperature °C	Ammongelatine (35% NG) m/sec, No. 8 detonator	Ammonium nitrate explosive (6% NG) m/sec, No. 8 detonator
−25	2300	3350
0	2450	3350
+35	2700	3600

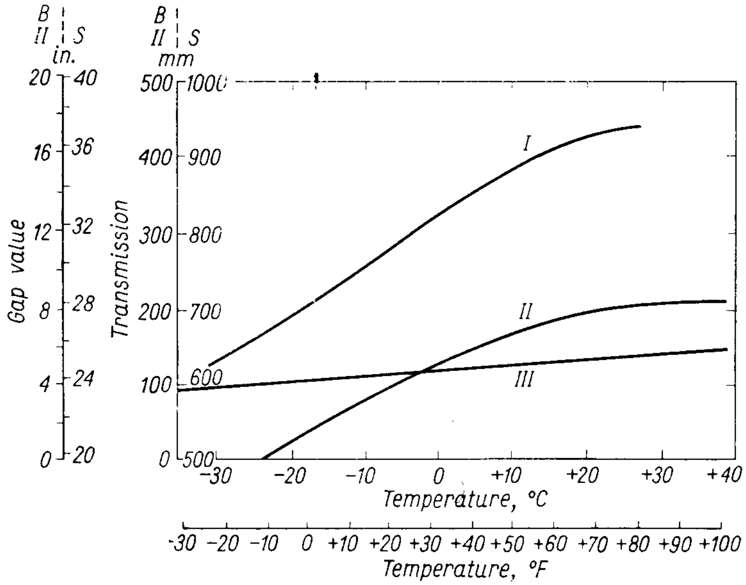

FIG. 147. Change in the transmission of detonation of explosives with temperature [71]; *I*—semi-plastic explosive, type S with 54% NG; *II*—ammonium gelatine, type B with 35% NG; *III*—ammonium nitrate explosive, type II with 6% NG and 76% NH_4NO_3.

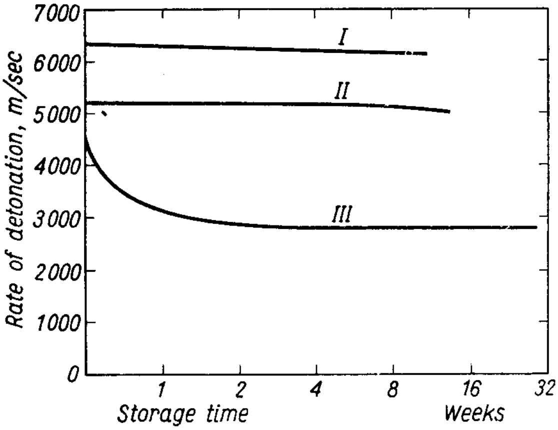

FIG. 148. Change in the rate of detonation of explosives on storage [71]; *I*—ammonia gelatin, iron tube 1 in. (25 mm) dia., type B with 35% NG; *II*—ammonium nitrate explosive, iron tube 1 in. (25 mm) dia., type II with 6% NG and 76% NH_4NO_3; *III*—ammonium gelatine, cardboard tube $1\frac{9}{16}$ in. (40 mm) dia., type B with 35% NG.

POWER OF EXPLOSIVES

The power of explosives is determined in a conventional manner. The most usual test is the determination of the lead block expansion and the rate of detonation. In some countries the crushing of lead and copper cylinders is determined.

In Anglo-Saxon countries a test in a ballistic mortar is also used. Tests for explosive power should be repeated occasionally for inspection purposes in production.

SAFETY TESTS WITH METHANE AND COAL-DUST

Explosives for use in coal mines containing methane or ignitable coal-dust must pass a test in a testing gallery. Different procedure is used in different countries. General data on galleries and methods of testing are summarized in Table 108.

Experimental gallery in Poland

The experimental gallery for testing explosives for use in the mining industry (Fig. 149) is a wrought-iron tube, circular in cross-section, 44.2 m long and 2.0 m in inner diameter. One end of the tube is open, while the other is closed with a concrete block. There is a cavity inside the concrete block in which a steel mortar is mounted (Fig. 150). The cavity is connected through the safety valve, vent shaft and air damper with a powerful electric ventilator for airing the gallery after the shot. The safety valve and air damper close the vent shaft and protect the ventilator from accidental damage when firing takes place.

Throughout the length of the gallery there is a floor of sheet iron with an empty space below filled with concrete except for the first three meters from the closed end, where the heating pipes are situated.

Inside the gallery, at a distance of 3.4 m from the closed end a ring is fixed to which a paper partition is fastened so as to form a chamber of 10 m^3. In the chamber a mixture of methane and air is prepared. In winter this is heated to a temperature of above 0°C by steam in the heating pipes beneath the floor.

In the wall of the gallery facing the observation post there are observation windows at intervals of 1 and 2 m along its whole length, through which the course of firing is watched.

Between the first windows at the firing end there are apertures for the firing leads and arrangements for measuring the temperature inside the gallery.

After the cables have been laid, the paper partition is fastened in place, and the cables are connected through the short-circuiting unit with the observation post.

The concrete block closing the firing end is situated in a compartment in which the methane dispensers and the ventilators are located.

At a distance of about 10 m from the gallery, half way along its length, an observation post is located, from which the charges are fired and the results observed.

In Poland the following standards established by Cybulski have been in force since 1950. Tests are made with cartridges 32 mm dia., placed in a mortar of 50 mm dia., unstemmed. When testing permitted explosives* in the presence of firedamp,

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* i.e. safe towards firedamp and coal-dust.

TABLE 108

Country	Locality	Dimensions of gallery		Capacity of gas chamber m	Gas			Shothole in the mortar		Stemming	Diameter of charges mm
		length m	diameter m		type %	concentration %	temperature °C	length cm	diameter mm		
Belgium	Pâturages	20	1.6	10	firedamp	9	15–20	50	55	no stemming	30
Czechoslovakia	Ostrava	24	1.8/1.4 (elliptical)	10	firedamp	8–9		60	55		
France	Verneuil	12	2.0	15.7	firedamp	8–9	day temperature	22	38	stemming with a steel disk	
		12	2.0	22				34			
Great Britain	Buxton	15	1.5	10	natural gas	9 ± 0.25		 120	55	stemming or no stemming no stemming	37
Japan	Nagata	34	1.55	6.8	methane	9	20 ± 10	120	55	no stemming	32
Germany	Derne	25	1.35	10	methane	8–9.5	28–30	60	55	no stemming	35
	Freiburg		1.8 (elliptical)								
Poland	Mikołów Institute of Mining Safety	44	2.0	10 or 20	methane	8–9.5		70 or 120	50	no stemming	33
U.S.A.	Bruceton	30.5	1.9	17.8	natural gas	8 and 4**	20–30	55	57	1 pound of dry clay or no stemming	32
U.S.S.R.	Makeyevka	a number of galleries	1.5–1.8	10–11	methane	8–10	−10 to +30	90*	55*	stemming of moist clay	31–32

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* The use of a mortar is permissible until the capacity of the shothole increases less than 50% in comparison with the initial capacity.

** 4% used only in conjunction with added coal-dust on shelves and on the floor of the gallery.

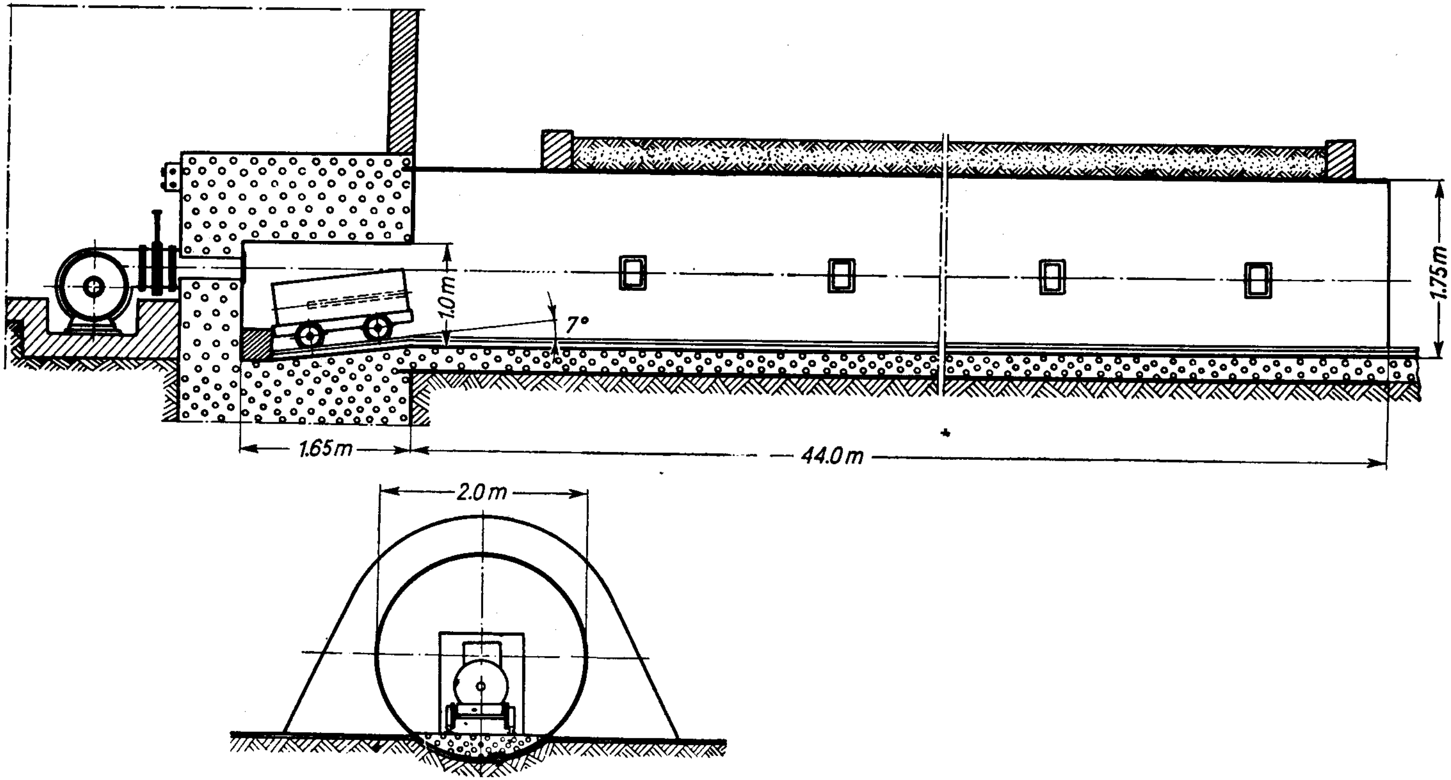

FIG. 149. Diagram of the experimental gallery at Mikołów (Poland).

10 shots, each of 500 g, are fired with the detonator placed at the front of the charge (i.e. initiated directly). The content of methane in the air is 8–9.5%. With special permitted explosives the requirements are much more stringent. The test involves 1 kg of explosive, fired by means of a detonator placed at the rear of the charge (i.e. inversely initiated). The number of shots should not be less than 20.

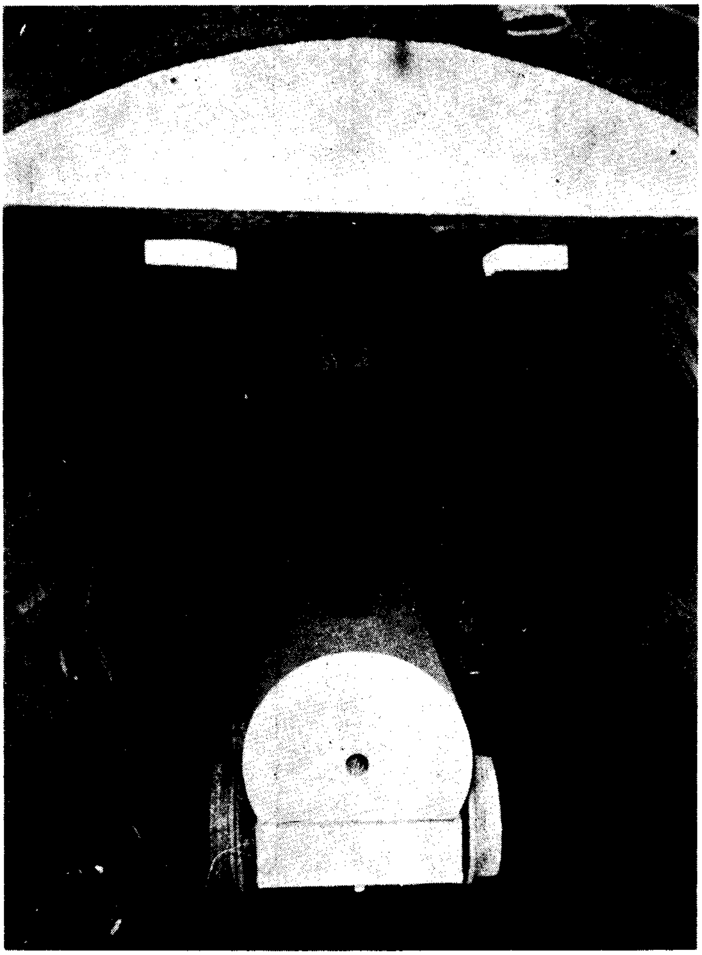

FIG. 150. The closed end of the experimental gallery simulating a coal-face, at Mikołów (Poland).

When testing the safety of normal and of permitted explosives (i.e. permitted Metanits and Karbonits) in the presence of coal-dust 10 shots, each of 500 g, directly initiated, are fired. A cloud of coal-dust is formed by firing small charges (5–7 g) of permitted explosive in bags with coal-dust, suspended in the explosion chamber of the gallery. This creates the most favourable conditions for the ignition of coal-dust, and is therefore a most rigorous test for the explosive. The shots in the bags are fired simultaneously, just 0.5 sec before the test shot.

The classical method of firing explosives in a testing gallery with the charge inside the mortar does not present a true picture of the safety of explosives towards coal-dust since the explosives commonly used fail to ignite coal-dust under such conditions. The angle shot mortar (Fig. 138) is therefore sometimes used as an unofficial auxiliary test.

Special permitted explosives are tested under much more drastic conditions. As previously stated 1 kg of inversely-initiated explosive is fired creating a cloud of coal-dust. The number of test shots should not be less than 20. Safety in the presence of coal-dust is also tested by a special method worked out by Cybulski, which consists in firing two charges, each weighing 1 kg, simultaneously from two opposite mortars. The distance between the mortars is 1 m. A cloud of coal-dust is obtained as described above. The charges are inversely initiated. The number of shots is 20. The test is considered exceptionally stringent. Such tests are repeated from time to time for inspection purposes.

In addition the flashes produced when the explosive charges are fired in the air, are recorded photographically, as an auxiliary test.

Experimental gallery in U.S.S.R.

In the U.S.S.R., tests to authorize permitted explosives for use in dangerous mines are carried out according to the standard specification—GOST 7140–54.

Each lot of the explosive manufactured is tested by drawing samples from 2% of the boxes.

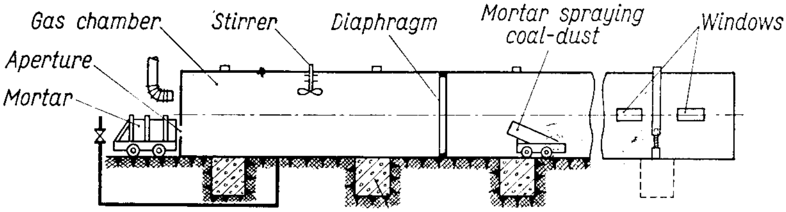

FIG. 151. Diagram of the testing gallery in the U.S.S.R., according to GOST 7140–54.

A testing gallery is shown diagrammatically in Fig. 151. The wall which closes the gallery is fitted with an aperture 300–400 mm dia., to which the mortar is brought on a truck.

The testing of explosives for use in the presence of methane–air mixture is carried out by firing a charge of 600 g. For those used in the presence of coal-dust a charge of 700 g is used.

Three tests are carried out on each lot of explosives intended for use in methane–air mixture and two tests on each lot for use in the presence of coal-dust; in one of these no coal-dust is present in the mortar, in the other 100 g of coal-dust are placed in the bore, most of it between the charge and the mortar's mouth.

Should the methane–air mixture or the coal-dust be ignited, repeat tests are carried out in duplicate on samples drawn from twice the number of boxes. If these tests again give unsatisfactory results, even only for one substance (gas or dust), the lot is rejected.

At least once a year every production plant sends samples (of not less than 60 kg each) of all permitted explosives manufactured there, to the Makeyevskii Scientific Institute of Safety in Coal Mines Research (MAKNII) for a check inspection.

Samples of permitted explosives for use in the presence of methane–air mixture or of coal-dust are tested by the MAKNII according to paragraph 5 of GOST 7140–54 and repeated in accordance with paragraph 6 of GOST 7140–54.

MAKNII carries out tests on experimental new substances or pilot production lots (to be authorized for handling and use) by firing 10 shots from each batch in methane–air, and 10 from each lot in coal-dust (5 with and 5 without coal-dust (100 g) in mortar).

The stemming used when testing explosives in the presence of methane is prepared as follows:

Plastic clay is dried to a moisture content of less than 5% and stemming material is made from it by mixing four parts by weight of the clay with one part by weight of water. The mixture is stirred carefully until a uniform paste is obtained.

50–55 g of clay so prepared containing 20–25% water is pressed into a cake 10 mm wide and 55 mm dia. to make the stemming (Fig. 152).

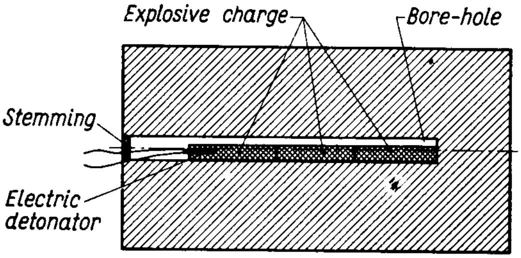

FIG. 152. Charged mortar with clay stemming, according to GOST 7140–54.

Method of testing in the presence of methane. An explosion chamber 10–11m^3 in capacity is separated by a gas-proof diaphragm within the experimental gallery.

The cartridges of explosive being tested are placed in the mortar end to end so that the charge reaches the bottom of the hole, with the last cartridge facing the mouth of the mortar not less than 5 cm away from it (Fig. 152).

A No. 8 instant fulminate–tetryl electric detonator is fixed to the cartridge next to the mouth of the mortar and the hole hermetically sealed with stemming of plastic clay.

The loaded mortar is moved through the window into the explosion chamber of the experimental gallery.

Gas (natural or synthetic methane) containing not less than 90% methane and not more than 8–10% hydrogen is introduced into the chamber.

Before firing the shot the methane–air mixture is stirred by a fan or a mixer and the methane content determined by a Sager pipette or gas analyser.

The temperature of the methane–air mixture in the chamber should lie between −10 and +30°C.

Method of testing in the presence of coal-dust. Testing in the presence of coal-dust is carried out in an experimental gallery without a diaphragm. The lay-out of the explosive cartridges and the electric detonator in the mortar is the same as that described above.

The coal-dust used for the tests is obtained by milling either coal from the Makeyevskii seam of the Tchaikino-South mine, which contains 29–35% volatile matter, less than 9% ash and less than 2% moisture, or another coal of the same composition.

According to GOST 4403–48 the coal should be ground so that the residue on a No. 15 sieve is less than 10% and that more than 50% of the dust passes through a No. 16 sieve.

Coal-dust is injected into the experimental gallery by means of a spray gun 500–700 mm long with a 150–220 mm bore, loaded with 50 ± 5 g of the explosive under test. The charge is fitted with a No. 8 fulminate–tetryl electric detonator in a paper or copper tube. 6 ± 0.1 kg of coal-dust is spread over the charge.

The spray gun is placed:

at a distance of 11.5 m from the bottom of a gallery 1500 mm dia.;
at a distance of 10.0 m from the bottom of a gallery 1600 mm dia.;
at a distance of 8.0 m from the bottom of a gallery 1800 mm dia.;
and at an angle of 20° to the horizontal axis of the gallery.

The charge of the explosive being tested, weighing 700 g, is located in the mortar.

A No. 8 fulminate–tetryl electric detonator in a paper or copper tube is located in the first cartridge. Coal-dust spraying is commenced 5–10 sec before the charge of explosive being tested is initiated.

If a 700 g charge fails to ignite coal-dust under the conditions described above, the explosive is considered to be safe in the presence of coal-dust.

If any residue of the explosive is found in the bore of the mortar or in the explosion chamber, the test is considered a failure irrespective of whether or not the coal-dust is ignited.

APPLICATION OF STATISTICS TO GALLERY TESTING OF EXPLOSIVES

During World War II Dixon and Mood [72] developed a special experimental method for testing the sensitiveness of explosives to impact. The method gave a statistical estimation of the mean value. It became known as the Bruceton up-and-down method. The primary advantage of the method is that it increases the accuracy with which the mean value can be economically determined. The method requires fewer tests than other methods.

It was used for dust-explosion gallery tests on "permissible" explosives at Buxton at the S.M.R.E. by Gibson, Grimshaw and Woodhead [73]. It is now accepted in the U.S.A. as a standard procedure for determining the charge limit of a safety explosive. Figure 153 gives a general idea of the method. Usually the charge (W_{50}) giving a 50% probability of explosion of firedamp or coal-dust is determined by this method [75].

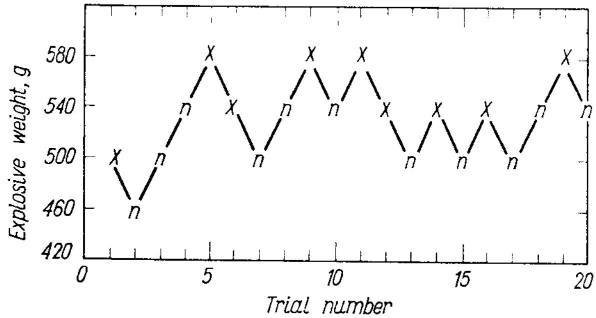

FIG. 153. Determination of incendiveness of a permitted (permissible in the U.S.A.) explosive in a firedamp atmosphere, by the up-and-down method, according to Grant and van Dolah [74].

STABILITY OF MINING EXPLOSIVES

The chemical stability of explosives depends on their ingredients. Those which do not contain nitroglycerine may be stored for long periods. Ammonium nitrate explosives must be protected against moisture and, if this is done, they may be stored for periods up to 6 months. In practice, all explosives containing nitroglycerine should be utilized fairly quickly (within 1–3 months, depending upon the regulations in force in a given country). It is very important to remember that ammonium nitrate always contains a certain amount of free nitric acid which, if not neutralized by the addition of suitable ingredients, has a deleterious effect on nitroglycerine, leading to its decomposition. Apart from chemical stability the constancy of physical properties is also of importance. E.g. cartridges of ammonium nitrate explosives often become hard and difficult to detonate and impossible to use due to the impracticability of introducing detonators into them (Vol. II, p. 459). Nitroglycerine explosives which do not contain nitroglycol or aromatic nitro compounds in a proportion sufficient to lower the freezing point may freeze at low temperatures and need to be thawed. This may involve the separation of nitroglycerine, thus creating an additional hazard (Vol. II, p. 72).

MINING EXPLOSIVES USED IN VARIOUS COUNTRIES

In the following lists the mining explosives used in the inter-war period and in current use in different countries are cited.

The lists are presented in alphabetical order:

1, Belgium. 2, Czechoslovakia. 3, France. 4, Germany. 5, Great Britain. 6, Hungary. 7, Japan. 8, Poland. 9, U.S.A. 10, U.S.S.R.

BELGIUM

In Belgium earlier mining explosives had the composition given in Table 109.

TABLE 109

BELGIAN MINING EXPLOSIVES

Ingredients	R II Centralite	B bis Sabulite	V bis Flamivore	Antigrisou Yonckite
Ammonium nitrate	62	51	59	42
Sodium nitrate	–	–	–	10
Ammonium perchlorate	–	–	–	12
Potassium perchlorate	–	10	–	–
TNT	14	15	–	14
DNT	–	–	1	–
Nitroglycerine	–	–	11	–
Nitrocellulose	–	–	0.05	–
Cellulose	–	–	4.85	–
Naphthalene	–	–	2	–
Carbon black	–	–	0.1	–
Sodium chloride	18	24	22	22
Sodium oxalate	6	–	–	–

The explosives in Belgium are now classified into 4 types, according to l'Association de Fabricants Belges d'Explosifs et le Centre de Recherches Scientifiques et Techniques pour l'Industrie des Produits Explosifs [76] (Tables 110–112).

Type I—dynamites and rock explosives. The chief ingredients of the latter are ammonium nitrate, nitroglycerine and TNT. Their rate of detonation at a density of 1.1 is about 3800 m/sec, their transmission distance 6 cm.

Type II—explosives which, when a 1400 g charge is fired in a steel mortar in an experimental gallery, fail to ignite a 9% methane–air mixture or coal-dust. They are used with an inert sheath in rock workings. Their rate of detonation is about 3300 m/sec (charge 30 mm dia.) at a density of 1.1, their transmission distance 6 cm.

Type III—the S.G.P. (Securité-Grisou-Poussières) explosives. These are used exclusively with an inert sheath and must not ignite methane or coal-dust in the following two tests:

(1) A shot of 1000 g, inversely initiated, fired in a mortar without stemming;

(2) A shot of 1400 g in an angle shot mortar fired at an angle of 90°.

Their rate of detonation at a density of 1.1 and 30 mm dia. is 3000 m/sec, their transmission distance 8 cm.

Type IV—explosives extra safe in use. Explosives in this group undergo the most stringent tests. In an experimental gallery a 2200–2400 g charge (depending on dimensions of the gallery) must not ignite methane or coal-dust.

Mixtures of this type are represented, among others, by Bicarbite mixtures, which are not explosives strictly speaking, but are used in cartridges together with cartridges of genuine explosives, to increase their safety (p. 431).

Common blackpowder or improved "poudre H" is also used in Belgium in opencast mines. The latter contains a certain amount of ammonium nitrate and is used only in mines when large charges of explosives are used. It is initiated exclusively by a detonating fuse.

The composition of modern Belgian explosives is given below.

Type I ammonium nitrate explosives may be represented by Ruptol consisting of:

Ammonium nitrate	73%
Nitroglycerine	10%
DNT	5.5%
Cellulose	5.5%
Woodmeal	4.0%
Aluminium	2.0%

The cartridges are 22, 25 and 30 mm dia.

TABLE 110

TYPE II BELGIAN EXPLOSIVES

Ingredients	Explosives		
	C. A. Fractorite	B Ruptol	003 Sabulite
Nitroglycerine	10	10	–
Ammonium nitrate	77	74.5	80
DNT	–	4	–
TNT	10	–	14.2
Sodium chloride	–	5	–
Calcium silicide	–	–	4
Kieselguhr	1.5	–	–
Woodmeal	–	6.5	1.8
Cellulose	1.0	–	–
Metal soap	0.5	–	–
Density	1.1	1.04	1.1
Diameter (mm) (of explosive core and with sheath)	26/36	23/36	23/37
Date of approval	1958	1957	1957

CZECHOSLOVAKIA

The explosives used in Czechoslovakia over the inter-war period were similar to those used in other Central European countries.

As rock explosives Dynamites and Donarits with the same composition as German Donarit were employed (the difference between Czechoslovak and German

TABLE 111

TYPE III S.G.P. BELGIAN EXPLOSIVES

Ingredients	Explosives						
	Cooppalite	Flammivore	Nitro-boncellite	V Nitrocooppalite	Matagnite	Sabulite	B Securite
Nitroglycerine and nitroglycol	35	10	10	10	10	—	35
Nitrocellulose	1.5	—	—	—	—	—	1.5
Ammonium nitrate	21.5	58	60	60	60	58.5	23.5
Potassium perchlorate	—	—	—	—	—	5	—
Trinitronaphthalene	—	—	—	—	—	1	—
TNT	—	—	—	—	—	14	—
Sodium chloride	42	25	23	23	23	20	40
Woodmeal	—	7	7	7	7	1.5	—
Density	1.5	1.0	1.05	1.0	1.0	1.15	1.4
Diameter (mm) (of explosive core and with sheath)	30	26/36 29/40	26/36	26/36	26/36	26/36	23/36
Date of approval	1955	1955	1953	1958	1955	1957	1955

TABLE 112

TYPE IV BELGIAN EXPLOSIVES

Ingredients	Explosives			
	Arionite	Ch. 41 Charbrite	VIII Nitrocooppalite	Bicarbite
Nitroglycerine	9.9	10	10.11	14.9
Nitrocellulose	0.1	—	0.09	0.1
Sodium nitrate	55.6	54.5	55.5	—
Ammonium chloride	34.4	34	34.3	—
Sodium hydrogen carbonate	—	—	—	85
Kieselguhr	1.5	—	—	—
Cellulose	1	—	—	—
Metal soap	—	0.5	—	—
Density	1.13	1.1	1.0	1.44
Date of approval	—	1957	1957	—

(pp. 267 and 457) Donarits was that the former contained 6% nitroglycerine and 12–16% nitroglycol).

As examples of safety explosives, Metanits may be cited (Table 113).

TABLE 113

CZECHOSLOVAKIAN PERMITTED EXPLOSIVES

Ingredients	Metanit A	Metanit N
Nitroglycerine	—	24–26
Nitrocellulose	—	0.6–1.0
Aromatic nitro compounds	6	—
Ammonium nitrate	71.5	23–27
Sodium chloride	20.5	42.8–49
Woodmeal	2	—
Calcium nitrate, 50% solution	—	2.5–3.5
Palatinol A	—	0.1–0.5
Density	0.98	1.65
Power (lead block test, cm^3)	240	168
Transmission (cm)	4	2
Rate of detonation (m/sec)	3850	5000

Rock and coal explosives with the composition tabulated below are now used (Table 114).

In addition, Gelatine-Donarit 1 (p. 455) is used as a rock explosive. TNT is also employed in opencast coal working and blackpowder is used where low power and a slow explosion giving large lumps are required.

TABLE 114

Ingredients	Rock explosives			Coal explosives	
	Gelatine	Dynamon I	Astralit I	Plastic* Metanit N	Bikarbit *
Nitroglycerine and nitroglycol	22	–	3	25	12.5
Nitrocellulose	0.8	–	–	0.8	–
Nitro compounds	–	14.1	12	–	–
Ammonium nitrate	61.9	82.9	82	25	–
Calcium nitrate, 50% aqueous solution	–	–	–	3	–
Sodium chloride	–	–	–	45.9	47
Sodium hydrogen carbonate	–	–	–	–	40.5
Woodmeal	–	2.75	2.5	–	–
Dyes	0.3	0.25	0.5	–	–
Diethylphthalate	–	–	–	0.3	–
Density	1.52	0.96–0.97	1.04	1.4	1.3
Oxygen balance (%)		+1.1	+3 to +5.5	+5.4	+0.4
Power (lead block test, cm³)	370–390	320–355	270–280	150–170	20–25
Transmission (cm)	15–20	5	5	2–6	2–3
Rate of detonation (m/sec)	6200–6500	3900–4200	3800–4800	3200–3800	2350
Heat of detonation (kcal/kg)		902	800	902	107

* Bikarbit is often used as an active sheath. The cartidges are composed of 52% Metanit and 48% Bikarbit.

A recent addition to the list of Czechoslovakian rock explosives [77] includes Geldonarit composed of:

Nitroglycol	22.0%
Collodion cotton	0.8%
Ammonium nitrate	61.9%
Cyclonite	15.0%
Dye	0.3%

Its properties are:

Density	1.52
Oxygen balance	+6.8%
Lead block expansion	370–390 cm³
Transmission of detonation	15–20 cm
Rate of detonation	6350 m/sec
Heat of detonation	960 kcal/kg

FRANCE

The more modern mining explosives employed in France (Table 115) do not differ in the main from those used earlier (see p. 403).

There have been modifications in explosives for coal work, in which 5% ammonium nitrate was replaced by potassium nitrate. These were called the saltpetre explosives (salpetré).

TABLE 115

Ingredients	Explosifs couche (for coal work)		Explosifs roche (for rock work only)	
	Grisou-naphthalite couche	Grisou-dynamite couche	Grisou-naphthalite roche	Grisou-dynamite roche
Ammonium nitrate	95	87.5	91.5	70
Nitroglycerine	–	12	–	29
Nitrocellulose	–	0.5	–	1
TNT	5	–	–	–
Dinitronaphthalene	–	–	8.5	–
Charge limit	500	500	1000	1000

Apart from explosives of this kind, others similar to those commonly used in other countries, i.e. permitted explosives containing sodium chloride, have more recently begun to be used in France.

There has also been a growing interest in ammonium chloride with sodium nitrate as ingredients of mining explosives in France.

TABLE 116

GROUP I. FRENCH EXPLOSIFS COUCHE AMELIORÉS

Ingredients	Dynamites			N Type	
	Grisou-dynamite chlorurée n°15	Noburex	Explosifs grisou chlorurés n°16	N n°64	N n°65
Nitroglycerine	20	20	12.3	–	–
DNT	–	–	0.7	–	–
Dinitronaphthalene	–	–	–	1.5	–
Penthrite	–	–	–	20	12
Ammonium nitrate	20	29	33	20	35.5
Sodium chloride	58	44	49	58.5	47
Woodmeal	2	–	–	–	3.5
Urea-resin foam	–	7	–	–	2
Peat	–	–	5	–	–
Properties					
Density	1.3	0.8	1.0	1.3	1.25
Power* (lead block test, picric acid = 100)	41	55	50	42	55
Transmission (cm)	10–50	6–12	5–10	4–8	3–7
Rate of detonation (m/sec)	2300	2000	2100	3000	3300
Date of approval	1949	1952	1954	1949	1950

* CUP = Coefficient d'utilisation pratique.

Finally, attempts are being made to use such ingredients as penthrite and cyclonite.

The most modern mining explosives employed in France are classified into four groups with regard to their safety in use:

I. Improved explosives for coal work (explosifs couche ameliorés). They may be used with delay detonators provided that the delay between the first and the last shot is less than 5 sec. In particularly dangerous places short-delay detonators should be used. The minimum initial charge is 1500 g in coal and 2000 g in rock.

II. Explosives for coal work (explosifs couche). They may be used only with instantaneous detonators. The minimum initial charge is 500 g in coal and 1000 g in rock.

III. Explosives for rock work (explosifs roche).

IV. Explosives permitted only in places where safety is not an important factor (explosifs à l'usage restreint).

With regard to composition they are divided into:

Dynamites, in which nitroglycerine is the chief ingredient;

Type N explosives, in which ammonium nitrate is the chief ingredient.

The most widely used of these explosives is Grisou-dynamite chlorurée n°15.

TABLE 117

GROUP II. FRENCH EXPLOSIFS COUCHE

Ingredients	Dynamites			N Type
	Grisou-dynamite chlorurée n°1	Grisou-dynamite chlorurée n°a	Minuret	N n°7
Nitroglycerine	20.5	20.5	20	–
DNT	–	–	–	7
Ammonium nitrate	55.5	–	17	76
Ammonium nitrate of low density	–	55.5	–	–
Sodium nitrate	–	–	34	–
Sodium chloride	21.5	21.5	–	15
Ammonium chloride	–	–	22	–
Woodmeal	2.5	2.5	–	2
Urea-resin foam	–	–	7	–
Properties				
Density	1.25	0.90	0.85	1.0
Power (picric acid = 100)	77	77	74	87
Transmission (cm)	10–40	6–20	5–15	2–6
Rate of detonation (m/sec)	3300	2500	2300	3700
Date of approval	1933	1954	1952	1933

The most extensively used of these explosives are grisou-dynamite chlorurée n°1 and N n°7.

TABLE 118

GROUP III. FRENCH EXPLOSIFS ROCHE

Ingredients	Dynamite	N type
	Grisou-dynamite roche à la cellulose ou cellamite	N n°1b grisou-naphthalite roche
Nitroglycerine	30	—
Dinitronaphthalene	—	8.5
Ammonium nitrate	67.5	91.5
Woodmeal	2.5	—
Properties		
Density	1.2	1.0
Power (picric acid = 100)	111	103
Transmission (cm)	10–30	2–6

Grisou-dynamite roche is in relatively wide use for blasting rocks.

TABLE 119

GROUP IV. FRENCH EXPLOSIFS À L'USAGE RESTREINT

Ingredients	Dynamites			N types				
	Dynamite gomme A	Dynamite gomme B Am	Nitro-baronite	N n°31	N n°30	N n°21	N n°0	N n°C
Nitroglycerine	92	60	22.75	—	—	—	—	—
Nitrocellulose	8	3	3	—	—	—	—	—
DNT	—	—	3	—	—	—	—	—
TNT	—	—	—	9.8	10.6	19.7	21.3	—
Dinitronaphthalene	—	—	—	—	—	—	—	12.6
Penthrite	—	—	—	2.5	—	4.9	—	—
Ammonium nitrate	—	31	69	78.5	80.2	75.4	78.7	87.4
Woodmeal	—	6	1.25	—	—	—	—	—
Aluminium	—	—	3	—	—	—	—	—
Bran	—	—	2	9.2	9.2	—	—	—
Properties								
Density	1.60	1.55	1.35	1.0	1.0	1.1	1.0	1.0
Power (picric acid = 100)	155	145	125	138	132	123	120	111
Transmission (cm)	1–15	5–15	5–15	8–12	6–10	8–12	6–10	3–6
Rate of detonation (m/sec)	2000* 7800	2000* 7500	4200	4200	4000	5100	4200	4200

* Depending on the strength of the detonators.

Dynamite gomme B Am is much used. Explosives n° 31, 30, 21 and 0 are very little used in coal mines.

GERMANY

German mining explosives are commonly divided into rock and coal explosives, the word "wetter" being added to their name if safe towards the firedamp ("Schlagendes Wetter" or "Schlagwetter").

The following explosives are for rock:

(1) Blackpowder type;
(2) Dynamites;
(3) Ammonium nitrate type;
(4) Perchlorate type;
(5) Chlorate type.

During the first few years after World War I these explosives were permitted for coal work if there was no methane or dangerous coal-dust in the mine. Soon, however, their use was restricted exclusively to rock work or in safe and opencast mines. Explosives of the blackpowder type (Table 120) were used in Germany even in mines with dangerous coal-dust, which led to a great catastrophe at the Heinitz mine in 1923. From then on the use of these explosives was restricted to rock work only. Some of the most dangerous explosives such as Ammonite 5 (with aluminium) were not permitted for use in rock work in coal mines but only in quarries. The most important types of German rock explosives are summarized in Tables 120 and 121.

TABLE 120

GERMAN EXPLOSIVES OF THE BLACKPOWDER TYPE

Name	Composition, %							
	Potassium nitrate	Sodium nitrate	Charcoal	Brown charcoal	Pitch	Sulphur	Cellulose	Carbon black
Sprengpulver 1	73–77	–	10–15	–	–	8–15	–	–
Sprengpulver 5	70–73	–	5–7	–	–	17–19	5–7	–
Sprengsalpeter 1	0–25	40–75	10–16	–	–	9–15	–	–
Sprengsalpeter 2	0–5	65–75	–	10–16	–	9–15	–	–
Sprengsalpeter 3	0–5	66–76	0–10	–	15–19	9–11	–	–
Sprengsalpeter 4	0–40 and 0–3 $FeSO_4$	25–70	–	–	–	8–12	10–15	8
Sprengsalpeter 5	0–40	30–75	5–7	–	–	17–19	5–7	–

During World War II Gelatine-Donarit 1 was extensively used, as was Dynamite 1 and Ammonite 1. The composition of Gelatine-Donarit 1 was:

Nitroglycol	22%
Nitrocellulose	0.8%
TNT	5%
DNT	6%
Ammonium nitrate	55%
Sodium nitrate	10%

Woodmeal	1%
Pyrites ash	0.2%

The oxygen balance of this explosive is +3.7%, its density 1.53. Its explosive properties are:

Heat of explosion	1030 kcal/kg
Rate of detonation	6150 m/sec
Lead block expansion	380 cm^3
Transmission	10 cm

The coal explosives, safe towards methane and coal-dust, are classified into 3 groups:

(1) Ammonium nitrate;
(2) Semi-gelatinous;
(3) Gelatinous.

Semi-gelatinous and gelatinous explosives are dynamites, adopted for coal work in the presence of methane and coal-dust due to their relatively high contents of "cooling" salts, mostly potassium or sodium chlorides (sometimes in the form of an aqueous solution of calcium nitrate).

Owing to the reduced sensitiveness to detonation of the ammonium nitrate coal explosives in the presence of the chlorides of alkaline metals, at least 4% nitroglycerine is added to these explosives. During World War I, when nitroglycerine was in short supply, it was sometimes replaced on the suggestion of Kast, by an admixture (5–10%) of potassium perchlorate as a sensitizing agent. The composition and properties of German coal explosives are listed in Table 122.

As can be seen, the gelatinous explosives of the Nobelite type, safe in the presence of methane, contain a small amount of calcium nitrate solution. Calcium nitrate was added to Nobelites to reduce the temperature of the flame of explosion. After World War I, small quantities of calcium nitrate in the form of a concentrated aqueous solution were added to the milled nitroglycerine powder (from the post-war surplus) used as a rock explosive. This was done to counteract dustiness; e.g. Nitroglycerinpulver 1 explosive had the following composition:

94-96% of milled nitroglycerine powder
4–6% of 50% calcium nitrate solution

Next Schwanke [78] published a patent in which he suggests the impregnation of woodmeal with a solution of calcium nitrate. The mixture is dried at temperatures from 90 to 130°C and compressed into tubes (resembling those of black blasting powder).

According to Chemisch Technische Reichsanstalt [79] a well-dried (64 hr at a temperature of 120°C) mixture having the composition:

Calcium nitrate	57%
Woodmeal	42%
Pyrites ash	1%

TABLE 121

GERMAN DYNAMITES AND AMMONIUM NITRATE, PERCHLORATE AND CHLORATE EXPLOSIVES

Name	Ammonium nitrate	Sodium nitrate	Potassium perchlorate	Nitroglycerine and nitroglycol	Nitrocellulose	Aromatic nitro compounds	Woodmeal	Various
Dynamite 1	—	25–29	—	61–63	1.5–4	—	6–9	0–2
Dynamite 2	—	25–30	—	59–61	4.5–9	0–4	3–8	—
Dynamite 3	—	44–54	—	34–39	1–6	6–10	1–6	—
Dynamite 5	—	50–74	—	16–20	0.5–2	2–12	1–6	0–12 (sodium chloride)
Ammonite 1 (Donarit 1)	67–85	Potassium nitrate 0–10	—	3–4	—	10–18	1–6	—
Ammonite 2	67–87	0–10	—	—	0–4	12–20	1–6	—
Ammonite 4	70–77	—	5–10	—	—	10–16	1–4	—
Ammonite 5 (not permitted in coal mines)	68–84	0–5	0–5	—	—	5–15	0–4	2–12 (aluminium)
Ammonite 6	82–88	—	—	3–4	—	3–8	1–6	—
		Potassium nitrate						
Perchloratit 2	0–10	0–10	52–75	—	0–4	20–30	1–8	—
Perchloratit 3	35–45	—	30–40	—	—	15–20	3–8	—
	Potassium or sodium chlorate							
Chloratit 2	50–85	—	0–20	—	—	10–20	1–5	3–5 (hydrocarbons, fats or oils)
Chloratit 3 (similar to Miedziankit)	88–91	—	—	—	—	—	0–3	8–12 (liquid hydrocarbons with a minimum ignition temperature of 30°C)

TABLE 122

GERMAN COAL EXPLOSIVES

Name	Composition, %									Explosive properties						
	Ammonium nitrate	TNT	DNT	Nitroglycerine	Nitroglycol	Nitrocellulose	Wood-meal	Sodium or potassium chloride	Calcium nitrate, 50% solution	Oxygen balance %	Heat of explosion kcal/kg	Density	Rate of detonation m/sec	Lead block expansion cm³	Transmission cm	Charge limit
Ammonium nitrate																
Wetter Detonit A (1936)	72	2	—	6	—	—	2	18	—	+10.4	516	1.06	3000	220	8	600
Wetter Detonit B	72	—	2	4	—	—	3	potassium chloride 19	—							800
Wetter Westfalit A	80.5	0.5	0.5	4	—	—	1.5	sodium chloride 13	—							
Semi-gelatinous																
Wetter Baldurit A	50	—	2	—	12 with nitrocellulose		2+ coal-dust 0.5	sodium chloride 33.5	—							
Gelatinous																
Wetter Nobelit A	32	—	2	—	25.4	0.6	1	36.5	2.5	+4.1	640	1.66	5750	205	6	700
Wetter Nobelit B	26.5	—	—	—	29.2	0.8	0.5	40	3	+6.2	570	1.69	5650	185		700
Wetter Wasagit A	30.5	—	—	—	27.8	0.7	0.3+ agar-agar 0.7	39.5+ talc 0.5	—							
Wetter Wasagit B	29.5	—	—	—	30	1	agar-agar 0.5	39	—							
Wetter Arit	29.0	2	—	29		1	—	39	—	3.9	657	1.44	5200	190	6	

gives an expansion in the lead block of 165–175 cm³ when a charge of 29–30 g is used; a charge of 46–47 g of black blasting powder gives a lead block expansion of 145–160 cm³.

The disadvantage of mixtures containing calcium nitrate lies in their high hygroscopicity, though the hygroscopicity of calcium nitrate is lower than that of ammonium nitrate. Hence more modern explosives containing calcium nitrate also contain ammonium nitrate. Such mixtures include Calcinite 1, an explosive safe towards methane, with the following composition:

35.5%	of ammonium nitrate
38%	of calcium nitrate
7.2%	of TNT
4.8%	of DNT
6%	of nitroglycerine
8%	of woodmeal
0.5%	of pyrites ash or dark dye or pigment

The more recent list of Germany rock explosives is given in Table 123 [80].

TABLE 123

Name	Nitroglycerine and nitroglycol with collodion cotton	Ammonium nitrate	Sodium nitrate	Aromatic nitro compounds	Woodmeal	Dye
Dynamit 1 (GFR)	65	–	27	–	8	–
Gelamon 1 (GDR)	32–35	40–45	12–15	4–6	3–6	0–2
Gelamon 2 (GDR)	27–30	47–52	10–13	7–10	2–5	0–1
Ammon Gellit 2 (GFR)	25–29	57–62	–	8–12	1–2	0–2
Ammon Gellit 3 (GFR)	18–23	61–67	10–15	–	1–2	0–1
Gelatine-Donarit (GDR)	20–22	55–57	10–15	9–12	0.5–2	0–0.5
Donarit 1 (GFR and GDR)	4–6	78–81	–	12–16	2–4	0.3–0.5
Donarit 2 (GFR and GDR)	4–6	80–82	–	3–5	8–10	0–0.5

Dekamon and Ammonex (ammonium nitrate with 5–6% Diesel-oil) are also in use in the German Democratic Republic and the German Federal Republic, respectively.

At present, permitted explosives in Germany are divided into 3 classes with regard to their safety in the presence of methane and coal-dust [80, 81].

Class I safety explosives (unsheathed) should fulfil the old safety requirements, namely that 600 g fired unstemmed in a 55 mm dia., 600 mm deep shothole in a steel mortar must not cause ignition of 9% methane–air mixture in five consecutive shots.

Class II safety explosives must fulfil new conditions when tested in an angle-shot mortar: 350 g of explosive fired in this mortar at a distance of 65 cm from the wall and at an angle of 40° must not ignite a 9% methane–air mixture. The charge is increased by increments of 25 g. The charge limit should not give an ignition in any of five consecutive shots.

Class III safety explosives must be safe in a 9% methane–air mixture when fired with the maximum number of cartridges that can be placed in a row in the 2 m long groove of the angle-shot mortar. The experiment starts with 1800 g charge. It is increased by 200 g increments. The charge limit is determined; this should not give any inflammation in five consecutive shots.

From the point of view of composition, German safety explosives are classified as formerly into three groups:

(1) Ammonium nitrate mixtures with a minimum of 4% nitroglycerine and cooling salts,

(2) Semi-gelatinous, with *ca.* 12% nitroglycol or nitroglycerine and nitroglycol and nitrocellulose.

(3) Gelatinous, with 25–30% nitroglycol or nitroglycerine and nitroglycol and nitrocellulose.

They do not differ essentially from those given in Table 122.

Interesting innovations are Wetter-Astralit and Wetter-Carbonit B (West Germany). Their composition is given in Table 124.

TABLE 124

Ingredients	Wetter-Astralit (used as an active sheath)	Wetter-Carbonit B
Nitroglycerine and nitroglycol	10	8.7 (with nitrocellulose)
Ammonium chloride	–	31.0
Potassium nitrate with tetryl	–	59.0
"Guar-meal"	–	0.95
Metal-soap	–	0.05
Aluminium hydroxide	–	0.3
Sodium chloride	65	–
Sodium hydrogen carbonate	25	–
Properties		
Oxygen balance (%)	0	No data available
Density	1.45	
Lead block expansion (cm^3)	22	
Rate of detonation (m/sec)	1750	
Transmision (cm)	15	
Heat of detonation (kcal/kg)	106	

In East Germany explosives trials should be completed by examination in the ballistic mortar (as in Anglo-Saxon countries).

GREAT BRITAIN

In Table 125 a list is given of explosives safe in the presence of methane and coal-dust (Permitted Explosives) used in Great Britain after World War I.

According to Cybulski [82] Polar Viking explosive with a density of 1.01 has the following rates of detonation depending on the test conditions:

unstemmed, charge 22 mm dia.	1930 m/sec
unstemmed, charge 44 mm dia.	2505 m/sec
in a steel tube 31.7/38 mm	3580 m/sec

The mining explosives in Great Britain are known by conventional names based on their composition. They may be divided into the following groups according to their chemical composition:

Dynamites, gelatine dynamites or gelatines—explosives with high contents of nitroglycerine. In the second group collodion cotton is used to form a gel with nitroglycerine.

Gelignites—plastic explosives with a lower content of nitroglycerine than dynamites and formerly including potassium nitrate as an oxidizing agent; this has gradually been superseded by sodium nitrate. The presence of sodium nitrate in explosives is indicated by the letters "N.S.", e.g. N.S. Gelignite.

In all explosives containing ammonium nitrate the names mentioned above are preceded by the prefix "Ammon", e.g. Ammon Gelatine Dynamite, Ammon Gelignite etc.

"Sheathed explosives" with an inert sheath, usually containing sodium hydrogen carbonate, are also employed. After World War II "Eq. S" explosives were introduced. These have already been mentioned (p. 429).

Under The Coal Mines (Explosives) Act 1951, Statutory Instruments No. 1675: 1951 states that all mining explosives used in Great Britain are divided into two groups with regard to their safety in use:

Non-permitted, for ordinary use where special safety precautions are not required (Table 126).

Permitted, which have passed special statutory tests as safety explosives, for use in coal mines, where methane–air mixtures or inflammable coal-dust are likely to be present.

In 1957 the National Coal Board [83] centralized the purchase of permitted explosives in Great Britain and introduced standardization of composition, cartridge sizes etc.

The testing gallery at the Ardeer factory of Imperial Chemical Industries Ltd., which is identical with the Official Home Office Testing Gallery, is shown in Fig. 154 and the testing mortar in Fig. 155.

TABLE 125

BRITISH MINING EXPLOSIVES SUITABLE FOR USE IN THE PRESENCE OF METHANE AND COAL-DUST

Ingredients	Ammonite No. 2	Antifrost Penrhyn Powder	Douglas Powder	Eversoft Tees Powder	Hawkite No. 3	Polar Dynobel	Polar Samsonite No. 3	Polar Saxonite No. 3	Polar Viking
Ammonium nitrate	77.5–80.5	58.5–61.5	70–73	58.5–61.5	58.5–61.5	51–54	–	37–40	71
Sodium nitrate	–	–	–	8–10	–	–	2.5–4.5	–	–
Barium nitrate	–	–	–	–	1–3	–	–	–	–
TNT	–	–	14–16	–	14–16	–	–	–	–
DNT	–	–	–	–	–	0.5–1.5	–	1–3	–
Dinitronaphthalene	4.5–6.5	–	–	–	–	–	–	–	–
Nitroglycerine Nitroglycol	–	7.5–9.5	–	9–11	–	14–16	57–59	24.5–26.5	9.5
Nitrocellulose	–	–	–	–	–	0.25–0.75	2.5–4.5	0.5–1	–
Woodmeal	–	7.5–9.5	–	–	–	4–6	–	–	8
Wheat flour	–	–	–	–	–	–	–	1–3	–
Kaolin	–	–	–	–	–	–	–	4.5–6.5	0.5
Borax	–	–	–	–	–	–	21–23	–	–
Sodium chloride	14–16	20.5–22.5	12.5–14.5	19–21	21.5–23.5	24–26	11.5–13.5	24–26	11
Ammonium phosphate	–	–	–	–	–	–	–	–	–
Moisture	0–2	0–2	0–2	0–2	0–2	0–2	0–2	1–3	–

FIG. 154. Experimental gallery at I.C.I.'s Ardeer factory, according to J. Taylor and Gay [4] (a replica of Home Office Testing Gallery).

The free suspension test and break gallery, described previously, are shown in Figs. 135, 136 and Fig. 140, respectively.

The Buxton Test, often called the Home Office Test, was introduced in 1932 and is at present the British Official Gallery Test.

When testing in the presence of firedamp two series are fired:

(1) Five shots of 8 oz each, unstemmed;

(2) Five shots of 28 oz each, stemmed with a 1 in. clay plug;

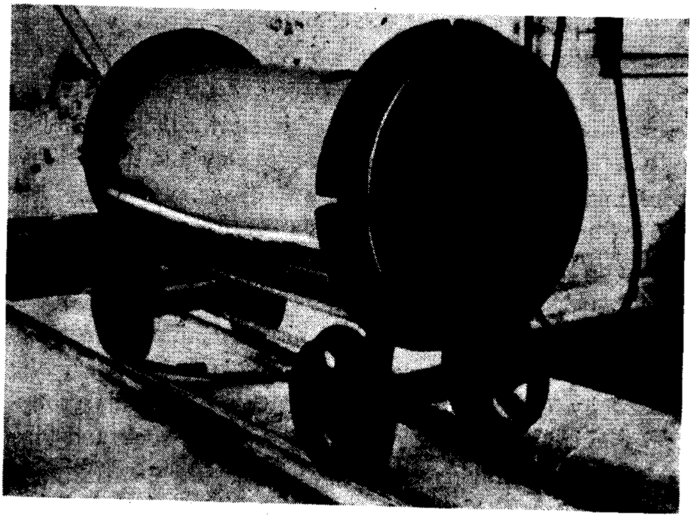

FIG. 155. Gallery mortar at I.C.I.'s Ardeer factory, according to J. Taylor and Gay [4].

For testing behaviour in coal-dust:

(3) Five shots of 28 oz are fired into a coal-dust suspension each stemmed with a 1 in. clay plug.

The permitted maximum shot-firing charge in dangerous mines was made the same for all explosives, i.e. 28 oz in any one shothole, but an exception is made in the case of certain low density explosives, where the maximum permitted charge is 18 oz.

The explosive has to satisfy certain requirements concerning sensitiveness to propagation of detonation.

A new test was introduced in 1953 for new types of permitted explosives: Eq. S. and sheathed explosives (see p. 429). For testing in a gas mixture it specifies:

(1) Five shots, each of 20 oz inversely initiated without stemming. (In sheathed explosives the charge includes the sheath.)

(2) Five shots directly initiated and stemmed with a 1 in. clay plug. For Eq. S. each shot is 36 oz and for sheathed explosives each shot is 28 oz (18 oz for low-density explosives.)

(3) The test applied for sheathed explosives only consists of five shots, each of 8 oz directly initiated, and fired unstemmed. (The weight does not include the sheath.)

For testing in a coal-dust suspension it specifies:

(4) Five shots, each of 20 oz inversely initiated are fired without stemming. (In sheathed explosives the charge includes the sheath.)

No ignition must occur with any shot. Since 1962 a new test was adopted. It involves mortar shots into gas, allowing no more than 13 ignitions out of 26 shots.

Modern Permitted Explosives used in Great Britain are divided into five groups.

I. TNT–Ammonium nitrate powders. These do not contain nitroglycerine. A typical representative of this group is Douglas Powder. Sheathed Douglas Powder was replaced by Unirend, where the equivalent weight of sodium hydrogen carbonate in the sheath was replaced by sodium chloride which was incorporated in the explosive. The safety of freely suspended cartridges is much less than that normally obtained with similar explosives containing nitroglycerine.

According to J. Taylor and Gay [4] this is probably due to a relatively high rate of detonation of mixtures manufactured in an edge-runner mill. The influence of edge-runner mixing on rate of detonation has already been discussed.

Explosives of this group are used for general coal work. They are medium to low water-resistant.

II. Nitroglycerine gelatine explosives. The nitroglycerine content (25% and over) and density (*ca.* 1.5) are high. A typical example is Polar Ajax. Sheathed Polar Ajax was replaced by Unigex and Unigel. Explosives of this group possess the highest power per unit volume. They are used for hard rock and blasting in hard coal or anthracite. They are highly water resistant.

III. Nitroglycerine semi-gelatinous explosives. The nitroglycerine content is *ca.* 15%, and density *ca.* 1.1. They are used for dealing with fairly hard coal. They

TABLE 126

COMPOSITION AND PROPERTIES OF SOME TYPICAL BRITISH NON-PERMITTED EXPLOSIVES (ACCORDING TO J. TAYLOR AND GAY [4])

Ingredients	Explosives					
	Ammonium nitrate powder	Ammonal	Ammon gelatine dynamite	Ammon gelignite	Semi-gelatine	Nitroglycerine powder
Nitroglycerine and nitroglycol	–	–	33.0	25.7	15.0	10.0
TNT	–	12	–	–	–	–
Nitrocellulose	–	–	1.3	0.9	0.3	–
Ammonium nitrate	92	83	59.2	57.8	78.7	80.0
Carbonaceous material	8	–	6.5	5.8	6.8	10.0
Aluminium	–	5	–	–	–	–
Inert ingredients	–	–	–	9.8	–	–
Properties						
Density	1.15	1.1	1.5	1.5	1.2	1.0
Power (as % of that of blasting gelatine	81	88	90	78	82	78
Physical form	powder	powder	rubbery plastic	plastic	cohesive	powder
Blasting uses in:	opencast work large diameter cartridges	quarries dry to damp conditions	hard rock	hard rock	average rock	quarries dry conditions

show medium water resistance. A typical example is Dynobel No. 2. An Eq. S. explosive equivalent to sheathed Dynobel is Unibel.

IV. Nitroglycerine powders. They contain *ca.* 10% nitroglycerine which is not gelatinized. The density is *ca.* 1.0. A typical example is Polar Viking. Its sheathed Eq. S. Explosive is Unifrax.

They are used for work with soft coal. They possess medium-low water resistance.

TABLE 127

COMPOSITION AND PROPERTIES OF SHEATHED PERMITTED EXPLOSIVES AND CORRESPONDING EQ. S. EXPLOSIVES (ACCORDING TO J. TAYLOR AND GAY [4])

Ingredients	Explosives			
	Sheathed Polar Ajax	Unigel	Unigex (initial)	Unigex (modified)
Low-freeze nitroglycerine	27.5–25.5	28.3–26.3	17.7–15.7	18.0–16.0
Nitrocellulose	1.1–0.1	1.4–0.4	1.1–0.1	–
Nitrotoluene	2.8–0.8	2.2–0.2	–	–
TNT	–	–	–	–
Ammonium nitrate	42.0–39.0	32.5–29.5	–	75.4–42.4
Sodium nitrate	–	–	46.5–49.5	–
Sodium chloride	25.5–23.5	30.3–28.3	–	27.7–25.7
Ammonium chloride	–	–	30.0–28.0	–
China clay	3.5–1.5	5.3–3.3	5.0–3.0	4.7–2.7
Woodmeal	–	–	3.0–1.0	3.7–1.7
Wheat flour	–	–	1.5–0.5	1.5–0.5
Oat husk meal	4.5–2.5	2.4–0.4	–	–
Diammonium phosphate	–	1.1–0.1	–	–
Acid Magenta	0.05–0.001	0.1–0.001	–	0.5–0.005
A. S. No. 2	0.01–0.001	0.01–0.001	–	0.01–0.001
Alcohol	0.5–0.0	–	–	–
Calcium sulphate	–	–	–	4.7–2.7
Sodium carboxymethyl cellulose	–	–	1.5–0.5	1.1–0.1
Calcium stearate	–	–	1.1–0.1	1.1–0.1
Barytes	–	5.3–3.3	–	–
Volatile matter	2.0–0.0	2.0–0.0	2.0–0.0	2.0–0.0
Gallery tests	Charge limit	Charge limit	Charge limit	Charge limit
Suspended in 9% methane–air (oz)	10–12		10–12	12
Fired from 47 in. bore mortar into gallery 9% methane–air (oz)	28	24	28	20–28
Density of unsheathed cartridge	1.12	1.7	1.3	1.15
Power (as % of that of blasting gelatine)				
unsheathed	62	44	42	*ca.* 40
sheathed	43	–	–	–

V. Nitroglycerine low-density powder. This is a modification of Group IV. Low density (*ca.* 0.7) is obtained by incorporating vegetable fibre or peat. A low density form of ammonium nitrate and sodium chloride may also be used. A 1 Rounkol is an example of an explosive of this group. Sheathed Rounkol has been replaced by Unikol. They are used for soft coal, for maximum lump production. Their water resistance is the same as that of Group IV.

TABLE 128

COMPOSITION AND PROPERTIES OF SHEATHED PERMITTED EXPLOSIVES AND CORRESPONDING EQ. S. EXPLOSIVES (ACCORDING TO J. TAYLOR AND GAY [4])

Ingredients	Explosives			
	Sheathed Polar Dynobel No. 2	Unibel	Sheathed Douglas Powder	Unirend
Low-freeze nitroglycerine	16.0–14.0	12.4–10.4	–	–
Nitrocellulose	1.1–0.1	1.1–0.1	–	–
Nitrotoluene	2.2–0.2	1.3–0.3	–	–
TNT	–	–	16.0–14.0	12.7–10.7
Ammonium nitrate	64.0–61.0	50.0–47.0	70.5–67.5	52.1–49.1
Sodium chloride	16.2–14.2	36.9–33.9	17.0–15.0	39.2–36.2
China clay	1.25–0.25	–	–	–
Woodmeal	6.0–4.0	4.8–2.8	–	–
Acid Magenta	0.05–0.01	0.05–0.01	0.05–0.01	0.1–0.001
A. S. No. 2	0.01–0.001	0.01–0.001	0.01–0.001	0.01–0.001
Volatile matter	2.0–0.0	2.0–0.0	2.0–0.0	0.5–0.0
Gallery tests	Charge limit	Charge limit		
Suspended in 9% methane–air (oz)	8–12	24–30	–	–
Fired from 47 in. bore mortar into gallery containing 9% methane–air (oz)	30	30	–	–
Density of unsheathed cartridge	1.15	1.15	1.15	1.2
Power (as % of that of blasting gelatine):				
unsheathed	66	42	56	42
sheathed	43	–	43	–

Recently Imperial Chemical Industries Ltd. developed a class of explosives known unofficially as "ultra-safe". The general principle of these compositions is that they contain a higher proportion of cooling salts, ground to a finer size, than is customary with other permitted explosives. They have proved considerably safer than any other permitted explosive.

However, increased safety has been accompanied by considerably reduction in power. In hard material the results were poor, but firing by delay detonators gave

TABLE 129

COMPOSITION AND PROPERTIES OF SHEATHED PERMITTED EXPLOSIVES AND CORRESPONDING EQ. S. EXPLOSIVES (ACCORDING TO J. TAYLOR AND GAY [4])

Ingredients	Explosives			
	Sheathed A 1 Rounkol	Unikol	Sheathed Polar Viking	Unifrax
Low-freeze nitroglycerine	11.0–9.0	11.0–9.0	11.5–9.5	13.2–11.2
Ammonium nitrate	57.0–54.0	37.1–35.1	72.2–69.2	51.4–48.4
Sodium nitrate	11.0–9.0	14.5–12.5	–	–
Sodium chloride	13.0–11.0	31.9–29.9	11.0–9.0	32.0–29.0
Woodmeal	–	–	9.8–7.8	–
Plant fibre	12.5–10.5	11.0–9.0	–	8.2–6.2
Diammonium phosphate	0.5–0.0	0.5–0.0	–	1.1–0.1
Resin	0.5–0.0	0.5–0.0	–	1.1–0.1
Acid Magenta	0.1–0.05	0.1–0.05	0.05–0.01	0.05–0.005
A. S. No. 2	–	–	–	0.01–0.001
Gallery tests	Charge limit	Charge limit	Charge limit	Charge limit
Suspended in 9% methane–air (oz)	8	8	8	8
Fired from 47 in. bore mortar into gallery containing 9% methane–air (oz)	28	28	24	24
Density of unsheathed cartridge	0.7	0.8	0.98	0.8
Power (as % of that of blasting gelatine):				
unsheathed	61	39	66	46
sheathed	38	–	47	–

satisfactory results. Their production and use still seems to be at the experimental stage (Wildgoose [84]). The new classification [98] includes: P-1 ordinary permitteds, P-2 sheathed permitteds, P-3 Eq. S., and P-4 the new class.

HUNGARY

The composition of coal mine explosives manufactured and used in Hungary is given in Tables 130 and 131.

Dynamite explosives of novel type ("Nidin") with nitroglycerine and nitroglycol mixtures seem to be particularly popular.

Ammonium nitrate explosives, both rock and permitted types, do not differ from those generally used in Central Europe.

JAPAN

As in European countries the development of explosives in Japan has had a chequered history. By the end of the nineteenth century dynamites and gelignites were used in mines. In 1899 a dreadful explosion occurred at Toyokuni resulting

TABLE 130

HUNGARIAN DYNAMITE TYPE EXPLOSIVES

Ingredients	Ammon-dinamit	Nidin 33	Nidin 40	Nidin 50	Nidin 60	Nidin 80
Nitroglycerine	30±1	–	–	–	–	–
Nitroglycerine and nitroglycol	–	33±0.5	40±0.5	50±0.5	60±0.5	80±0.5
Collodion cotton	1.25±0.1	1.5±0.2	2±0.2	3.1±0.2	4±0.2	7±0.3
Nitrotoluenes	3.75±0.1	0±0.3	–	–	–	–
TNT	5±0.5	–	–	–	–	–
Woodmeal	1±0.1	2±0.3	4.5±0.3	3.7±0.2	5.5±0.2	2±0.2
Ammonium nitrate	58.8±1.5	57.6±1	51.8±1	42.5±1	31.8±1	–
Sodium nitrate	–	–	–	–	–	10.3±0.5
Magnesium oxide	0.6±0.02	0.3±0.01	0.3±0.01	–	–	–
Aluminium hydroxide	0.6±0.02	0.1±0.01	–	–	0.2±0.02	0.2±0.02
Ferric oxide	–	0.3±0.01	0.3±0.01	0.3±0.01	0.3±0.02	0.3±0.01
Sodium hydrogen carbonate	–	–	0.1±0.01	0.4±0.01	0.2±0.02	0.2±0.01
Glycerol	–	1.2±0.2	–	–	–	–
Dibutylphthalate	–	–	1±0.2	–	–	–
Density	1.4±0.2	1.42±0.2	1.5±0.2	1.48±0.2	1.54±0.2	1.56±0.2
Oxygen balance (%)	+0.38	+1.68	+2.6	+4.8	+1.61	+0.3
Lead block expansion (cm^3)	415±20	390±20	370±20	420±20	420±20	480±20
Transmission of detonation (cm)	7±2	7±2	7±2	7±2	7±2	10±2
Rate of detonation (m/sec)	5600±200	5500±200	5800±200	5900±200	6100±200	6600±200
Heat of detonation (kcal/kg)	1160	1140	1180	1240	1345	1270

in the loss of 210 lives. Further great catastrophes ensued in 1903, 1906 and 1907, the last one (also at Toyokuni) causing the death of 365 people. It was caused by the explosion of coal-dust initiated by the explosion of a methane–air mixture.

This led to the manufacture of Anzen-Bakuyaku ammonium nitrate safety explosives on the lines of European compositions, but later modified to suit the damp climate of Japan (Yamamoto [85]). The production of the following new explosives began in 1913:

Ume (plum bossom) dynamite derived from British Saxonite; Matsu (pine tree) dynamite, a kind of blasting gelatine; Ran (orchid flower), derived from Carbonite and Kaede (maple leaf), a modification of Belgian Grisoutite. The last two were soon withdrawn from use due to their undesirable products of explosion. The composition of the above explosives is tabulated below (Table 132) (according to Yamamoto [85]).

TABLE 131

HUNGARIAN AMMONIUM NITRATE EXPLOSIVES

Ingredients	Paxit 3	Nitrocertuszit
Ammonium nitrate	82 ± 1.5	72 ± 1.5
Di- and trinitrotoluene (1 : 9)	5.4 ± 0.5	4.9 ± 0.5
Nitroglycerine	5 ± 0.5	4 ± 0.5
Collodion cotton	0.1 ± 0.002	1.0 ± 0.002
Woodmeal	3 ± 0.2	0.5 ± 0.1
Charcoal	1.7 ± 0.2	–
Wheat meal	2.5 ± 0.2	1.5 ± 0.2
Sodium chloride	–	17 ± 1
Aluminium hydroxide	0.1 ± 0.02	0.1 ± 0.02
Lubricating oil	0.3 ± 0.02	0.7 ± 0.01
Ferric oxide	0.1 ± 0.002	1.0 ± 0.002
Density	1.04	1.08
Oxygen balance (%)	+4.55	+7.02
Lead block expansion (cm^3)	385 ± 20	235 ± 20
Transmission of detonation (cm)	7	3
Rate of detonation (m/sec)	3950 ± 200	3600 ± 200
Heat of detonation (kcal/kg)	955	603

TABLE 132

JAPANESE MINING EXPLOSIVES

Ingredients	Explosives				
	Anzen Bakuyaku No. 1	Anzen Bakuyaku No. 2	Ume dynamite	Ran dynamite	Kaede dynamite
Nitroglycerine	–	–	58	30	44
Nitrocellulose	–	–	4	–	–
DNT	70	12	–	–	–
Ammonium nitrate	70	88	–	–	–
Potassium nitrate	–	–	17	30	–
Sodium nitrate	28	–	–	–	–
Barium nitrate	–	–	–	–	–
Woodmeal	–	–	7	33	12
Kieselguhr	–	–	–	2	2
Ammonium oxalate	–	–	14	–	–
Sodium sulphate	–	–	–	–	42

Recently rock explosives mainly for use in opencast mining, composed of ammonium nitrate with fuel oil (as invented in the U.S.A. see p. 482) were introduced in Japan.

In 1915 the Regulation for Preventing Coal Mine Explosions was issued. In 1917 an official experimental gallery was erected at Nogata.

After World War I it was found that the mining explosives used till then in Japan did not pass the more stringent tests in the experimental gallery (e.g. those with a 400 g charge). Over the period 1922–24 new, safer explosives appeared which were classed into three groups.

(1) Ume dynamite which was improved by adding a considerable quantity of borax thus making it similar to the British Samsonite.

(2) Shōan dynamite (Shōan is the abbreviation of Shōsan-ammonia, i.e. ammonium nitrate). Shōan dynamite is semi-gelatinous and resembles British Dynobel.

(3) Shōan Bakuyaku, a kind of Ammonite (Table 133).

A new modern experimental gallery (modelled on the one at Buxton in Great Britain) was constructed in 1927 and the explosives which passed the gallery test with the charge of 400 g were designated Permitted Explosives (Kentei Bakuyaku).

During World War II the composition of some explosives was altered due to lack of raw materials such as borax. Ume-dynamite was therefore replaced by Shiraume-dynamite into which ammonium nitrate and sodium chloride were introduced.

After World War II new testing galleries were erected at the factories, facilitating improvements in the manufacture of explosives. The following new types were also introduced. Taketoyo Factory (Japan Oil and Fat Co., Ltd.) introduced new kinds of Toku (special) permitted explosives which contain dried pulverized seaweeds as a cooling agent. Seaweeds contain halogen (Cl, Br, I) and alkali (Na, K) ions (*ca.* 10% by weight) in a finely divided form.

TABLE 133

NEWER JAPANESE MINING EXPLOSIVES

Ingredients	Explosives				
	Ume dynamite A	Shōan dynamite A	Shōan dynamite B	Shōan Bakuyaku A	Shōan Bakuyaku B
Nitroglycerine	49–51	19–21	7–11	4.0–4.5	–
Nitrocellulose	1.5–2.0	0.5–0.7	0.1–0.3	–	–
DNT	–	–	–	6–8	7–9
Ammonium nitrate	–	44–48	62–65	70–72	74–76
Potassium nitrate	8–12	–	–	–	–
Woodmeal	1–3	3–6	4–7	2.5–3.5	1.6–2.5
Starch	–	1.0–2.5	1.5–2.5	–	–
Sodium chloride	–	26–28	19–22	19–21	14–16
Borax	34–36	–	–	–	–
Charge limit (g)	600	800	700	600	500
Ballistic pendulum swing (mm)	54	56	59	56	60

Another improvement consisted of preparing low density explosives (L.D. explosives) which contain ammonium nitrate in the form of bulky, porous crystals

(Vol. II, p. 460). Some of the L.D. explosives can be classified as Eq.S. explosives. S-Shōan dynamite contains powdered talc besides ordinary cooling salts and possesses a high degree of safety.

The following tests for safety in the presence of methane and coal-dust have now been introduced in Japan [86].

Gas test. The charge loaded into the mortar is 400 g. A No. 6 electric detonator is detonated near the mouth of the mortar. The test is repeated ten times without stemming. No ignition should occur.

To investigate new explosives, various charges over 400 g are used. Some of the permitted explosives do not cause any ignition with a charge of up to 800 g. These explosives are classified as:

"no ignition at 500 g"
"no ignition at 600 g" etc.

Coal-dust test. 1500 g coal-dust is uniformly scattered on the four shelves fixed to the walls of the explosion chamber of the gallery, and stirred by the air current produced by a fan. One minute after stopping the fan, the charge is fired. Relative humidity in the explosion chamber is kept below 80%. The test is repeated five times under the same conditions as those in the methane test. No ignition should occur.

Ballistic pendulum test. 100 g charges should give a swing of more than 40 mm to the five tons pendulum.

TABLE 134

JAPANESE PERMITTED GELATINE AND SEMI-GELATINE DYNAMITES

Ingredients	Explosives			
	Shiraume dynamite	Shōan dynamite	Toku Shōan Shin dynamite	L. D. Shōan dynamite
Nitroglycerine (and nitroglycol)	33.0	8.0	8.0	8.0
Nitrocellulose	1.3	0.2	0.3	0.2
Ammonium nitrate	32.8	63.0	69.7	66.6
Woodmeal or starch	2.4	8.0	4.0	8.2
Oil	0.5	–	–	–
Seaweed	–	–	10.0	–
Sodium chloride	30.0	20.8	8.0	17.0
Properties				
Density	1.57	0.95	0.90	0.70
Charge limit (g)	–	–	700	700
Swing of ballistic pendulum (mm)	66	58	–	–
Rate of detonation (m/sec)	6030	3000	–	2200
Lead block expansion (cm^3)	260	250	–	240
Relative power (% of blasting gelatine	63.1	56.0	–	57.0
Gap test: cartridge diameters (32 mm)	7	6	–	3

More stringent tests, not yet approved officially, are applied to new explosives showing a high margin of safety.

The tests listed above resemble those employed in Europe, and consist of:

(1) detonating a charge freely suspended in methane–air atmosphere,

(2) detonating a charge mounted in various ways: plain steel plate, an angle bar, steel rail, an angle-shot mortar, or an angle-shot mortar with a ricochet plate,

(3) detonating a charge suspended in a kraft-paper tube, with or without a slit,

(4) firing from a mortar into the gallery by inverse priming, with an expansion chamber.

The composition and properties of the most typical Japanese explosives are summarized in Tables 134 and 135 (according to Yamamoto [85] and Yokogawa [86]).

TABLE 135

JAPANESE PERMITTED AMMONIUM NITRATE EXPLOSIVES

Ingredients	Explosive			
	Ko Shōan Bakuyaku	Toku Shōan Bakuyaku	L. D. Shōan Bakuyaku E_2	Shin D Shōan Bakuyaku
Ammonium nitrate	64.5	72.8	–	76.2
Low density ammonium nitrate	–	–	73.9	–
Nitroglycerine	5.96	4.7	5.0	–
Nitrocellulose	0.04	0.1	0.1	–
DNT	–	1.92	2.0	–
TNT	2.0	–	–	3.0
Nitronaphthalene	–	1.28	–	–
Dinitronaphthalene	–	–	–	6.0
Woodmeal	–	–	7.0	–
Starch	5.5	6.2	2.0	2.8
Seaweed	4.0	–	–	–
Sodium chloride	18.0	5.0	10.0	5.0
Potassium chloride	–	8.0	–	7.0
Properties				
Density	0.96	0.95	0.70	1.00
Swing of ballistic pendulum	69	–	–	65
Rate of detonation (m/sec)	3010	–	–	4000
Relative power (1% of blasting gelatine	63.8	–	–	67.4
Gap test: cartridge diameters (32 mm)	5	–	–	4

For blasting and quarrying rock blasting blackpowder or ammonal type explosives are used. A typical feature of Japanese explosives is the admission of a few ammonium perchlorate explosives, named Carlits (inventor Carlson). E.g. Midori (green) carlits are permitted for coal mining while Kuro (black) and Murasaki (purple) carlits are rock explosives unsuitable and suitable, respectively, for underground use. Toku Kaba (special brown) carlit—also a rock explosive—is marked by producing non-toxic fumes and is recommended for underground work where ventilation is inadequate.

The composition of some carlits is tabulated below.

TABLE 136

JAPANESE PERCHLORATE EXPLOSIVES

Ingredients	"Carlit" explosives				
	Kuro	Murasaki	Toku Kaba	Midori	
				III GO	V GO
Ammonium perchlorate	72–77	81–86	46–51	5–9	4–9
Ammonium nitrate	–	–	–	58–63	59–64
Sodium nitrate	–	–	33–31	3–7	2–7
Dinitronaphthalene	–	–	8–13	1–5	1–5
TNT	–	–	–	6–11	6–10
Oil	1–5	1–3	1–3	–	–
Woodmeal	4–9	3–7	2–6	1–5	1–6
Ferrosilicon	14–18	8–12	–	–	–
Sodium chloride	–	–	–	11–16	10–15
Properties					
Density	1.05	1.11	1.15	1.05	1.06
Swing of ballistic pendulum (mm)	82	80	70	68	67
Rate of detonation (m/sec)	4400	4400	4000	3000–4300*	3000–4300*
Lead block expansion (cm³)	485	465	320	285	285
Relative power (% of) blasting gelatine	90	90	60	50	50
Gap test: cartridge diameters (32 mm)	5	6	4.5	4.5	4.5

* Different figures according to various sources.

Explosives with a safety sheath are also used. The safety sheath must correspond to Japanese Industrial Standard M 7609 (1952). Two kinds are used: (1) a sheath wrapper into which the cartridge is rolled, and (2) a sheath tube made in the form of a pipe into which a cartridge is inserted.

Safety sheaths undergo gas and coal-dust tests in the gallery in which the sheath covers 450 g of a standard explosive composed of:

Ammonium nitrate	83.7%
Nitroglycerine	8%
Collodion cotton	0.3%
Woodmeal	8.0%

The power of sheathed explosive is tested using the sheath to cover a standard explosive composed of:

Ammonium nitrate	64.8%
Nitroglycerine	8.0%
Collodion cotton	0.2%
Woodmeal	7.0%
Sodium chloride	20.0%

The swing of the ballistic pendulum should be 55 mm or more and the gap distance 3.5 times the diameter or more.

POLAND

After World War I German explosives were used to some extent in Poland. Detonating powder, black blasting powder, dynamites, ammonites and chloratits were used as rock explosives. Chloratit 3 with a composition corresponding to that of Miedziankit of Łaszczyński (p. 278) ranked high among rock explosives. Explosives safe in the presence of methane and coal-dust, such as ammonium nitrate, Lignozyts, Bradyts, semi-gelatinous and gelatinous Bradyts were also employed.

Polish safety explosives for coal mining included Bradyt F. Its composition was developed by T. Urbański [87]:

77.5% of ammonium nitrate
4% of potassium perchlorate
4% of TNT
4% of nitroglycerine
9% of sodium chloride
1.5% of woodmeal

A feature of Bradyt F was the introduction of potassium perchlorate which increased the safety of the explosive by virtue of the potassium chloride formed on explosive decomposition. This proved effective in the experimental gallery. However, after being in use for many years, explosives of this type were withdrawn because of their comparatively high power (lead block expansion *ca.* 280 cm^3) which was considered much too high for coal working, when more stringent regulations were introduced.

There are now four groups of mining explosives in use:

A. Rock explosives, which are divided into 3 subgroups according to their chemical composition:

(1) Ammonium nitrate explosives (ammonites);
(2) Nitroglycerine explosives (dynamites);
(3) Blackpowder.

They may be used only for rock, where there is no coal and no risk of gas. They may also be used, exceptionally, in mines where gas can be present, provided that the content of methane is less than 0.1% at faces situated 50 m away in slightly dusty areas, and 150 m away in very dusty ones.

B. Coal explosives. They may be used only in non gassy coal seams. Their use is limited to strictly determined areas where dangerous coal-dust occurs. They may also be used instead of explosives of group A.

TABLE 137

A. POLISH ROCK EXPLOSIVES (AMONITS)

Ingredients	Explosives				
	Amonit skalny 0	Amonit skalny 2	Amonit skalny 5	Amonit skalny 6	Amonit skalny 8
Ammonium nitrate	90	84.5	83.5	80.9	81
Nitroglycerine	–	–	–	4	4
DNT	–	2	2	–	2
TNT	10	11.8	7.5	8	5.5
Woodmeal	–	1.5	–	2	–
Ferric oxide	–	0.2	–	0.1	–
Aluminium	–	–	7	5	7.5
Lead block expansion (cm^3)	–	330	–	400	400
Rate of detonation (m/sec)	–	3300–3700	–	–	–
Transmission of detonation (cm)	–	4	–	8	8

TABLE 138

A. POLISH ROCK EXPLOSIVES (DYNAMITS)

Ingredients	Explosives						
	Dynamit skalny 1	Dynamit skalny 1G	Dynamit skalny 2GI	Dynamit skalny 3GH waterproof	Dynamit skalny 5A	Dynamit skalny 5G1	Dynamit skalny 5G2
Nitroglycerine	63	45.75	17.1	55	22	17.2	11
Nitroglycol	–	15.25	4.9	15.4	–	4.8	11
Nitrocellulose	2	3	1	4.5	0.8	0.8	1.3
DNT	–	–	2	–	4	4	4
TNT	–	–	5	–	7	7	7
Ammonium nitrate	–	–	68.5	–	50	50	49
Sodium nitrate	27	28	–	–	14.8	14.8	15.6
Potassium nitrate	–	–	–	19.3	–	–	–
Woodmeal	8	8	1	5.7	1	1	1
Ferric oxide	–	0	0.1	0.1	0.1	0.1	0.1
Glycerine	–	–	0.4	–	–	–	–
Glycol	–	–	–	–	0.3	0.3	–
Density	–	1.45	1.45	1.37	1.45	1.45	1.45
Lead block expansion (cm^3)	–	390	330	440	320–350	320–350	320–350
Rate of detonation (m/sec)	–	5000	6100	6100	2400	2500	2500
Transmission of detonation (cm)	–	12	7	8	8	10	10

C. Permitted explosives, which are divided into 2 subgroups according to their chemical composition:

(1) Ammonium nitrate explosives;

(2) Nitroglycerine explosives (permitted dynamites).

Both may be used in coal mining where the content of methane in the air is less than 1%. In more dangerous areas only ammonium nitrate explosives are permitted. Both may also be used wherever A and B explosives are permitted.

D. Permitted special explosives. They may be used in coal mines where the content of methane in the air is less than 1.5% and in mines where particularly sensitive coal-dust occurs.

The explosives used in Poland should not be prone to deflagration (this is discussed on p. 417).

Those permitted for use in gassy and dusty mines should meet the requirements outlined on p. 439.

TABLE 139

B. POLISH COAL EXPLOSIVES (KARBONITS)

Ingredients	Explosives				
	Karbonit węglowy D2	Karbonit węglowy D29	Karbonit węglowy D3	Karbonit węglowy D4	Karbonit węglowy D49
Ammonium nitrate	72	72	68.5	75	75
Nitroglycerine	4	2	4	4	3
Nitroglycol	–	2	–	–	1
DNT	2	2	2.5	1.5	1.5
TNT	4	4	6.5	5.5	5.5
Woodmeal	3	3	3.5	3.5	3.5
Sodium chloride	15	15	15	10.5	10.5
Density	1.03	–	–	–	–
Lead block expansion (cm^3)	255	–	270–285	270	–
Rate of detonation (m/sec)	2600	–	1900–2200	–	–
Transmission of detonation (cm)	5	–	4–5	4–5	–

Since these explosives may be used safely only in mines where little or no gas occurs, Cybulski has recently formulated explosives which may be used in mines where much gas is present and where ordinary permitted explosives are not generally approved. Two such explosives are used: permitted special Metanit A and permitted special Metanit B. They are ammonium nitrate explosives with a very high content of cooling salt (e.g. up to 50% sodium chloride). Permitted special Metanits are very safe in the presence of firedamp and coal-dust. They stand up to the tests described above and do not ignite firedamp even with a 1.5–2 kg charge suspended

TABLE 140

C. POLISH PERMITTED EXPLOSIVES (AMMONIUM NITRATE-TYPE METANITS)

Ingredients	Explosives						
	Metanit powietrzny D2	Metanit powietrzny D29	Metanit powietrzny D2G1	Metanit powietrzny D3	Metanit powietrzny D39	Metanit powietrzny W1	Metanit powietrzny W1G
Ammonium nitrate	63	63	63	67.5	67.5	55	55
Nitroglycerine	4	2	3.64	4	3.12	5	4.55
Nitroglycol	–	2	0.36	–	0.88	–	0.45
DNT	1	1	1	1	1	1	1
TNT	3.5	3.5	3.5	4	4	3.5	3.5
Woodmeal	3.5	3.5	3.5	3.5	3.5	3.5	3.5
Sodium chloride	28	25	25	20	20	27	27
Ammonium chloride	–	–	–	–	–	5	5
Density	1.0	–	–	–	–	1.0	–
Lead block expansion (cm^3)	190–230 (average 210)	–	–	–	–	18–230 (average 205)	–
Rate of detonation (m/sec)	1700	–	–	–	–	1800	–
Transmission of detonation (cm)	3–5	–	–	–	–	3–5	–
Charge limit (g)	500	–	–	–	–	500	

TABLE 141

C. POLISH PERMITTED EXPLOSIVES (DYNAMITE-TYPE BARBARYTS)

Ingredients	Explosives			
	Barbaryt powietrzny A1	Barbaryt powietrzny AG1	Barbaryt powietrzny AG2	
Nitroglycerine	23	17.2	14	
Nitroglycol	–	4.8	8	
Nitrocellulose	0.5	0.5	0.8	
DNT	3	2.5	–	
TNT	–	–	2	
Ammonium nitrate	32.5	30.5	21	
Sodium nitrate	4	4	6	
Sodium chloride	35.5	38	45	
Talc	1	1.5	1	These ingredients are used to "soften" the mixtures and to facilitate mixing and cartridging
Glycerine	–	1	1	
Glycol	0.5	–	–	
Saturated aqueous solution of ammonium nitrate	–	–	1.2	
Density	1.45	1.45	1.45	
Lead block expansion (cm³)	190	190	160	
Rate of detonation (m/sec)	2300	2200	2200	
Transmission of detonation (cm)	4–10	4–10	3–8	

TABLE 142

D. POLISH PERMITTED SPECIAL EXPLOSIVES (SPECIAL METANITS)

Ingredients	Explosives	
	Metanit powietrzny specjalny B	Metanit powietrzny specjalny C
Ammonium nitrate	42.5	47.5
Nitroglycerine	6	6
TNT	3.5	3.5
Woodmeal	3	3
Sodium chloride	45	40
Density	1.0	
Lead block expansion (cm³)	130–170 (average 140)	
Rate of detonation (m/sec)	1600	
Transmission of detonation (cm)	4–6	
Charge limit (g)	1000	

in an explosive mixture of firedamp. Permitted special Metanits correspond to the British Eq. S. explosives.

In Poland, as in all parts of the world, blasting gelatine consisting of 92–94% nitroglycerine and 8–6% dynamite collodion cotton is used for work in hard rock.

U.S.A.

The rock explosives used in the U.S.A. are similar in composition to those used in Europe. In addition to blackpowder (with Chilian saltpetre) dynamites with the composition tabulated below are used extensively. The oldest are the "straight dynamites" designated by percentage expressing the content of nitroglycerine. The latter is not gelatinized but only adsorbed by woodmeal and the like.

TABLE 143

U.S.A. STRAIGHT DYNAMITES

(% EXPRESSES THE RELATIVE POWER OF THE EXPLOSIVE)

	20%	30%	40%	50%	60%
Nitroglycerine	20.2	29.0	39.0	49.0	56.8
Sodium nitrate	59.3	53.3	45.5	34.4	22.6
Sulphur	2.9	2.0	–	–	–
Carbonaceous combustible material (e.g. woodmeal, starch)	15.4	13.7	13.8	14.6	18.2
Antacids (calcium carbonate, zinc oxide etc.)	1.3	1.0	0.8	1.1	1.2
Moisture	0.9	1.0	0.9	0.9	1.2

A mixture with nitroglycol is now generally used instead of pure nitroglycerine. Gelatine dynamites are similar in composition. They contain nitroglycerine (and nitroglycol) and are gelatinized with nitrocellulose.

TABLE 144

U.S.A. GELATINE DYNAMITES (% EXPRESSES THE RELATIVE POWER OF THE EXPLOSIVE)

	20%	30%	40%	50%	60%	80%	100%*
Nitroglycerine (+nitroglycol)	20.2	25.4	32.0	40.1	49.6	65.4	91.0
Nitrocellulose	0.4	0.5	0.7	0.8	1.2	2.6	7.9
Sodium nitrate	60.3	56.4	51.8	45.6	38.9	19.5	–
Sulphur	8.2	6.1	2.2	1.3	–	–	–
Carbonaceous combustible material	8.5	9.4	11.2	10.0	8.3	10.1	–
Antacids	1.5	1.2	1.2	1.2	1.1	1.7	0.8
Moisture	0.9	1.0	0.9	1.0	0.9	0.7	0.1

* 100% gelatine dynamite is usually called "blasting gelatine".

Since the high price of nitroglycerine makes the use of straight or gelatine dynamites rather costly in relation to their power, it may be partly substituted by ammonium nitrate, giving "ammonium dynamites" and "ammonium gelatines" (Tables 145 and 146. The percentage expresses the relative power of the explosive.)

TABLE 145

U.S.A. AMMONIUM DYNAMITES

	20%	30%	40%	50%	60%
Nitroglycerine	12.0	12.6	16.5	16.7	22.5
Ammonium nitrate	11.8	25.1	31.4	43.1	50.3
Sodium nitrate	57.3	46.2	37.5	25.1	15.2
Sulphur	6.7	5.4	3.6	3.4	1.6
Carbonaceous combustibles	10.2	8.8	9.2	10.0	8.6
Antacids	1.2	1.1	1.1	0.8	1.1
Moisture	0.8	0.8	0.7	0.9	0.7

TABLE 146

U.S.A. AMMONIUM GELATINES

	30%	40%	50%	60%	80%
Nitroglycerine	22.9	26.2	29.9	35.5	38.3
Nitrocellulose	0.3	0.4	0.4	0.7	0.9
Ammonium nitrate	4.2	8.0	13.0	20.1	34.7
Sodium nitrate	54.9	49.6	43.0	33.5	19.1
Sulphur	7.2	5.6	3.4	—	—
Carbonaceous combustibles	8.3	8.0	8.0	7.9	4.3
Antacids	0.7	0.8	0.7	0.8	0.9
Moisture	1.5	1.4	1.6	1.7	1.8

It is characteristic of many of these explosives that most of them contain sulphur, unlike European explosives.

As in Europe, ammonium nitrate explosives consist of mixtures of ammonium nitrate with various ingredients:

(1) explosive, such as nitroglycerine or nitrostarch,

(2) combustible, but non-explosive.

In the first group there are mixtures with the following composition:

Ammonium nitrate 40–80%
Nitroglycerine or nitrostarch 3–10%
(less frequently aromatic nitro compounds are employed)

made up with woodmeal and antacid ingredients.

The second group is represented by a mixture of:

Ammonium nitrate	92.5%
DNT	4.0%
Paraffin wax	3.5%

Its rate of detonation varies with the diameter of the cartridge from 3500 to 5000 m/sec. The gap test gives a value of 12–45 cm.

In the U.S.A. in 1956 a new class of rock explosives was tried for the use in opencast mines, based on a patent taken out by Lee and Akre [88]. They are low cost explosives composed of ammonium nitrate and an inexpensive fuel such as carbon black. Rapid development took place in 1957–58 and their use was extended to certain underground operations. Fuel oil was next used as a combustible ingredient (AN–FO) explosives.

AN–FO explosives are usually made in the mine ("do-it-yourself" explosives) thus saving the cost of explosives transport.

Usually prilled ammonium nitrate is used as it facilitates detonation of the explosive and the porosity of the granules help to retain the liquid ingredient.

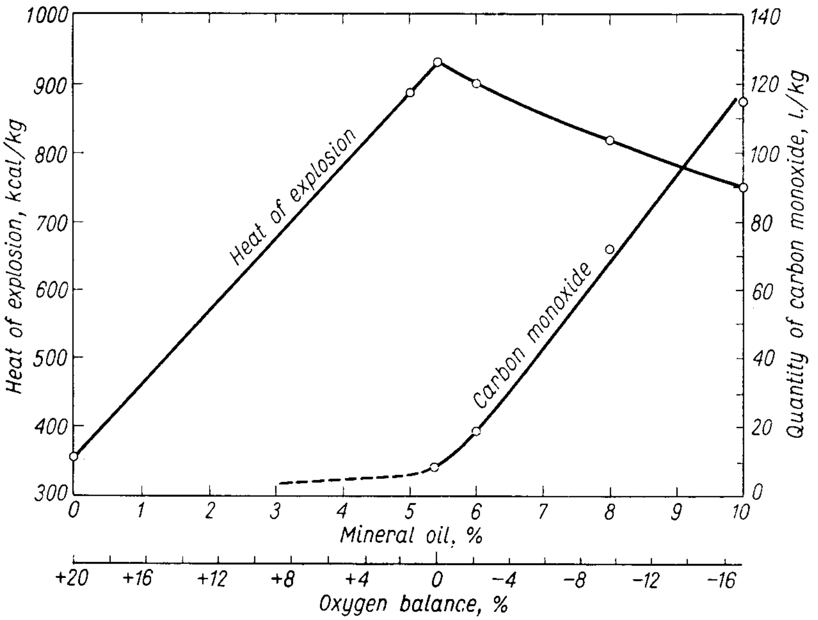

FIG. 156. Explosive properties of ammonium nitrate–mineral oil mixtures as a function of mineral oil content [71].

The ratio of ammonium nitrate to fuel oil giving a zero oxygen balance is *ca.* 95/5. The highest rate of detonation (*ca.* 3300 m/sec using a 100 mm dia. cartridge in a steel tube) is reached when the fuel oil content is 5–6% [89]. The rate of detonation can be raised to 6000 m/sec by detonating a PETN fuse all along the cartridge. Very often initiation is strengthened by adding a cartridge of a readily detonating explosive, e.g. 60% dynamite. The most easily initiated mixture contains 2% of fuel oil. With 10% of fuel oil the ease of detonation is considerably impaired.

Wetterholm [71] gives a summary of explosive properties of ammonium nitrate–mineral oil mixtures as a function of the oil content (Fig. 156). Another diagram by the same author (Fig. 157) gives a minimum charge diameter for stable detonation of ammonium nitrate–Diesel oil mixtures with 5% water or without water, against the composition of the mixtures (Diesel oil content).

It is advisable to use ammonium nitrate with as little as possible of the inert material usually added to ammonium nitrate to prevent its caking. According to the same source, the quantity of inert material should not exceed 0.4% of NH_4NO_3 (fertilizer grade ammonium nitrate usually contains 2–5% added matter).

The diameter of the cartridges used for opencast mining is usually 100 mm, which evidently facilitates detonation.

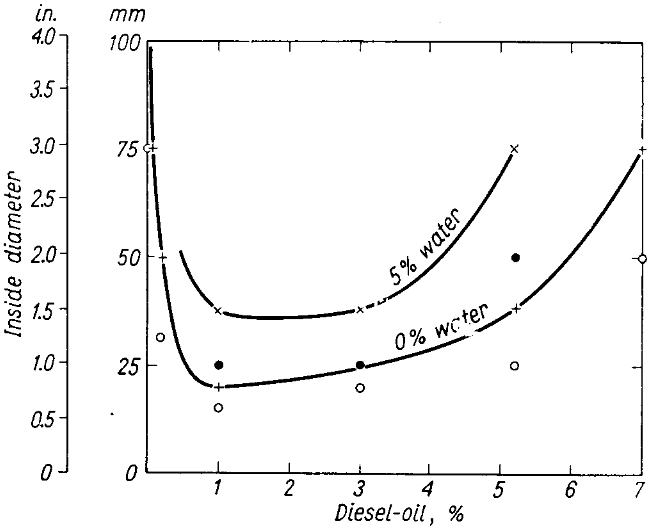

FIG. 157. Minimum charge diameter for stable detonation in iron tubes (wall thickness 3 mm). Initiation by No. 8 detonator and 27 g compressed TNT; 5% water: † — detonation, ● — miss; 0% water: + — detonation, ○ — miss [71].

As mentioned before, preparation of AN–FO explosives is usually carried out where they are to be used. The methods are described later in the chapter on the manufacture of mining explosives.

AN–FO explosives are approximately twice as cheap as the usual ammonium nitrate rock explosives and three times cheaper than dynamites.

They have become very popular not only in the U.S.A. but also in Canada, U.S.S.R., Japan and Sweden.

More information is to be found in papers presented at an International Symposium in Rolla, Missouri [90].

A modified type of AN–FO explosive has been suggested in the U.S.A., made by mixing ammonium nitrate with nitromethane (*ca.* 5%)which is itself explosive. They have a higher rate of detonation than AN–FO (e.g. 3900 m/sec). However, they have not been widely used because of their higher price.

The other types of cheap ammonium nitrate explosives to made on the spot by mixing ammonium nitrate with cheap solid fuel such as carbon black, peat, brown coal etc. were also suggested in the U.S.A. They are much less popular than AN–FO.

Safety explosives

Safety exsplosive are known in the U.S.A. under the name of Permissible Explosives or simply permissibles. As in European countries their chief ingredient is ammonium nitrate. Permissibles may or may not contain nitroglycerine.

According to Taylor and Rinkenbach [91] permissible Monobel contains:

Ammonium nitrate	80%
Nitroglycerine	10%
Combustible and other material	10%

No detailed information is available about the compositions of permissibles, which are kept secret by the producers.

An ammonium nitrate explosive in widespread use is Nitramon (Kirst, Woodbury and McCoy [92]) containing ammonium nitrate with DNT. It is not classified as “permissible”.

U.S.S.R.

Mining explosives are classified in the U.S.S.R. into the following groups:

(I) Approved for opencast works;

(II) Approved for opencast and underground works in non-gassy and non-dusty mines;

(III) Approved for rock work in gassy and dusty mines;

(IV) Approved for rock and coal work in gassy and dusty mines;

(V) Approved for sulphur mines.

Groups (I) and (II) comprise non-permitted explosives, groups (III)–(V)—permitted explosives.

The permitted explosives are tested in experimental galleries in the presence of methane and coal-dust (explosives of groups (III) and (IV)), or in the presence of sulphur dust (explosives of group (V)). The explosives intended for use in oil fields are tested for safety towards petroleum vapours.

The non-permitted explosives and those permitted for works in sulphur and oil fields have cartridges 31–32 mm dia.

The explosives of group (IV) have cartridges 36–37 mm dia. The compressed Ammonits have a cartridge diameter not less than 36 mm.

The composition and properties of some of these explosives are given in Tables 147–153.

Explosives for underground work are not usually allowed to contain more than 0.5% moisture. The requirements for explosives for opencast work are not so stringent and a moisture content of up to 1.5% is approved.

TABLE 147

U.S.S.R. NON-PERMITTED EXPLOSIVES
ROCK EXPLOSIVES FOR OPENCAST WORK (GROUP I)

Ingredients	Explosives	
	Ammonit No. 9	Ammonit No. 10
Ammonium nitrate	87	85
TNT	5	8
Woodmeal or powdered peat, or powdered cottonseed cake or asphaltite	8	7
Density	0.8–0.9	0.85–0.95
Lead block expansion (cm^3)	300–330	300–330
Transmission of detonation (32 mm dia.) cm	2–3	2–4
Rate of detonation (m/sec)	3000–3500	3200–3600
Heat of detonation (kcal/kg)	857	905

TNT in various forms (flakes, pressed or cast charges) is also approved for opencast mining.

TABLE 148

U.S.S.R. ROCK EXPLOSIVES FOR OPENCAST WORK

Ingredients	Explosives				
	Ammonit No. 6			Ammonit No. 7	Dinaftalit No. 1
Ammonium nitrate		79		81	88
TNT		21		14	–
DNT		–		–	12
Powdered bark		–		5	–
	Form				
	Powder	Corned	Pressed		
Density	1.0–11	1.0–1.15	1.25–1.35	1.0–1.1	1.0–1.1
Lead block expansion (cm^3)		360–380		350–370	320–360
Transmission of detonation when dry (cm)	5–10	4–8	5–10	4–6	3–6
when moist (cm)	3–5			2–3	2–5
Rate of detonation (m/sec)	3600–4200	3600–3800	4600–5500	3600–3900	3500–4500
Heat of detonation (kcal/kg)	1028	1028	1028	962	950–976

Dinitronaftalit No. 1 Zh V and No. 1 V and Ammonits No. 6 Zh V and No. 7 Zh V comprising ammonium nitrate partly waterproofed are also used. All these explosives are required to transmit detonation after storage under water at a depth of 1 m for 1 hr. The transmission figures when moist are given above.

Rock Ammonits No. 1, No. 1 Zh V (water-proof) and No. 2 are also used.

They are more powerful than the Ammonits described above and are manufactured in the form of compressed cartridges 36 and 45 mm dia. (250 and 400 g of weight, respectively) or powdered material 60–210 mm dia. The compressed cartridges are supplied together with the initiators fitted with detonator pockets.

The properties of rock Ammonits are given in Table 149.

TABLE 149

U.S.S.R. ROCK AMMONITS

Properties	Ammonits				
	Rock No. 1		Rock No. 1 ZhV		Rock No. 2
	Powder	Pressed	Powder	Pressed	Pressed
Density	0.95–1.1	1.45–1.5	0.95–1.1	1.45–1.51	1.5–1.6
Moisture (max)	0.2		0.2		0.2
Oxygen balance (%)	−2.2		−0.7		+0.13
Lead block expansion (cm³)	450–480		450–480		420–440
Transmission of detonation when dry (cm)	6–10	4–8	7–12	5–9	7–10
after being kept in water (1 m depth) for 1 hr (cm)	4–6	3–8	5–8	5–9	7–10
Rate of detonation (m/sec)	4000–5000	6000–6500	4000–5000	6000–6500	6500–7000
Heat of detonation (kcal/kg)	1270	1270	1290	1290	1166

Another group of very powerful non-permitted explosives are the Ammonals: VA-2, VA-4, VA-8. All are water-proof. They are characterized by the presence of aluminium powder. Their properties are similar to those of rock Ammonits.

The non-permitted explosives include low-freezing 62% dynamite composed of:

Nitroglycerine	37%
Nitrodiglycol (DGDN)	25%
Nitrocellulose	3.5%
Sodium or potassium nitrate	32%
Woodmeal	2.5%

It is manufactured in cartridges with diameters of 31–32 mm (200–250 g) and 44–45 mm (500–550 g).

Its properties are:

Density	1.40–1.45
Lead block expansion	380–420 cm³
Transmission of detonation when dry	8–10 cm
and after being kept in water	(the same)
Rate of detonation	6000–7000 m/sec
Heat of detonation	1200 kcal/kg

Low density Ammonit No. 14 is a relatively new explosive — it was first tested in 1954. It contains low density ammonium nitrate and 7% nitroglycerine. Its properties are:

Density	0.75–0.80
Oxygen balance	−0.2%
Lead block expansion	320–350 cm^3
Transmission of detonation	4–8 cm
Rate of detonation	1800–2500 m/sec
Heat of detonation	900 kcal/kg

Cheap ammonium nitrate–fuel oil explosives (p. 482) are also in use in the U.S.S.R. under the name of Igdanit.

TABLE 150

U.S.S.R. PERMITTED EXPLOSIVES

PERMITTED AMMONITS

Ingredients	Explosives		
	Ammonit No. 8	Ammonit AP-1	Ammonit AP-2
Ammonium nitrate	68	65	68.5
TNT	10	14	15
Woodmeal	–	–	1.5
Powdered bark	2	1.5	–
Sodium chloride	20	19.5	–
Potassium chloride	–	–	15
Density	1.00–1.15	1.00–1.15	1.00–1.15
Lead block expansion (cm^3)	240–280	260–290	285–310
Transmission of detonation (cm)	3–5	4–7	4–8
Rate of detonation (m/sec)	2500–3000	3000–3500	3200–3700
Heat of detonation (kcal/kg)	690	800	855

A water-proof modification of a permitted Ammonit is water-proof Ammonit PZh V-20. It is more easily detonated than Ammonit No. 8. The other water-proof Ammonits are: AP-4 ZhV and AP-5 ZhV. They are used in damp conditions.

The permitted explosives Pobedits (Pobeda = Victory) are widely used: rock and coal Pobedit PU-2; water-proof Pobedit VP-1; Pobedit No. 6; water-proof Pobedit VP-2.

All are of low nitroglycerine content (5–9%).

Their properties are given in Table 151.

Pobedit P-8 is an ammonium nitrate sheathed explosive with 7% nitroglycerine. The sheath is composed of potassium chloride powder.

The properties of this explosive are:

Density	1.0–1.15
Lead block expansion	285–310 cm^3
Rate of detonation	3500–4000 m/sec

TABLE 151

POBEDITS

Properties	Pobedit PU-2	Pobedit VP-1	Pobedit No. 6	Pobedit VP-2
Density	1.00–1.10	1.15–1.30	1.00–1.10	1.15–1.30
Oxygen balance (%)	−0.53	+0.51	−0.14	+0.3
Lead block expansion (cm^3)	250–280	265–290	285–310	320–340
Transmission of detonation				
when dry (cm)	5–10	6–20	5–15	6–20
after storage in water (cm)	–	5–15	–	5–14
Rate of detonation (m/sec)	2800–3500	3200–3700	3500–4000	3800–4300
Heat of detonation (kcal/kg)	800	813	870	910

The explosive part of the cartridge has 28 ± 0.5 mm dia., and a weight of 132 ± 7 g. With the sheath its diameter is 36 ± 1 mm and weight 225 ± 15 g.

The transmission of the detonation figure for the complete cartridge is 4–7 cm.

Pobedit P-8 is tested not only in a steel mortar in a gallery, but also suspended free in methane atmosphere and in the presence of coal-dust.

Ammonit No. 15 is a low density permitted explosive, containing 8% nitroglycerine. Its properties are:

Density	0.7–0.8
Oxygen balance	−0.03%
Lead block expansion	240–260 cm^3
Transmission of detonation	3–6 cm
Rate of detonation	1700–2300 m/sec
Heat of detonation	800 kcal/kg

It is supplied in two dimensions:

31–32 mm dia., weight 150 g
and 36–37 mm dia., weight 200 g

TABLE 152

U.S.S.R. SULPHUR AMMONITS

Properties	Sulphur Ammonit No. 1	Sulphur Ammonit No. 2
Density	0.95–1.05	0.95–1.05
Oxygen balance (%)	−0.8	−0.5
Lead block expansion (cm^3)	200–220	150–170
Transmission of detonation (cm)	5–8	4–7
Rate of detonation (m/sec)	2500–3000	2000–2500
Heat of detonation (kcal/kg)	720	600

Permitted explosives for various purposes

In sulphur mines. Sulphur Ammonits No. 1 and No. 2 are used. They contain 5% nitroglycerine. They are recommended when the sulphur content of an ore is lower and higher than 20%, respectively.

Their properties are given in Table 152.

In oil fields. Petroleum Ammonits are ammonium nitrate explosives with a low (4–9%) nitroglycerine content. Their properties are given in Table 153.

TABLE 153

U.S.S.R. PETROLEUM AMMONITS

Properties	Neftyanoy Ammonit No. 1	Neftyanoy Ammonit No. 2	Water-proof neftyanoy Ammonit No. 3
Density	0.95–1.05	0.95–1.05	1.1–1.3
Oxygen balance (%)	−0.2	+0.1	−0.3
Lead block expansion (cm³)	220–230	230–250	220–240
Transmission of detonation when dry (cm)	5–8	5–10	3–7
after storage in water at a depth of 40 cm for 1 hr (cm)	–	–	2–5
Rate of detonation (m/sec)	2000–2500	2500–3200	2500–3200
Heat of detonation (kcal/kg)	634	690	700

Petroleum ammonits No. 1 and No. 2 are recommended where there is a danger of petroleum vapours or of petroleum plus methane.

COMBINED BLASTING AND WATER INFUSION FOR COAL BREAKING

As a further stage in the effort to reduce the risk involved in the use of explosives in mines, an old idea was recently reintroduced. It was decided that safety in use may be increased by surrounding the charge with a layer of water (e.g. in a paper container, circular in cross-section). As long ago as 1876 this method suggested by MacNab [24] was recognized as effective for diminishing the danger of gas ignitions.

Water infusion applied at high pressure in holes drilled in the coal face was used to mine coal in some Westphalian collieries in 1914, and in some mines in South Wales in 1942.

Besides being safe in themselves, these methods considerably reduce coal-dust concentrations.

Demelenne [93] experimented in Belgium with small charges of explosives, using the gas pressure that developed as the motive force to obtain the desired infusion. A considerable reduction of coal-dust (by *ca.* 40%) was claimed.

The new technique of pulsed infusion shot-firing was then introduced in Great Britain. It required the development of highly water-proof explosives. Polar Ajax was originally suggested, but it was only capable of withstanding a water pressure of *ca.* 20 lb/in^2 for a few hours, whereas ability to withstand up to 800 lb/in^2 water pressure was required. Earlier work had shown that barium sulphate increases the sensitiveness of nitroglycerine gelatine explosives under high water pressure. This property had been applied in geophysical investigation and existing explosives for deep seismic prospecting therefore provided a basis for the new development.

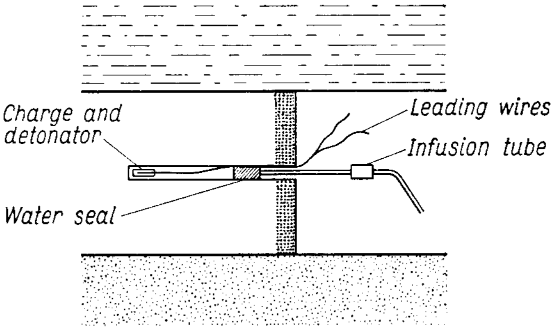

FIG. 158. Blasting coal, employing combined blasting-water infusion technique, according to J. Taylor and Gay [4].

Eventually a new explosive Hydrobel was developed by Haslam, Davidson and Hancock [94] (Table 154). Submarine-type electrical detonators for short holes (Fig. 158) and Cordtex detonating fuse for long (up to 150 ft) holes are used to

TABLE 154

HYDROBEL

Nitroglycerine and nitroglycol	40.9–37.9
Nitrocellulose	3.0–1.0
Ammonium nitrate	21.0–19.0
Sodium chloride	28.1–26.1
Barytes	10.7–8.7
Chalk	1.0–0.1
Diammonium phosphate	0.8–0.1
Woodmeal	1.6–0.6
Acid Magenta	0.05–0.001
A. S. No. 2 (optional)	0.01–0.001
Volatile matter	2.0–0.0
Density	1.7
Power (in % of blasting gelatine)	48
Rate of detonation of unconfined explosive in 1¼ in. diameter cartridges (m/sec)	6000

detonate the charge. A Cordtex detonating fuse consists of a high-explosive core surrounded by textile layers made water-proof by an outer plastic. To increase safety, the fuse is coated with a balata composition, in which one sixth of the weight consists of finely ground cryolite.

The new technique of mining coal is based on the introduction of water at a pressure ranging from 100 to 400 lb per sq. in. The water is forced by the infusion pump into the shothole which is loaded with Hydrobel explosive and sealed with stemming.

This technique of coal-getting by combined blasting and water infusion eliminates the need for undercutting. It is known that undercutting is largely responsible for the formation of coal-dust. The hazard is considerably reduced by wetting the coal-dust before it is suspended in the air. In addition the toxicity of the fumes is reduced as some of the toxic constituents, such as N_2O_4, are soluble in water.

LIQUID OXYGEN EXPLOSIVES (OXYLIQUITS)

Oxyliquits are explosives consisting of combustible materials impregnated with liquid oxygen. They were invented by Linde [95] and were originally prepared by impregnating such substances as sawdust, carbon black etc. with liquid air. These mixtures, however, were hard to detonate since, as appeared later, they were incapable of adsorbing a sufficient amount of the liquid and so did not contain enough oxygen. Substances with highly adsorptive properties then began to be added, for instance activated coal, or incombustible adsorbents such as kieselguhr.

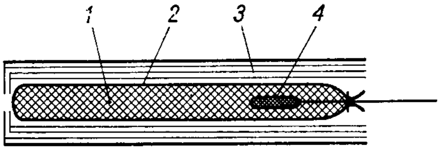

FIG. 159. Section of the oxyliquit charge.

The disadvantage of employing liquid air is that it usually contains less than 33% oxygen which is not always enough for complete combustion. Moreover the composition of liquid air undergoes continuous alteration on storage. Liquid air has therefore been superseded by 98% liquid oxygen.

A charge of oxyliquit is shown in longitudinal section in Fig. 159. Adsorbent combustible mixture (*1*) is enclosed in a cotton or paper bag (*2*) 30–50 mm dia. (the use of smaller diameters is not recommended since the charge looses rapidly oxygen by evaporation). The bag with the combustible mixture is placed within a double-walled envelope (*3*) made of corrugated and ordinary cardboard which stiffens the cartridge and constitutes a thermal insulator. The outer diameter of the cartridge plus envelope is 35–60 mm, its length—300 mm. In ignition cartridges the inner bag includes a detonator with electric fuse (*4*). Safety fuses cannot be fired in coal mines for fear of premature explosion which may result from the sparking the safety fuse or ignition of the molten pitch insulating the braid of the safety fuse.

Before firing the prepared cartridges are dipped in a Dewar vessel containing liquid oxygen. The cartridge absorbs the oxygen and gradually sink in it, after which the explosive charge is ready for use (impregnation lasts for about 20 min). The prepared cartridges are placed into the shothole (one of them should have a detonator with an electric fuse) and further procedure is then routine. The shot must not be fired later than 10–15 min (depending on the composition of the cartridge) after the cartridges have been taken out of oxygen.

The efficiency of oxyliquits depends on:

(1) the composition of the absorbent (combustible);

(2) the quantity of oxygen adsorbed;

(3) the time from the moment of impregnation with oxygen to the moment of shotfiring;

(4) the losses due to the evaporation of oxygen.

The composition of the combustible mass. The power of oxyliquits depends on the composition of the absorbent. D oxyliquits are very strong explosives with a performance resembling that of dynamite; A oxyliquits have a performance equal to that of ammonium nitrate explosives; P oxyliquits have a relatively slow action similar to blackpowder.

Kast and Haid [96] report figures characteristic of the absorbent on the explosive properties of some oxyliquits (Table 155).

TABLE 155

D OXYLIQUITS

Properties	Absorbent				
	Karben*	Carbon black	Cork dust	Woodmeal	Peat
Density of prepared explosive	1.04	0.72	0.63	0.82	0.53
Heat of explosion (kcal/kg)	2180	1995	1660	1535	1670
Gas volume (V_0, l./kg)	615	535	700	700	700
Calculated temperature of explosion (°C)	5750	6500	4195	4095	4385
Lead block expansion (cm^3)	535	530	510	450	485
Rate of detonation in the open, m/sec)	4760	4680	3300	3610	3275

* Alias "Kupren" – absorbent obtained by the polymerization of acetylene on a copper catalyst at temperatures 200–280°C.

The explosives enumerated in Table 155 are very powerful type D oxyliquits. Their power may be reduced by the addition of inert cooling substances, e.g. sodium chloride, kieselguhr etc. An explosive is then obtained with a performance similar to that of coal explosives, e.g.:

Petrol	12%
Carbon black	63%
Kieselguhr	25%

This oxyliquit has a rate of detonation of 3430 m/sec.

If the power of oxyliquits is to be increased to obtain rock explosives, this may be achieved by the addition of aluminium.

A disadvantage of mixtures of liquid oxygen with combustible substances lies in their high sensitiveness to impact and friction. This property depends largely on the composition of the combustible material used. Oxyliquits containing sawdust show the lowest sensitiveness, while those containing hydrocarbons (e.g. naphthalene) pitch or petrol are more sensitive.

Explosives with liquid oxygen were used in Poland in some Upper Silesian mines during the inter-war period. To increase their safety, cartridges of Badowski's invention composed of 35% woodmeal and 65% sodium chloride were used. A cylindrical piece of ice was also introduced into the bottom of the shothole. A similar extinguisher was inserted at the mouth of the shothole. This did in fact give greater safety against coal-dust.

The amount of oxygen absorbed. The effect of the oxygen content absorbed by the combustible mass in the liquid phase on the explosive power is represented in Table 156.

TABLE 156

Oxygen content in liquid phase %	Lead block expansion cm^3
35	no explosion
40	9
50	30
55	147
98	384

The amount of oxygen adsorbed by various combustible substances and, for the sake of comparison, that required for the combustion of the substance is shown in Table 157.

TABLE 157

Combustible substance	Amount of oxygen adsorbed by 1 g of the substance, g	Amount of oxygen required for combustion of 1 g to CO_2+H_2O, g
Sawdust	2.4	1.37
Cotton	3.0	1.18
Carbon black	2.3	2.7
Charcoal	2.67	2.67
Kieselguhr	3.0	

Losses due to the evaporation of oxygen. The time which elapses from the moment of removing the cartridge from the Dewar vessel up to shotfiring affects the explosive considerably, since it weakens with the loss of oxygen. In addition a considerable amount of toxic carbon monoxide may be evolved on explosion. The greatest possible efforts should be made, therefore, to minimize the evaporation of oxygen. This begins immediately after removal of the cartridge from the liquid. The rate of evaporation depends on the type of adsorbent used and the insulation. The larger the specific surface of the adsorbent, the less evaporation occurs; e.g. charcoal and carbon black, with a very large surface, give an explosive which loses oxygen, and thus explosive power, very slowly. On the other hand, sawdust loses oxygen much more quickly, since the oxygen is rather weakly adsorbed. The rate of evaporation of oxygen depends also on the diameter of the cartridges and the stemming.

In the U.S.S.R. an absorbent of milled cane is used since it has very good adsorptive properties. The relationship between the rate of evaporation of oxygen from the cane cartridges, their diameter, and type of stemming is shown in Table 158.

TABLE 158

Diameter of charge and mode of stemming	Time of evaporation to give combustion	
	to CO_2	to CO
32 mm in the open	10 min	18 min
180 mm in the open	42 min	70 min
180 mm in the shothole	4 hr	7 hr

Charges of oxyliquit, 33 mm dia., containing carbon black (density about 0.3) give complete combustion to CO_2 within 5 min after removal from liquid oxygen and have a power 15% higher than that of standard dynamite; in 25 min their strength is 35% lower than that of dynamite.

A mixture of kieselguhr and petrol, in the ratio of 60 to 40, has 10% less power than dynamite, with a rate of detonation of approximately 3000 m/sec; after 45 min its power falls to 45% that of dynamite.

Loss of oxygen by evaporation does not particularly affect the rate of detonation of an explosive. For charcoal oxyliquit, for instance (Kast and Haid [96]), the following figures have been found:

After	Rate of detonation
3 min	4930 m/sec
6 min	4670–4750 m/sec
10 min	4780 m/sec

The fall in the rate of detonation is insignificant.

Despite the drawback arising from the need for haste, the loss of power caused by the evaporation of oxygen has a great advantage. In the event of a misfire, the unfired charge loses its explosive power in a few hours, so that a shothole may be drilled again in the same place.

The other advantage of oxyliquits lies in their safety during transport: the explosives are manufactured on the spot, just before the use. One of their most serious drawbacks, as mentioned before, lies in the fact that an explosive which has lost too much oxygen, may give rise to a considerable amount of toxic carbon monoxide on detonation.

SOME OTHER PEACEFUL APPLICATIONS OF EXPLOSIVES

Among various applications of explosives to engineering work such as tunnel and road building, water front, harbour and river regulation etc., explosive working of metals was recently added to the list of peaceful uses of explosives [97].

Another application is in geological investigation by seismographic methods, much used in the search for underground sources of liquids, such as oil.

These applications, which form the subject matter of specialist books, will not be discussed in the present work.

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CHAPTER VI

THE MANUFACTURE OF MINING EXPLOSIVES

THE MANUFACTURE OF AMMONIUM NITRATE EXPLOSIVES

Raw materials

THE properties and purity standards of ammonium nitrate — a chief ingredient of these mixtures—have been discussed earlier (p. 463, Vol. II), and so has the purity of potassium nitrate (p. 343). The other ingredients should meet the requirements of high purity demanded in the commercial products.

The quality of an explosive depends to a great extent on the uniformity of the mixture, i.e. on the milling of the ingredients and on their mixing. The careful preparation of ingredients is therefore an essential requirement. Mills of the disintegrator type are best suited for this purpose (Excelsior, Perplex etc.). Not infrequently the ingredients are dried before milling. The drying of non-explosive ingredients, such as all salts other than ammonium nitrate, is fairly straightforward. It is usually carried out in ordinary shelf driers heated from below by warm air convection. Since the salts become lumpy on drying, they are then screened, if necessary, being crushed between the rollers before screening. To prevent hygroscopic salts (sodium nitrate, sodium chloride) from absorbing moisture, a temperature of 25–30°C is maintained in the premises.

More recently driers based on the fluid-bed principle were introduced. Figures 160 and 161 give diagrammatic presentations of sodium nitrate and woodmeal fluid-bed driers.

Ammonium nitrate may also be dried in the same driers. Since, however, very large quantities of this substance are processed in factories, the use of a high output drier is necessary. The very low sensitiveness of ammonium nitrate to friction and impact permits the use of steel machinery.

Various drum type driers are very popular. A typical example with a stationary drum is shown in Fig. 162. In this arrangement the substance passes through the mill to the elevating conveyer which carries it to the end of the drier. A screw conveyer inside the drum moves the substance through the drier. Hot air (60–80°C) is sucked from above by a fan. The dried substance is poured into the screening

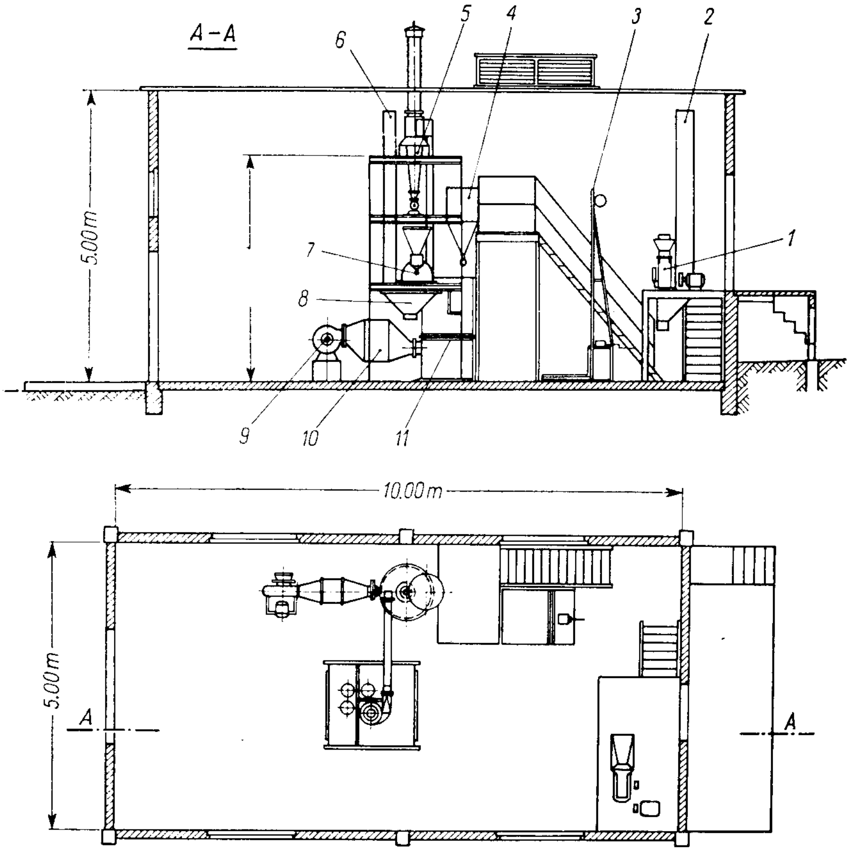


FIG. 160. Sodium nitrate fluid-bed drier (Courtesy H. Orth G.m.b.H., Ludwigshafen-Oggersheim, G.F.R.); *1*—filter tube, *2*—mill, *3*—lift, *4*—feeder, *5*—outlet cyclone, *6*—filter tube, *7*—end-mill, *8*—discharge funnel, *9*—ventilator, *10*—calorifuge, *11*—fluid-bed drier.

drum. Lumps formed during drying are recycled to the mill and drier. Rotary driers (Fig. 163) and shelf driers of the Schielde type are also in use (Vol. II).

More modern fluid bed driers are now much in use. A diagrammatic presentation of such a drier is given in Fig. 164 and the general view in Fig. 165.

Mixing of ingredients

There are various methods of mixing. They depend on the traditions of a given factory or country and on the ingredients included in the mixture. Explosives containing nitroglycerine are mixed differently from those without nitroglycerine. Nitroglycerine explosives are usually mixed in two stages: first all the ingredients with the exception of nitroglycerine are mixed together and then the nitroglycerine is added in a different mixer.

Mixing of ingredients without nitroglycerine. These may be mixed either cold or hot. In the cold, the ingredients previously dried and milled either in iron drums with wooden balls or in kneaders of the Werner–Pfleiderer type (Figs. 206, 207, 208) are mixed for about 1 hr. In France an edge runner is commonly used of a construction similar to that for the manufacture of blackpowder (Fig. 94). In the edge runner the explosive is not only mixed and milled but also crushed. It may thus reach a higher density which is particularly advantageous when intended for military purposes (making Amatol 80/20 for shell filling). Mixing in an edge runner makes it possible to obtain a higher rate of detonation which is of importance for rock explosives and ammonium nitrate mixtures intended for military purposes.

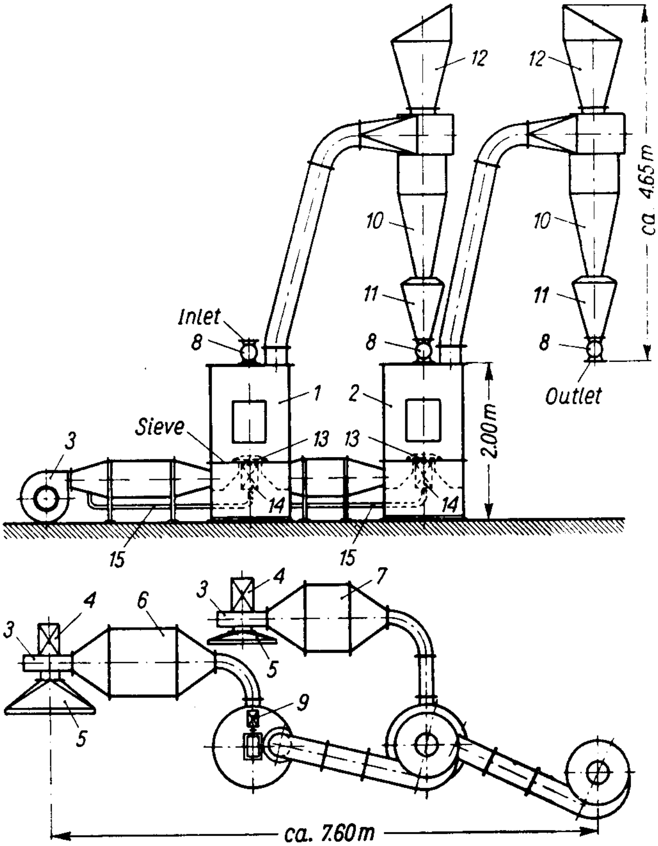


FIG. 161. Woodmeal fluid-bed drier, 200 kg/hr (Courtesy H. Orth G.m.b.H., Ludwigshafen-Oggersheim, G.F.R.); *1*—pre-drier, *2*—final drier, *3*—blowing engine, *4, 9, 14*—electric motors, *5*—air filter, *6*—air heater for the pre-drier, *7*—air heater for the final drier, 8—feeding and discharging valves, 10 and *11*—cyclones, *12*—air stream breakers *13*—air screw wheels, *15*—air coolers.

Schneiderite, for instance, consisting of a mixture of ammonium nitrate and **dinitronaphthalene, is mixed in an edge runner in batches of 60 kg. The mixing**

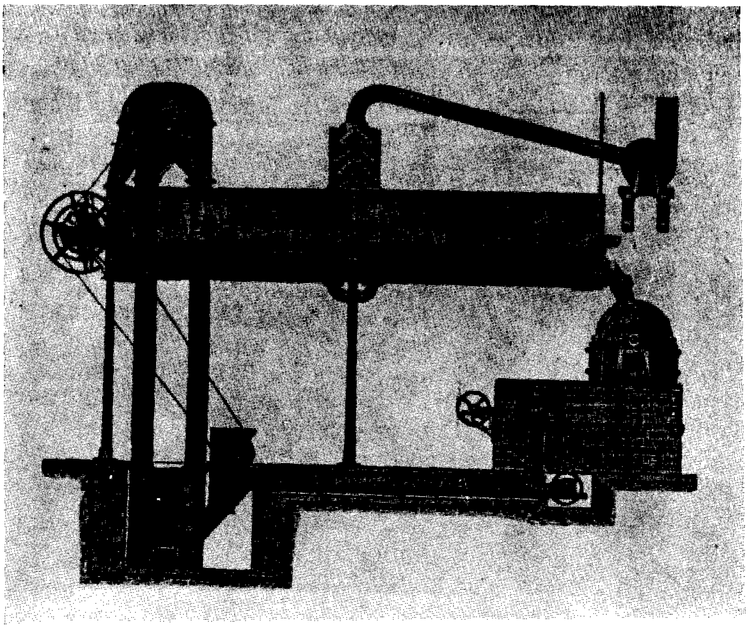


FIG. 162. Schematic view of a drier with a stationary drum.

lasts for about 40 min. Since it is necessary to protect ammonium nitrate against the absorption of atmosphere moisture a temperature of approximately 30°C must be maintained and the material must be dried to about 0.4% moisture content. Two edge runners can manufacture 1500 kg of Schneiderite in 24 hr. If the explosive is to be used for filling shells, and thus requires a considerable density, the charge from the edge runner is sifted through a 5-mm mesh sieve; coarse grains are pressed

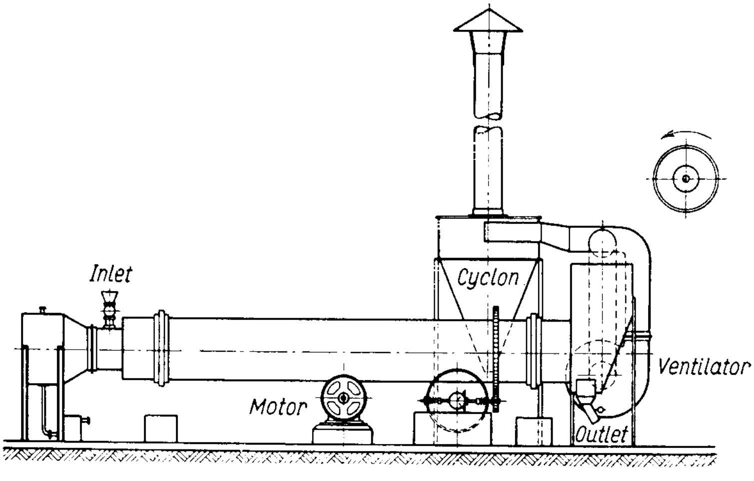


FIG. 163. Schematic view of a rotary drier.

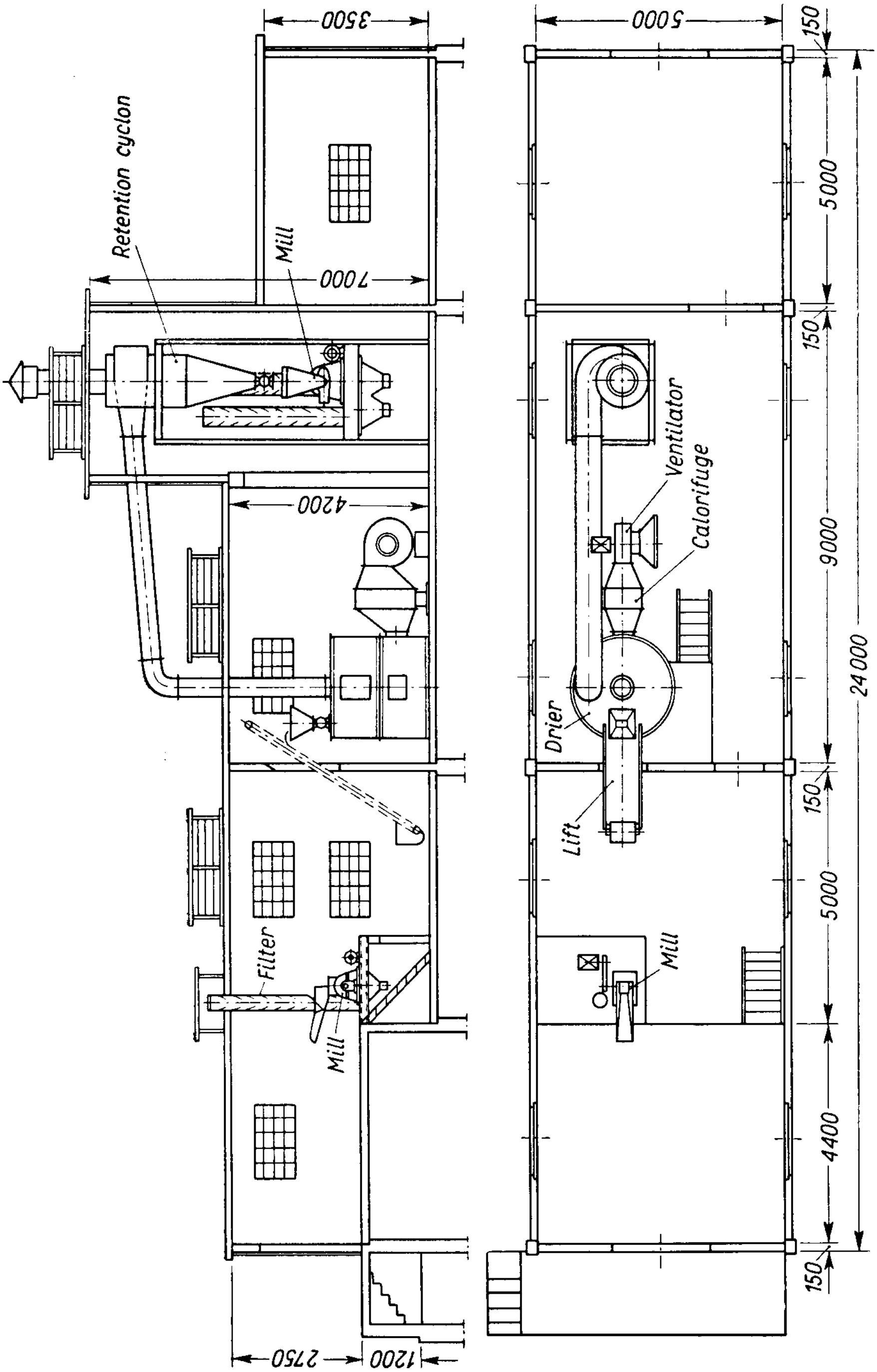


FIG. 164. Diagram of a fluid-bed drier for ammonium nitrate (Courtesy H. Orth G.m.b.H., Ludwigshafen-Oggersheim, G.F.R.).

in a hydraulic press (60 kg/cm^2) while fine grains, together with dust, are recycled to the edge runner. The layer of explosive to be pressed must be such as to achieve a thickness of 6.5 mm by the end of the operation.

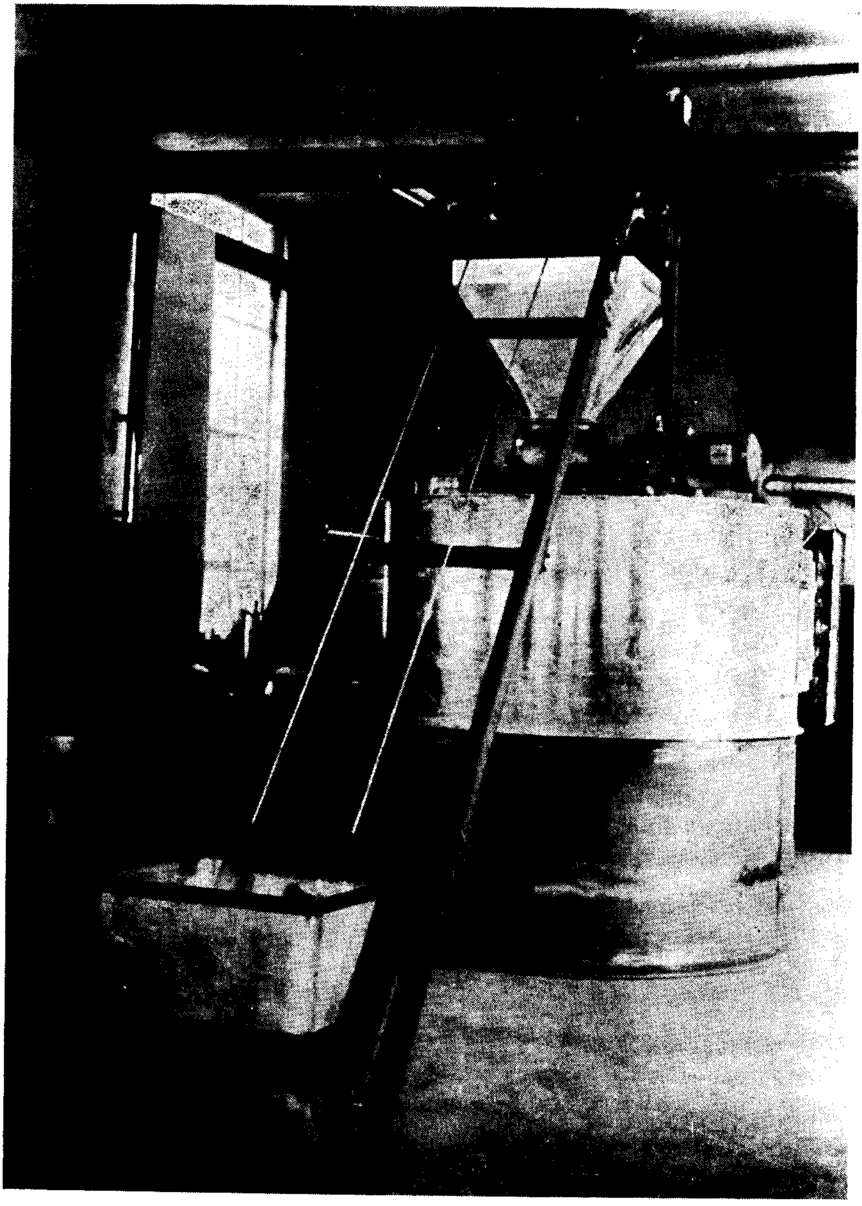


FIG. 165. General view of a fluid-bed drier for ammonium nitrate (Courtesy H. Orth G.m.b.H., Ludwigshafen-Oggersheim, G.F.R.)

The pressed cakes of explosive are broken up in a corning mill, the construction of which is shown in Fig. 166. After passing through breaking rollers (*1*) and (*2*) the material passes through a leather sleeve to sieves (*3*) (13 mm mesh) and (*4*) (6 mm mesh). Material with grains of the correct size constitutes 50% of the whole. It is collected in receiver (*5*). The dust (from container (*6*)) and coarse grains (from vessel (*7*)) are recycled to the edge runner.

Schneiderite so obtained has a specific gravity of 1.5–1.6, number of grains per kilogramme 1500–2000 and a rate of detonation approximately 5400 m/sec.

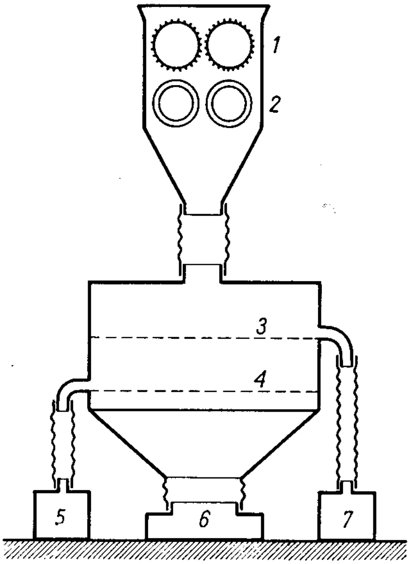


FIG. 166. Schematic view of a corning mill for ammonium nitrate explosive.

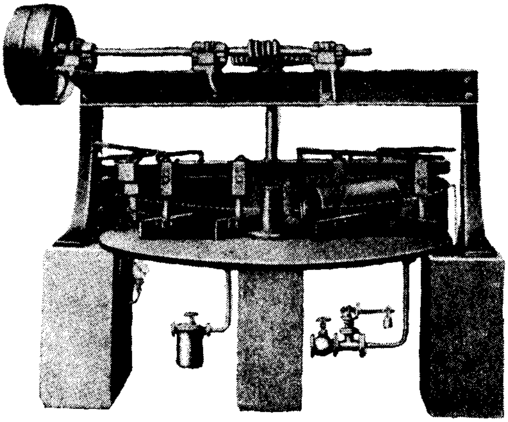


FIG. 167. Disk mixer.

Hot mixing may be conducted either in kneaders of the Werner–Pfleiderer type with a heating jacket or in disk mixers (Fig. 167). These mixers consist of a round plate of copper, brass or bronze, approximately 2 mm dia., with beaded edges, which is heated with hot water to a temperature of 80–90°C. The material is mixed with bronze blades and kneaded with a bronze roller.

The operation in kneaders or disk mixers begins with the mixing of all the ingredients, except those which sensitize the mixture to impact and friction, e.g. potassium or ammonium perchlorates. Molten TNT or another nitro compound (DNT) is then poured in, the whole is carefully stirred and cooled while stirring. Only when the temperature has fallen to 40–50°C, are the perchlorates added. When the material is cooled down to a temperature of 25–30°C, it is stirred for a certain time, then unloaded and transported in sheet metal or wooden boxes to the storeroom.

It usually takes a long time (3–4 hr) to cool a mixture, especially when operating the kneaders, so that some factories have adopted a more economic method of mixing by preparing separately, hot, a mixture of ammonium nitrate (two parts) with TNT (one part), called "triamon".

A certain amount of this mixture is stored at temperatures of 25–30°C, to be used cold as the need arises for the preparation of the finished product by one of the methods described above.

Médard and Le Roux [1] examined the influence of various methods of mixing on the properties of ammonium nitrate explosives ("Explosifs du type N"). They found that mixing in heavy (5 ton) edge-runners gives explosives of higher sensitiveness and rate of detonation than the same explosives mixed in kneaders of the Werner–Pfleiderer type.

The difference can be seen from the Table 159 which refers to Explosive N No. 31 (see Table 119).

TABLE 159

	Mixed	
	in kneaders	in edge-runners
Density	0.95	1.00
Sensitiveness to initiation in grammes of fulminate		
at density 1.00	0.30	0.25
1.30	2.00	0.50
1.50	no detonation	0.80
Transmission of detonation (cm)		
at density 1.00	6.5	8
1.30	0.5	4
Rate of detonation (m/sec)		
at density 1.00	3350	3900
1.30	3690	4800

Mixing either hot, or hot and cold alternately, has the advantage over mixing only in the cold that the crystals of ammonium nitrate are coated with a layer of nitro compound due to contact with molten TNT or DNT, which somewhat reduces their hygroscopicity. Mixing in the hot requires careful temperature control as the explosive leaves the kneader or mixer after being cooled. This temperature should under no circumstances be higher than that of the change of crystal form of ammonium nitrate, i.e. +32.1°C for pure substance. If the explosive has a temperature higher than +32°C after leaving the kneader, the change in crystal form may produce caking in later stages of manufacture, i.e. in the stored boxes or (at worst) in the paper cartridges.

Caking during storage is not of great consequence except that additional screening is then needed. On the other hand, caking in the finished charges is much more serious, since charges of hardened explosive are not suitable for use as their sensitiveness to detonation is impaired and it is difficult to introduce detonators into them.

Mixing of ingredients with nitroglycerine. Ammonium nitrate explosives containing 4–6% nitroglycerine are mixed in two stages. First, all the ingredients other than nitroglycerine are mixed by one of the methods described above and, secondly, nitroglycerine is added at a temperature of 30–32°C and carefully stirred. Mixing can also be carried out at 40°C and ended at 30°C. The temperature change is required for the reason given above. Mixing with nitroglycerine is carried out either in Werner–Pfleiderer (Fig. 206) or Drais type (Fig. 173) kneaders.

Cartridging

Free-flowing ammonium nitrate explosive is loaded into cartridge cases usually 32 mm dia., made of paraffin paper. The cartridge cases are handmade or manufactured on Hesser machines (in which they are numbered and paraffined at once) or on Niepmann machines (Fig. 179). The cartridges generally produced weigh 100 and 50 g. For loading, machines are usually employed in which the explosive is poured into a funnel fitted with a rotating screw that pushes the explosive towards the mouth of the funnel onto which the paper cartridge case is placed. There another rotating screw feeds the explosive into the cartridge case. After filling the open end of the cartridge case it is sealed (Fig. 168).

Paraffining and packaging

Formerly cartridge cases were made of non-paraffined paper and were paraffined after filling by dipping into melted paraffin, lignite wax (montan wax) or a mixture of both. A mixture of paraffin with rosin in the ratio of 70/30–90/10 was preferable to paraffin alone. The amount of coating should not exceed 2.5 g per 100 g of explosive. It was found, however, that paraffin may penetrate too deeply inside the cartridge and desensitize the explosive. Moreover, hot paraffin may induce a change of crystal form in the ammonium nitrate and cause the cartridges to harden. This method was therefore abandoned and the cartridge cases are now paraffined before being filled. The prepared cartridges are then placed into cardboard boxes, wrapped with paper and paraffined, together with the whole box. The latter usually contain 2–2.5 kg of explosive.

To help identify the explosives according to their safety, and to avert serious errors, cartridges are packed in various colours which in Poland are:

rock explosives—red,
coal explosives—blue,
permitted explosives—cream-coloured,
special permitted explosives—cream-coloured with the two black stripes and black bordering.

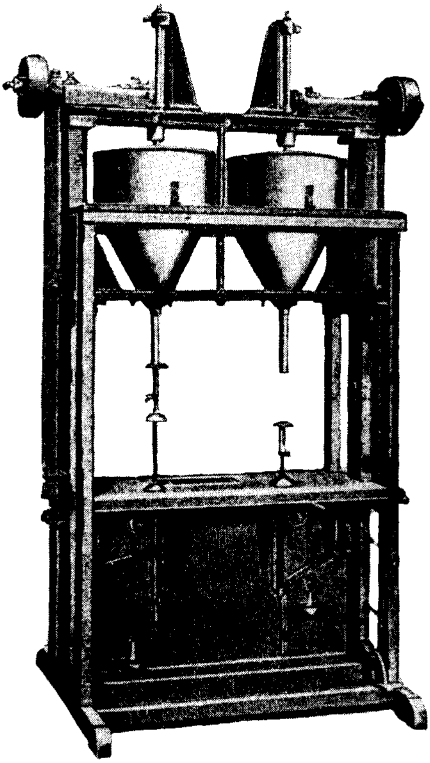


FIG. 168. Cartridging machine for free-pouring mining explosives.

In the U.S.S.R.:

explosives approved for opencast mines have white paper cartridges,
explosives approved for non-gassy and non-dusty mines —red,
rock explosives approved for gassy and dusty mines —blue,
coal and rock explosives approved for gassy and dusty mines —yellow,
explosives approved for sulphur mines —green.

AMMONIUM NITRATE–FUEL OIL MIXTURES
(AN–FO)

Various methods have been used for mixing ammonium nitrate with fuel oil on site at opencast mines. Some were very primitive and consisted of simply adding fuel oil to a polyethylene bag of ammonium nitrate and allowing the mixture to stand long enough for the ammonium nitrate to be soaked with oil. Then the mixture was poured into vertical shotholes.

Another method consisted of charging the shothole with a definite quantity of ammonium nitrate and pouring a measured quantity of fuel into it through a funnel.

Although these methods do not require any special equipment, they cannot guarantee uniform and reliable results.

Some users organized a plant where the AN–FO mixture was prepared, packed into multiwall paper or polyethylene bags, and stored until moved by company trucks to the mine or quarry.

The mixing and packaging equipment and procedures were as follows [2]. Dry ammonium nitrate prills are dumped into a sheet-metal hopper, approximately 4×4×4 ft in size with a sloping bottom, which feeds a 5 in. pipe through which an auger, driven by an electric motor through reducing pulleys, move the prills past a second, smaller bin into which oil is sprayed. The flow of oil is controlled by a hand-operated valve. A short distance beyond the point at which the oil is added, the auger discharges into a bucket elevator which raises the mixture to the top of a hopper approximately 5×5×5 ft in size. The top of this hopper is approximately 10 ft above the floor. At the bottom of the hopper, four filling tubes, closed by means of simple slide valves, control the flow of the mixture into packages. Usually the mixture is repackaged into the multiwall paper bags in which the ammonium nitrate had been received or into polyethylene tubes.

Sewing, heat sealing and tying equipment is available for closing the packages of explosive.

Fire followed by a disastrous detonation occurred in a plant near Norton, Va. According to van Dolah and Malesky [2] the accident demonstrated the importance of the many safety recommendations issued earlier by the Bureau of Mines [3]. In brief, all typical safety regulations for explosives factories and stores should be observed, i.e.: blasting agents should not be stored with ammonium nitrate or explosive mixtures, no smoking or open flames should be permitted in any of the buildings, the floors should be cleaned frequently to prevent any accumulation of ammonium nitrate, fuel oil or explosive mixtures, no more than one day's production of fuel-mixed ammonium nitrate should be permitted in or near the mixing and packaging plant, all electrical equipment should conform to safety regulations and all switches, controls, motors etc. should be outside the buildings.

Some opencast mines in the U.S.A. and Canada worked out special equipment for production of AN–FO. Some of these designs are given below, according to the literature [4].

Figure 169 gives an idea of the apparatus which seemed to be in use at Bingham Mine, Utah. It permits charging horizontal, skew and vertical shotholes with an ammonium nitrate–fuel oil mixture. Ammonium nitrate (45.4 kg) is placed in the vessel. Fuel oil (3.78 l.) is introduced from a measuring tank. The ammonium nitrate and fuel oil are moved by compressed air (2.6 and 1.9 atm respectively). Mixing occurs in the lower part of the vessel and immediately afterwards the mixture is fed into the shothole.

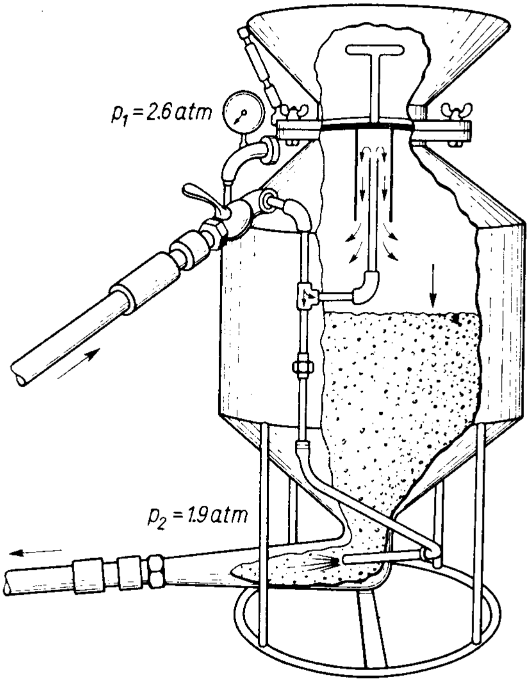


FIG. 169. Diagrammatic presentation of mixing equipment used in Bingham Mine, Utah, U.S.A. [4].

Another design, used in Canada, is shown in Fig. 170. It consists of a funnel provided with a number of nozzles supplying the liquid fuel. Ammonium nitrate passes through a sieve (*1*) and an exit (*2*) on a divergent cone (*3*) into the mixing chamber where the liquid fuel is injected by four nozzles—one of them (*4*) is shown. Uniform flow of the liquid is automatically maintained.

Another method also used in Canada is presented diagrammatically in Fig. 171. Ammonium nitrate passes through a mill and a sieve (*1*) and is transported to a mixing house through a stainless steel tube by means of compressed air. Liquid fuel enters the same mixing house from a tank. Mixing occurs in a rotating hopper. The mixture is loaded onto a special lorry (Fig. 172), which is equipped with a compressor, a screw conveyer, and a dosage valve. Shotholes are loaded straight from the lorry. The explosive from the lorry is delivered to the shothole by means of a compressed air.

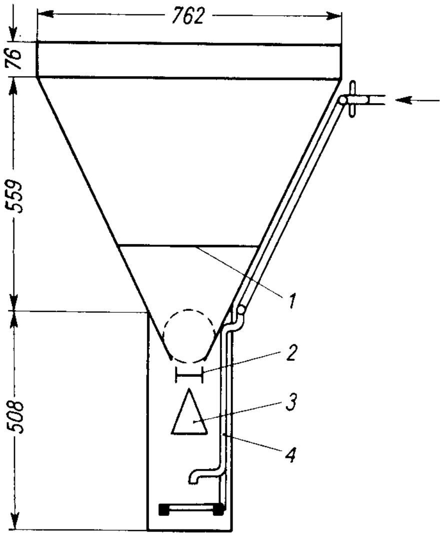


FIG. 170. Diagrammatic presentation of mixing equipment used in Canada [4].

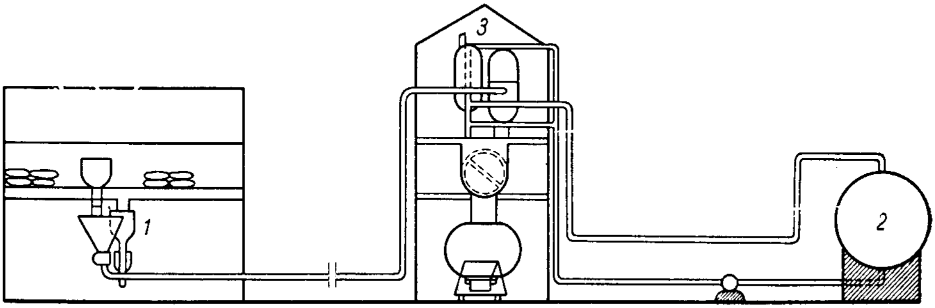


FIG. 171. Diagrammatic presentation of a mixing plant in Canada [4]; *1*—ammonium nitrate compartment, *2*—fuel oil tank, *3*—mixing house.

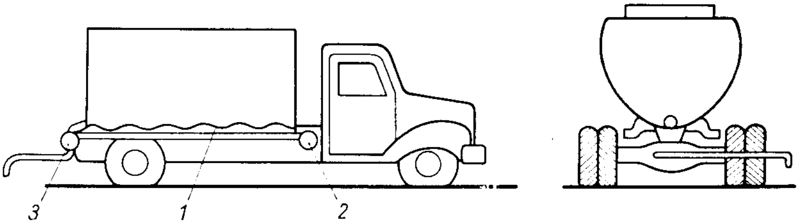


FIG. 172. Lorry for ammonium nitrate-fuel oil explosive [4]; *1*—screw conveyer, *2*—lifting device, *3*—dosage valve.

THE MANUFACTURE OF DYNAMITES

Raw materials

Methods for the manufacture of raw materials of requisite purity for nitroglycerine, nitroglycol and nitrodiethylene glycol production and for dynamite collodion cotton have already been described (Vol. II, pp. 87, 145, 152 and 409).

The oxidizing agents, such as sodium or potassium nitrates, were described in the section on blackpowder (p. 342) and ammonium nitrate in Vol. II, p. 450.

The other ingredients should meet the requirements for commercial products of high purity. Salts should be dried and milled.

Collodion cotton is a dynamite ingredient of very great importance. Before use each lot of collodion cotton should be checked. For this purpose a small sample of blasting gelatine made of nitroglycerine, or of nitroglycerine with nitroglycol used in manufacturing should be prepared. The suitability of nitrocellulose for manufacturing purposes is judged by the properties of the gel, notably by its chemical stability and consistency particularly at an elevated temperature (40–50°C). The gel should not give any exudation of nitroglycerine at this temperature.

Collodion cotton is supplied wet to dynamite factories with a water content up to 30–35%. Some factories use it directly in this form, although the presence of water is detrimental to the uniformity of the gel produced. In the majority of factories nitrocellulose is dried before use.

As will be discussed later (pp. 573, 642) the drying of nitrocellulose is dangerous since when dry it is ignited with unusual readiness by sparks, friction or impact. The drying operation therefore requires great care and is usually carried out in a separate building surrounded by safety walls. The amount of nitrocellulose to be dried at a time must not be too large (less than 100 kg). In the premises a temperature of 45–50°C should be maintained by radiators heated with hot water. The temperature is controlled from outside. The moist nitrocellulose is spread in a thin layer (4–5 mm) over the shelves of wire cloth stretched on carefully-earthed, metallic frames. Wooden frames with muslin stretched over them may also be used, provided that a lower temperature of drying is maintained (e.g. 40°C) and too fast an air circulation (e.g. mechanical ventilation) is avoided, otherwise high static charges may build up on the nitrocellulose. Drying lasts for approximately 24 hr and is ended at a 1.2–2% moisture content since complete drying may be dangerous. After the drying process is completed, the heating is turned off, the drying room opened and the nitrocellulose is unloaded after cooling.

Mixing of ingredients

The dynamite ingredients are mixed with a solution of collodion cotton in nitroglycerine prepared separately or in a mixture of nitroglycerine with nitroglycol. The drying and milling of the ingredients are preparatory operations.

Dissolution of collodion cotton. The collodion cotton used for the manufacture of dynamite gives solutions of very high viscosity. Since it dissolves very slowly, to avoid delays in production, dissolution is usually divided into two stages, viz. initial dissolution and mixing.

Formerly, the initial dissolution was carried out in the following way. Nitroglycerine was weighed in ebonite or bronze cans and was poured into a wooden tub, lined with ebonite or lead sheet, having a capacity of 25 kg of nitroglycerine. Next collodion cotton was poured in and the whole was stirred by hands protected with rubber gloves so as to obtain a mass as uniform as possible. The contents of the tub were allowed to stand for a few hours (the last batches over-night). During this time the nitrocellulose dissolved in the nitroglycerine and the mass became transparent, but not yet uniform. A uniform solution was obtained only by using stirrers or kneaders.

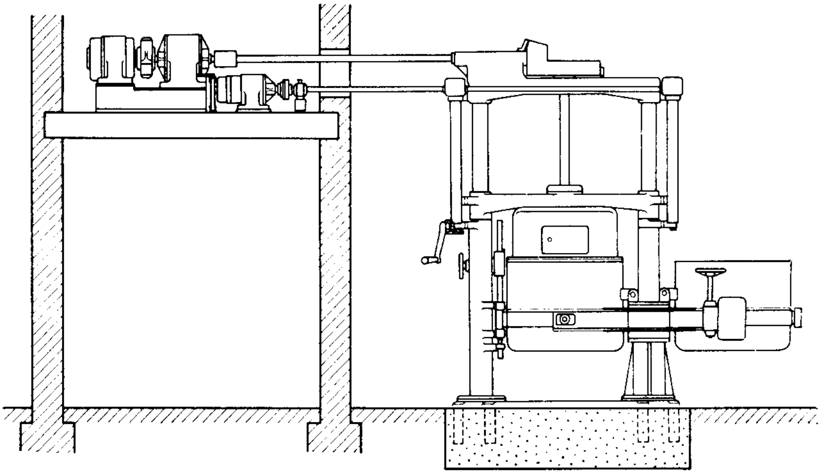
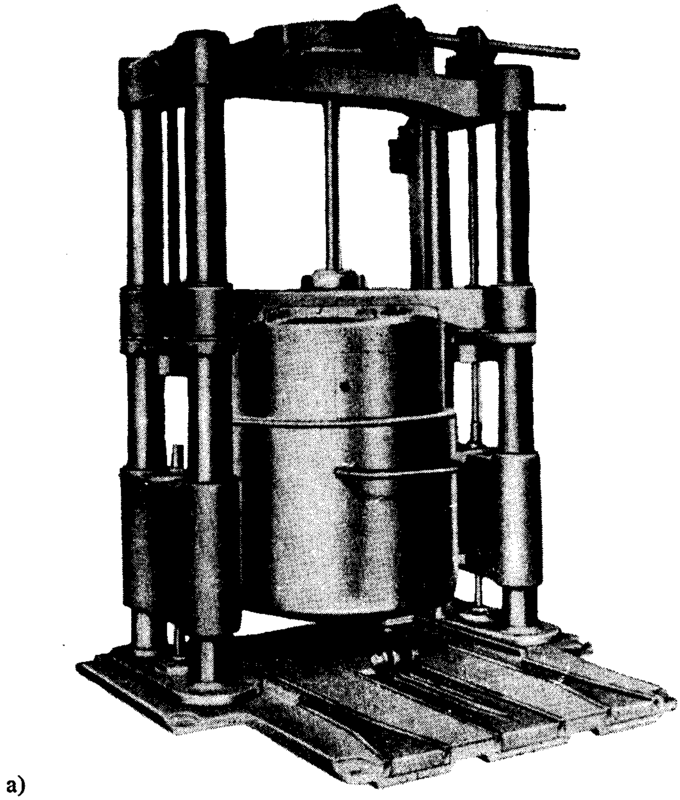


FIG. 173. Diagrammatic illustration of a Drais mixing and kneading machine with two tanks. The drive and switchgear is in an adjacent room for safety reasons (Courtesy Draiswerke Maschinenfabrik G.m.b.H., Mannheim-Waldhof, G.F.R.).

The initial dissolution is now usually carried out in copper tubs with a water jacket which maintains a temperature of 45–50°C in the tub. The tubs contain 100 kg of a mixture of nitroglycerine and nitrocellulose. Their contents are stirred with wooden paddles and then allowed to stand for 20–30 min. This is sufficient time for complete dissolution of nitrocellulose at this temperature.

Mixing. For mixing the solution of collodion cotton with the other dynamite ingredients vertical kneaders of the Drais type are commonly used (Figs. 173 and 174). The kneader of this type consists of stirrers and a vertical cylindrical tank provided with thermal insulation. The stirrers are fitted with a mechanism enabling them to be lifted and lowered. The toothed wheels which drive the mechanism are


a)

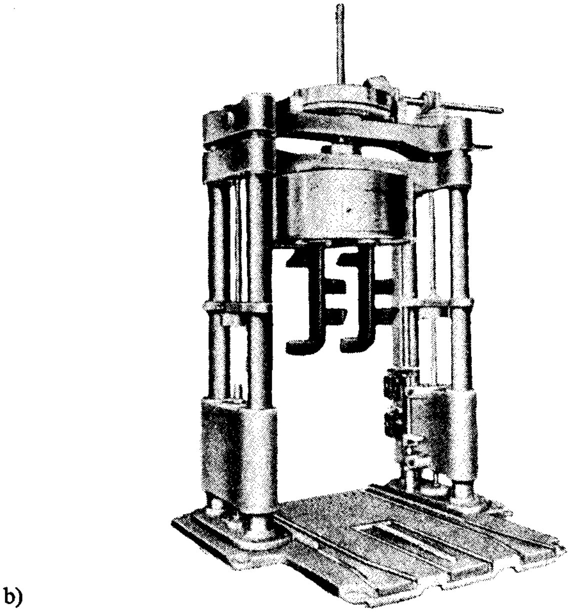

b)

FIG. 174. General view of a Drais mixing and kneading machine (Courtesy Draiswerke Maschinenfabrik G.m.b.H., Mannheim-Waldhof, G.F.R.); *a*—with stirrers dipped in the tank, *b*—with stirrers lifted, tank removed.

protected from dust by means of an air-tight casing. Drais type kneaders with two or three replaceable tanks are also known (Fig. 175).

The tanks have a capacity of 300–450 l. and hold approximately 200–300 kg of dynamite. They are suitable for the initial dissolution of collodion cotton (in a separate room) and for efficient mixing of the collodion cotton with nitroglycerine by hand (in rubber gloves) or with a hand-operated paddle. After the initial dissolution stage the tank is moved to the stirring equipment, where the other ingredients are added and the final mixing is carried out. The remaining dynamite ingredients are then added and stirred with the same stirrers. Since one set of stirrers is provided for several tanks, continuity of work may be maintained and the prolonged initial dissolution does not cause any delays in the manufacture.

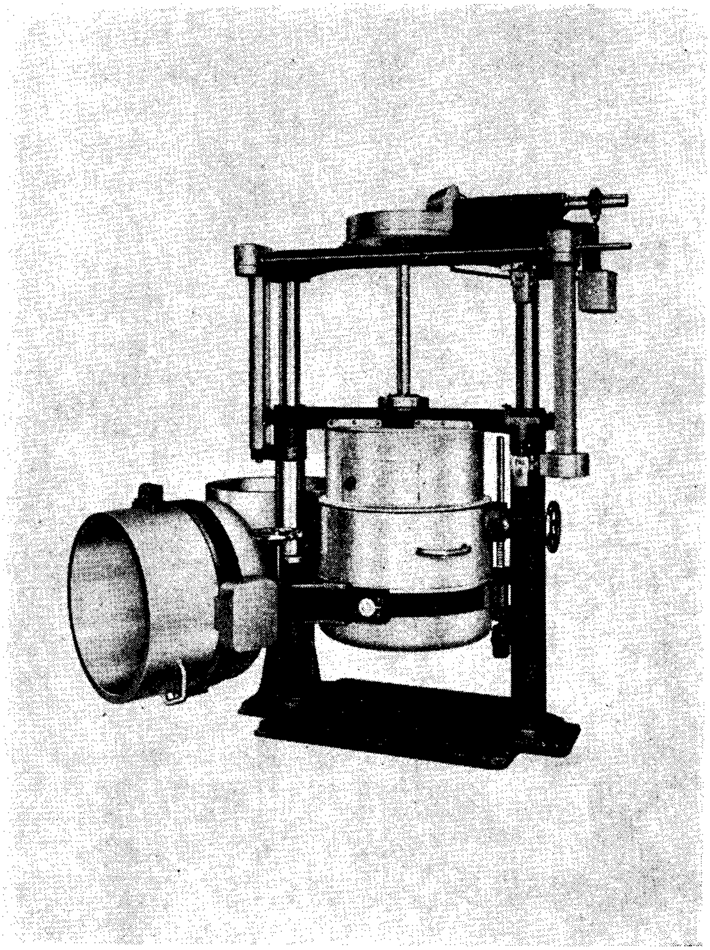


FIG. 175. Drais mixing and kneading machine with three tanks (Courtesy Draiswerke Maschinenfabrik G.m.b.H., Mannheim-Waldhof, G.F.R.).

For the manufacture of dynamites, kneaders of the Werner–Pfleiderer type may also be employed. They are widely used in the manufacture of smokeless powder (Fig. 206). Drais kneaders however, have the advantage over the Werner–Pfleiderer type in that they are safer to handle, and hence more suitable for mixing materials sensitive to friction and impact, such as dynamites.

Safety in the operation of vertical kneaders is achieved by ensuring that:

(1) The points where there is friction between the stirrers and their bearings are not in contact with the explosive mass.

(2) The distance between the paddles and the interior of the vat in which the stirring is carried out is relatively large.

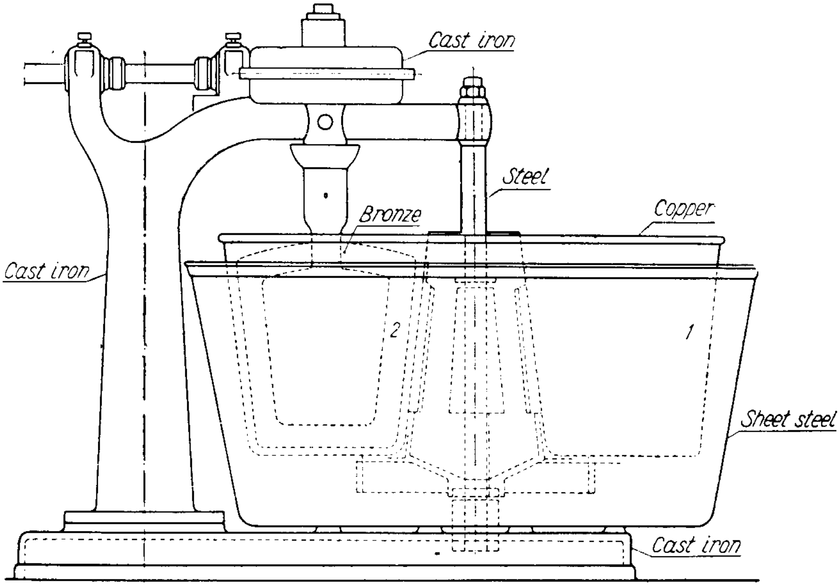


FIG. 176. A kneader used in France for the manufacture of blasting gelatine and dynamites [5].

In Werner–Pfleiderer kneaders this distance is very small so that if a hard object (metallic part, screw, nut etc.) penetrates into a kneader, an explosion may occur due to seizing. Werner–Pfleiderer kneaders have a capacity of 50–200 kg of dynamite.

In some countries other types of plant are used for mixing dynamites. In France, for instance, a kneader constructed as shown in Fig. 176 is used for the manufacture of blasting gelatine and dynamites rich in nitroglycerine. Here a copper vat (*1*), lined with lead and located in a heating jacket of sheet steel, rotates about a vertical axis. A bronze stirrer, (*2*), can rotate about another vertical axis. The charge in the kneader is 166 kg of nitroglycerine and 11–12 kg of collodion cotton. At the beginning a temperature of 15–20°C is maintained and it is then raised to 45–50°C.

After 15 min during which the collodion cotton is dissolved, the remaining ingredients (e.g. 24 kg of potassium nitrate) are added. After stirring, the contents of the vat are cooled to a temperature of 20–25°C.

For mixing dynamites, in particular those containing less nitroglycerine, wooden edge runners of a special design are employed in France (Fig. 177). The tub (*1*) has the base of ebonite plates (*2*). The wheels of the runner are also covered with ebonite bands (*3*).

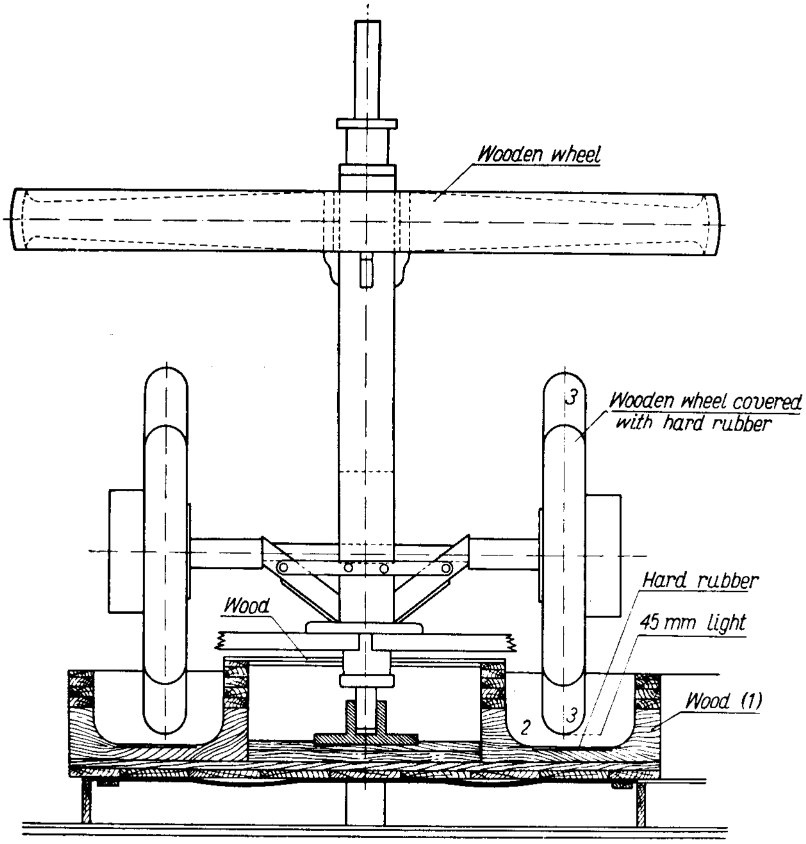


FIG. 177. Wooden edge runner for the manufacture of dynamite [5].

Cartridging

Dynamite from edge runners is transported in trucks to a separate room for cartridging. Figure 178 represents a diagram of one of the oldest and simplest designs for a hand operated machine for cartridging. Dynamite of plastic consistency is loaded by hand into the tapered body (*1*), through funnel (*2*). The rotation of the crank handle driving shaft (*4*) with worm (*5*) pushes out the explosive mass through the nozzle (*3*). There are ribs (*6*) inside the tapered body which prevent the mass from turning. The mass in funnel (*2*) should be pressed with a peg to facilitate its exit through nozzle (*3*). This nozzle has a brass orifice that holds a paper cartridge case. The dynamite passes through the orifice, pushing the bottom of the paper cartridge case and filling it while in motion. When the paper cartridge case has moved forward a distance corresponding to the required length of the cartridge, the dynamite is cut off and the cartridge closes. A new paper cartridge case is then attached to the orifice and the operation is repeated.

The explosive may also be extruded in the form of a long rod which is then cut into pieces of the required length on a table covered with a copper or brass sheet. The pieces are then put into paper cartridge cases which should be made of paraffined paper.

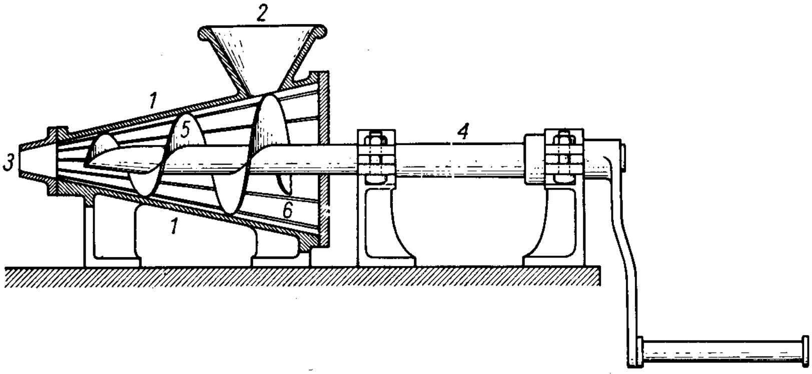


FIG. 178. Machine for the cartridging of dynamite [6].

In machines of the design described above a certain danger is created by the pressure caused by the decreasing area of taper. The increase of the pressure leads to greater friction and this, in turn, may cause the ignition of the dynamite. In a machine of better design, therefore, the body in which the worm rotates is cylindrical. It may be equipped with several brass orifices, so that several cases may be cartridged at a time. Since this attachment is safer, it may be fitted with a power drive. Loading the funnel with dynamite and fitting the orifices are the only manual operations.

Highly efficient machines are also available for mechanized cartridging. In the U.S.A., for instance, there are machines in use, operated by two people and capable of processing 6800 kg of dynamite in 8 hr. Mechanization, however, is not always advisable since it may decrease safety.

In Germany a machine of the Niepmann type has been adapted for cartridging dynamite [7]. A schematic view of its operation is shown in Fig. 179. The explosive supplied through funnel (*1*) is pushed out through worm (*2*) into conduits (*4*) and (*5*), from which it is ejected by pistons (*3*). The empty paper cases are fed by conveyer (*9*) into slots on the rotating table (*7*). When the cases reach position (*8*), a charge of plastic material, extruded from the orifice (*6*), is slipped into them. Further rotation severs the rods of dynamite while the cases, already filled, are passed to slanting receptacles (*11*) and (*12*). As there are few movable parts this method of cartridging is fairly safe. The machine processes 2400 cartridges of 100 g each, per hour.

A general view of a modern dynamite plant in the U.S.A. is given in Fig. 180.

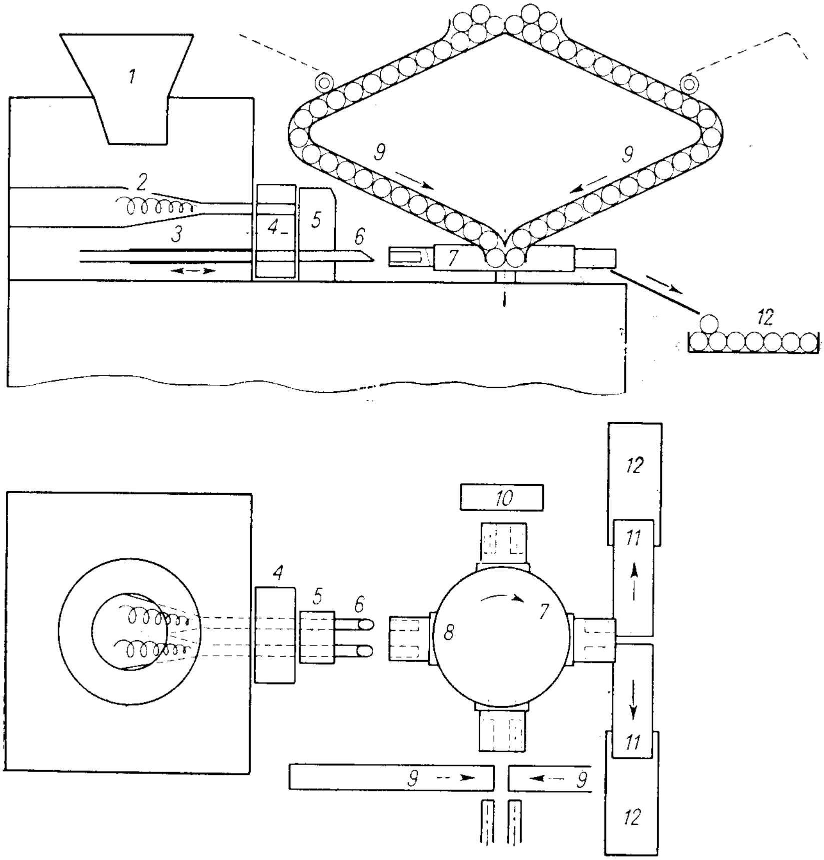


FIG. 179. Schematic view of the operation of a Niepmann type machine for dynamite cartridging [7].

Thawing of dynamites

Dynamites that contain nitroglycerine but no nitroglycol can easily freeze at low temperatures. Temperatures below 6°C should be regarded as undesirable and any temperature below 0°C will freeze the dynamite cartridges.

Although crystalline nitroglycerine is less sensitive to shock and can detonate at a higher rate than the liquid substance, the hard frozen cartridges are troublesome to handle, as it is difficult to insert a detonator into them. When such cartridges are warmed crystalline nitroglycerine separates from the gel as it melts and readily flows out of the cartridges. This can create a danger as nitroglycerine spilled on to the floor is subject to shock and friction.

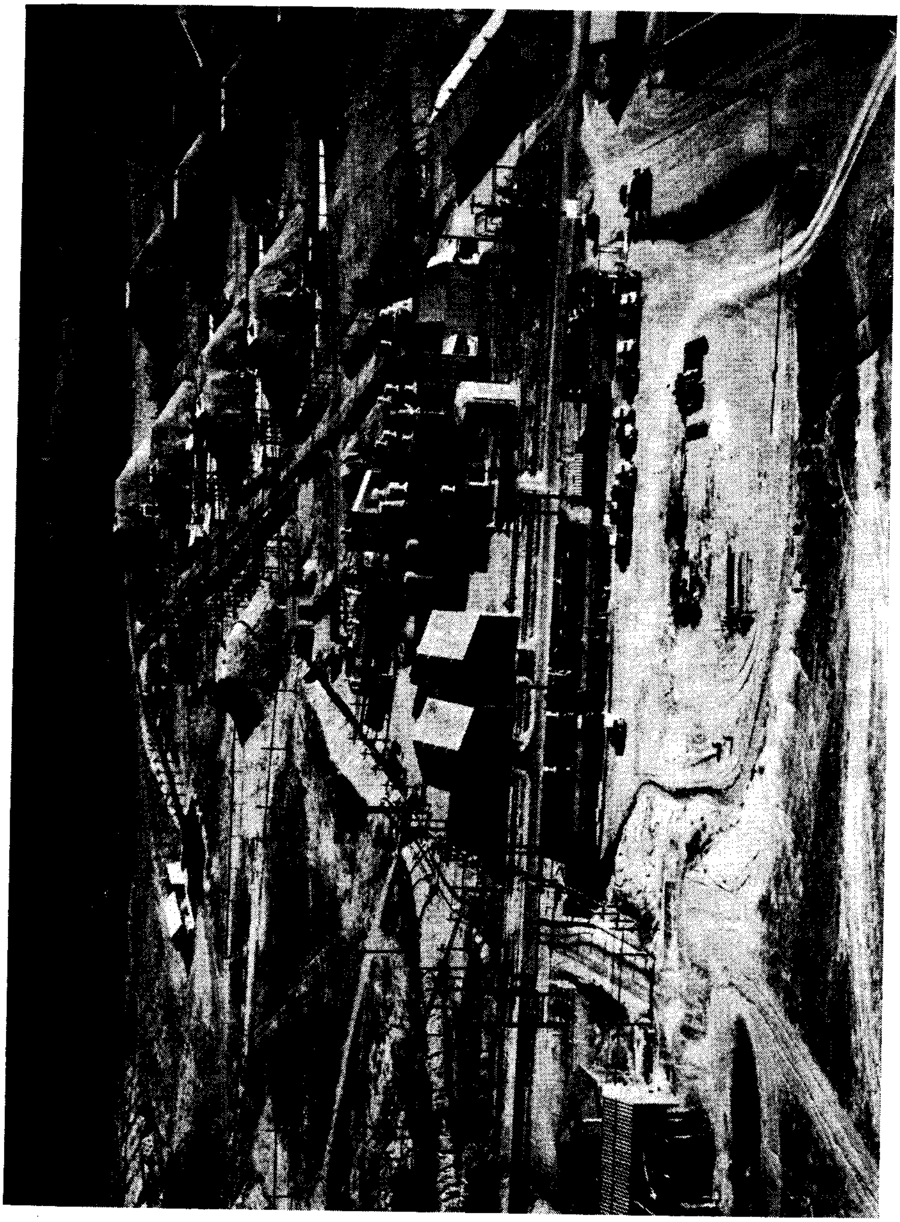


FIG. 180. General view of a modern dynamite plant of du Pont de Nemours in West Virginia, U.S.A. (Courtesy du Pont de Nemours).

Several accidents have occurred in the course of thawing frozen dynamite cartridges. In France, 1250 kg of dynamite caught fire and detonation occurred in a coal mine at Merlebach, in 1925. Commission des Substances Explosives [8] investigated the accident. The wooden cases with frozen dynamite were placed over steam heated calorifuges. In spite of the fact that the temperature in the compartment for defreezing the dynamite did not exceed 21°C, according to the recording thermometer, the dynamite caught fire after 40 hours' warming. Most likely this was due to superheating.

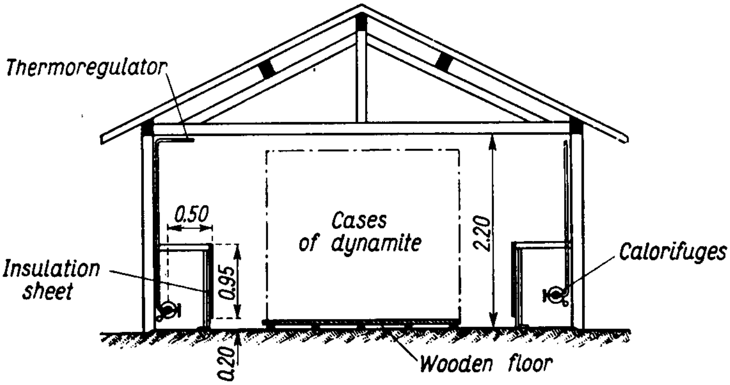


FIG. 181. Schematic design of a building for thawing (decongelation) of dynamites [8].

The Commission recommended several safety precautions, such as:

(1) keeping the temperature of calorifuges below 100°C preferably by heating with hot water to *ca.* 50°C,

(2) keeping the temperature inside the defreezing compartment below 30°C,

(3) using compartments for thawing dynamite so designed that the cases containing explosive are placed away from the calorifuges (Fig. 181).

Although modern dynamites contain mixtures of nitroglycol–nitroglycerine they should be considered to be only comparatively unaffected by a low temperature. Particularly heavy frost may freeze these explosives and the recommendations of the Commission des Substances Explosives should be observed.

THE MANUFACTURE OF CHLORATE AND PERCHLORATE EXPLOSIVES

To avert the danger arising from the mechanization of mixing appliances, chlorate mixtures are usually prepared either by primitive manual methods or in machines made chiefly of wood.

Chlorate explosives of the Cheddite type (p. 277, Table 61) are manufactured in an enamelled vat with a double bottom, heated by steam. First the organic ingredients are mixed and melted at 80°C (e.g. nitro compound with castor oil, paraffin with vaseline etc.). Finely-crushed chlorate is then added while stirring continuously with a wooden paddle. After a uniform mixture has been obtained, the hot mass is discharged onto a table covered with sheet brass and rolled with a wooden roller. As the mass solidifies, it becomes brittle and crumbles. It is then rubbed through a sieve. Finally the sieved mass is graded by sifting out the dust which is recycled.

If the explosive contains a liquid organic substance, it is prepared, as stated above, by filling the paper cases with chlorate and dipping them into the liquid.

Miedziankit is manufactured in this way, i.e. the milled and dried potassium chlorate is filled into paper cases by the machines for cartridging (Fig. 168). The cases are made either of non-glued, absorbent paper or of ordinary, densely-perforated paper. The cartridges filled with chlorate (90 g of weight and 30 mm dia.) are taken to another room in which they are saturated with kerosene. Here troughs mechanically fed with kerosene from a movable tank are placed on tables. The cartridges of chlorate are put into the troughs which rotate every few minutes so that each cartridge is uniformly saturated. After half an hour, when the cartridges are sufficiently saturated with liquid, they are taken out of the troughs and placed in containers made of parchment paper.

Careful, fine milling of the potassium chlorate is a very important factor in the manufacture of chlorate explosives. Opinions are divided on the question of the safety of the milling of chlorate. In Germany chlorate is milled like ammonium nitrate in common mills of the disintegrator type. A pre-requisite for such a procedure, however, is a high purity of chlorate (free from traces of combustible material, especially organic substances); milling impure chlorate is exceedingly dangerous. In France wooden edge runners are used for milling chlorate similar to those for dynamite (Fig. 177).

When manufacturing chlorate explosives, it is of extreme importance to observe the safety code which demands the highest possible purity, the removal of all chlorate dust settling on furniture, clothes etc. The workers' foot-wear should be wooden soled, since nails in soles not infrequently cause accidents. The floor in the premises should be covered with linoleum or magnesia cement.

The manufacture of perchlorate explosives is similar, but due to the lower sensitiveness to impact of perchlorate explosives, some operations as e.g. mixing, may be conducted in Drais kneaders (Figs. 173–175) or even in kneaders of Werner–Pfleiderer type (Figs. 206–208).

CARDOX, HYDROX AND AIRDOX CARTRIDGES

The hazards involved in the use of explosives in coal mining have necessitated constant efforts to improve the safety of blasting in coal mines, using other methods, i.e. the Cardox, Hydrox and Airdox methods of blasting. The Cardox and Hydrox cartridges function in a way similar to explosives.

Cardox. These are steel cartridges (Fig. 182) containing liquified or solidified gas and a pyrotechnic composition. On burning, the pyrotechnic mass emits a great amount of heat and converts the liquid or solid into a gas at a high pressure sufficient to blow out the walls of the shothole. Cardox was invented in the U.S.A. in 1920 by Helmholz, Farrel and Crawford and received Bureau of Mines U.S.A. approval in 1928 [10].

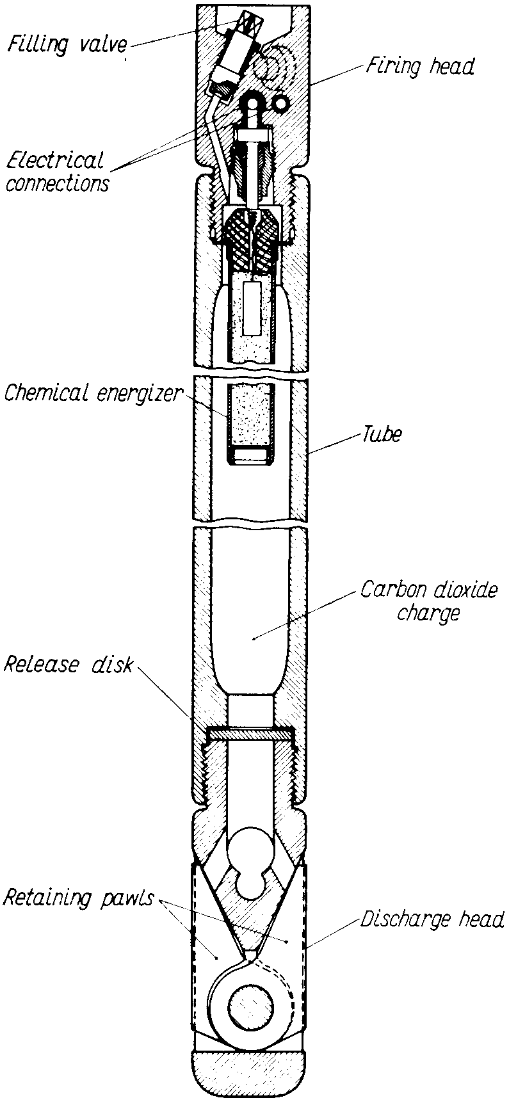


FIG. 182. Cardox blasting cartridge, according to J. Taylor and Gay [9].

In Cardox charges liquid carbon dioxide is the ingredient providing the gas pressure. The pyrotechnic charge consists of chlorate mixtures that evolve a great amount of heat, such as either sodium chlorate, powdered charcoal and aluminium dust or 10% naphthalene and 90% potassium chlorate. The mass is ignited by an electric detonator. The reaction proceeds according to the equation:

$$C_{10}H_8+8KClO_3 \rightarrow 10CO_2+4H_2O+8KCl+471 \text{ kcal}$$

In Great Britain a safer mixture was evolved (Payman [11]) with the following composition:

Potassium perchlorate	85%
Asbestos	1.5%
Nitrotoluene	4.5%
Kerosene	8.5%
Castor oil	0.5%

or

Potassium perchlorate	84%
Phenol-formaldehyde resins	16%

Due to the heat of reaction carbon dioxide evaporates very quickly. A high pressure (700–2000 atm) is produced which blows out a steel disk closing the chamber. Theoretically the pressure may increase to 4000–5000 atm. The steel cartridge is used again since it is not destroyed. Due to high cost the use of Cardox has nearly disappeared.

Hydrox. Hydrox charges (Fig. 183) are loaded with a mixture that usually consists of 56% sodium nitrite and 44% ammonium chloride. They carry a charge of cap mixture ignited electrically, the composition of which is similar to that of pyrotechnic mixtures. The heat of combustion of the latter charge causes the mixture of sodium nitrite and ammonium chloride to react according to the equation:

$$NaNO_2 + NH_4Cl \rightarrow NaCl + 2H_2O + N_2$$

Another possible reaction mechanism is:

$$NaNO_2 + NH_4Cl \rightarrow NH_3 + HCl$$

$$NaNO_2 + HCl \rightarrow NaCl + HONO$$

$$HONO + NH_3 \rightarrow N_2 + 2H_2O$$

The pressure of nitrogen and steam produced shears the bursting disk and releases the gases into the shothole.

The reaction may stop at an intermediate phase. In fact, the presence of ammonia can usually be detected in the reaction products.

Theoretically reaction takes place at a temperature of 1300°C. In reality the temperature in the cartridge only slightly exceeds 800°C due to its high thermal capacity.

Since the temperature may become too high in certain cases and may cause the ignition of methane in mines (especially when the cartridge is defectively assembled, without the bursting disk, that encloses the charge) a mixture of ammonium nitrate with organic combustible substances and salt hydrates is sometimes employed. Such a mixture is incapable of self-sustained reaction at atmospheric pressure but will decompose in the cartridge, when the pressure rise due to the combustion of an initiating charge composed of guanidine nitrate and an alkali metal persulphate. The initiating charge is fired by a pyrotechnic mixture, initiated, in turn, by means of an electric current.

About 1953 a modification of the Hydrox device, called Chemechol, was introduced in the U.S.A. In this design the electric detonator of the initiator is protected from ignition by stray currents. By this method a pressure of 18,000–22,000 lb per sq. in. (1200–1500 kg/cm^2) is attained. However it has been withdrown from the market mainly due to high costs.

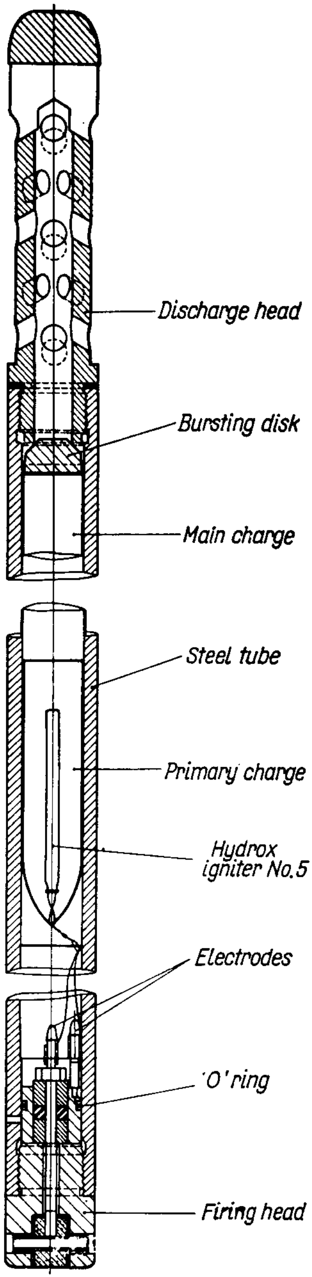


FIG. 183. Hydrox blasting cartridge, according to J. Taylor and Gay [9].

A mixture of sodium nitrite with ammonium chloride may decompose with time to form unstable ammonium nitrite. The presence of moisture and of acids favours the decomposition of a mixture of sodium nitrite with ammonium chloride. On the other hand, alkaline reaction and absence of moisture stabilize the system. Experiments have shown that for all practical purposes the mixture is best stabilized by the addition of 2% sodium carbonate. Ammonium carbonate or magnesium oxide may also be used.

Thermochemical data on a Hydrox mixture stabilized with the addition of 2% sodium carbonate are tabulated below (according to J. Taylor [12]).

TABLE 160

State of water	Conditions	Heat of reaction at 25°C kcal/kg	Temperature of reaction °C	Gas volume l./kg
Vapour	constant pressure	420	1120	537
Liquid	constant pressure	589	1120	
Vapour	constant pressure	435	1310	537
Liquid	constant pressure	594	1310	

Products of complete reaction of Hydrox mixture are:

NaCl	46.7%
N_2	22.4%
H_2O	28.8%
Na_2CO_3	2.1%

The total amount of gas produced comprises 51.2% (by weight) of all products.

A Hydrox mixture can be initiated either by heating it at one point by a heat-producing fuse, by an electrically-heated wire or a blackpowder igniter. A few drops of acid produce a self-sustained reaction, after an induction period. The induction period depends on the nature of the acid solution, its concentration and on the amount of alkaline stabilizer in the Hydrox powder.

Concentrated hydrochloric acid induces vigorous reactions which are partly "Hydrox reactions", and partly reactions which give rise to the evolution of NO (according to J. Taylor [12]).

$$3NaNO_2 + 3HCl \rightarrow 3NaCl + HNO_3 + 2NO + H_2O \tag{1}$$

$$3NaNO_2 + 2HCl + NH_4Cl \rightarrow 3NaCl + NH_4NO_3 + 2NO + H_2O \tag{2}$$

Neither hydrochloric nor nitric acid initiates a self-sustained reaction in powder stabilized with sodium carbonate or magnesium oxide.

This is probably caused by resulting reactions which destroy the acids too rapidly.

J. Taylor has described a method of igniting Hydrox powder stabilized with 2% sodium carbonate: it consists of adding 0.2 cm^3 of 50% solution of chromic acid.

Both Cardox and Hydrox devices should be subjected to tests before permission is granted for their use in coal mines, because the essential components of these devices are mixtures similar in nature to explosives. Faulty assembly, such as omission of a bursting disk may bring hot gases in contact with a methane–air mixture or coal-dust.

The greatest advantage of Cardox and Hydrox methods lies in their safety towards methane and coal-dust. They also contribute to the getting of coal in large pieces. In comparison with explosives, however, shotfiring with Cardox and Hydrox devices is more expensive.

Before World War II, in the U.S.S.R, another kind of Hydrox was suggested by Komar [13]. It consisted of modifying Cardox cartridges by replacing carbon dioxide with water. Water has a critical temperature (374°C) and total heat of evaporation much above the critical temperature (31°C) and heat of evaporation of carbon dioxide. Therefore water requires a much higher heat to be supplied by the burning composition. This created difficulty and therefore Hydrox with water did not seem practicable.

Podbelskii [14] suggested using salts which readily undergo dissociation into gaseous products instead of carbon dioxide.

Airdox. The use of Airdox charges is based upon an entirely different principle. A steel cartridge, closed at one end and connected with an air-compressor at the other, is introduced into the shothole. The air is fed in up to 700 atm and when it reaches the required pressure the bursting disk closing the charge is ejected so that the air is discharged and the shothole shattered.

The Airdox method was introduced in mines in the U.S.A. in the early 1930s.

Towards 1938 a modification of this method was introduced under the name of the Armstrong Airbreaker [9]. In this system the air is compressed up to 800 kg/cm^2 and introduced by opening a blow-out valve; this ruptures the bursting disk and blows up the shothole.

The Airdox device is very safe towards methane and coal-dust. Safety is especially increased by the improvement of the bursting disk which is fitted with a plastic plug closing the charge.

The Airdox device is widely used in the U.S.A. The Armstrong Airbreaker has been employed in very gassy mines in Great Britain, France the U.S.A. and Poland.

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CHAPTER VII

SMOKELESS POWDER

HISTORICAL

A FEW years after the discovery that the treating of cellulose with nitric acid converts it into a combustible substance, the idea arose of using nitrocellulose as a propellant instead of blackpowder. Schönbein's experiments [1], repeated by Pelouze [2], showed the high energy of nitrocellulose. It was found that a charge of nitrocellulose endows a projectile with a penetrating effect similar to that of a triple charge of blackpowder.

The primary difficulty in exploiting this property lay in finding a method for manufacturing nitrocellulose. It was not until large-scale manufacture of nitrocellulose was achieved by Lenk [3] that propellant charges could be used for Austrian artillery. Shortly afterwards, however, this method proved to be unsatisfactory, due to the variable results obtained and to the excessive pressure developed when firing nitrocellulose charges, which in many instances damaged or even blew up the cannon.

Earlier observations that nitrocellulose burns very quickly in a confined space— much more quickly than blackpowder— were confirmed. Since it is difficult to reduce the burning rate by physical methods only, e.g. by compressing the nitrocellulose to increase its density, attempts were made to slow down the rate of burning by the addition of "phlegmatizing" substances, such as glues, waxes, fats etc.

Partly successful results were obtained by Schultze [4] who prepared his powder by the following method. Wood cut into 1–2 mm grains was purified by boiling in sodium hydroxide solution and bleaching with calcium hypochlorite. It was then nitrated with a mixture of nitric and sulphuric acids. The nitration product was stabilized by boiling in a sodium carbonate solution, then dried and impregnated with a solution of either potassium or barium nitrate. After drying the grains were polished in a drum with paraffin wax to form a powder of the following composition:

50%	nitrocellulose and nitrated hemicelluloses
13%	non-nitrated wood pulp
33%	potassium and barium nitrates
4%	paraffin

This powder, however, was still too fast-burning for use in military rifles, but was found suitable for use in shot guns, and was a forerunner of propellants of the "Schultze type" used in some countries (chiefly Great Britain) as sporting powders.

A few years later it was discovered that nitrocellulose dissolves in organic solvents, such as acetone, ethyl acetate and in mixtures of alcohol with ether, leaving on evaporation of the solvent a highly dense, transparent film, which burns more slowly than nitrocellulose itself (Hartig [5]).

Some investigators tried to make use of this property. Volkmann [6] improved Schultze's powder by dipping nitrated grains of wood into a mixture of ether and alcohol and then either mixing them with blackpowder to prevent caking and coating them with a layer of this explosive or compressing the sticky grains into larger cubes. In spite of the encouraging results obtained in using this powder (the size of charges required was half of that of blackpowder) the Austrian authorities stopped manufacture on the formal grounds that the plant concerned infringed their blackpowder monopoly.

A number of patents were then registered for various methods of using solvents to prepare granular powder from nitrocellulose (Spill [7], Reid [8], Wolf and Förster [9]). None of those methods, however, found practical application, except for a short time in the work of Duttenhofer at Rottweil [10]. Duttenhofer nitrated slightly carbonized cellulose, stabilized it and saturated the nitrocellulose so obtained with ethyl acetate until a gelatinized mass was formed. After being dried the horn-like mass was broken up in a corning mill and the grains so obtained were graded. Clearly, Duttenhofer employed virtually the same production method as that used to manufacture blackpowder.

Duttenhofer's powder was used for a certain time in Germany under the name of RCP (Rottweil Cellulose Pulver). Its greatest disadvantage was the irregularity of the shape of the grains which prevented it from burning as uniformly as the smokeless powder [11] invented by Vieille at about the same time.

Vieille developed his powder as the result of systematic investigations. In 1879 he began a study of the burning of explosives in a manometric bomb which he invented together with Sarrau.

In the course of studying the burning of blackpowder Vieille found that it can burn in parallel layers provided that its specific gravity is approximately 1.80 or more (p. 340). He extended his experiments (1882–1884) to nitrocellulose, and tested its behaviour at various densities. Since it turned out that high specific gravity nitrocellulose cannot be achieved simply by pressing, Vieille made use of the recognized method of increasing its specific gravity by treatment with various solvents. He formed the dough-like mass into flakes and thin sheets which on drying showed a fairly high specific gravity (about 1.65). By experiments in the manometric bomb, Vieille demostrated that the flakes of the new powder burn in parallel layers and that this property makes their time of burning dependent upon their smallest dimension i.e. upon their thickness. Hence by altering this the total time of burning of the flakes may be controlled, and the "coefficient of the vivacity" (coefficient de vivacité) of the powder

$$\left(\frac{dp}{dt}\right)_{\max}$$

where p is pressure produced by burning the powder, t is time of burning, may be determined in the manometric bomb. Thus powders of an adequate vivacity adjusted to a given calibre of arms may be easily standardized.

Shortly afterwards (1885) Vieille's powder was introduced in France under the name of B powder (Poudre B). Vieille utilized two types of nitrocellulose for its manufacture: collodion cotton CP_2 (Vol. II, p. 373), soluble in a mixture of ether and alcohol and forming the powder dough; cotton CP_1, insoluble in a mixture of ether and alcohol, incorporated into the powder mass in the form of unchanged fibres.

In Russia, Mendeleyev [12] worked out a method for the manufacture of smokeless powder from pyrocellulose, i.e. relatively high-nitrated (12.5% N) nitrocellulose soluble in a mixture of ether and alcohol. In 1892 the manufacture of this powder was started for naval guns. Nitrocellulose powder of this type was soon adopted for military purposes in the U.S.A., where nitrocellulose powder became known as "single base powder".

A second type of smokeless powder, ballistite, was invented by Alfred Nobel [13] in 1888. He took advantage of the ability of nitroglycerine to dissolve nitrocellulose and thus replaced a volatile, non-explosive solvent (ether and alcohol in former powders) by a non-volatile explosive solvent—nitroglycerine. The ratio of nitrocellulose to nitroglycerine was 45:55. This is a relatively small amount of nitroglycerine which dissolves nitrocellulose with difficulty. Abel and Dewar [14] however succeeded in adapting acetone for the manufacture of nitroglycerine powder. This is a solvent of both the active ingredients: nitrocellulose and nitroglycerine. The product—British Cordite—has not been used outside the British Commonwealth. The powders made of nitrocellulose, nitroglycerine and a mixture of ether and alcohol as a solvent achieved only temporary success. The use of any solvent was troublesome and proved a drawback in manufacture, so that nitroglycerine powder without a volatile solvent, derived from ballistite, aroused much greater interest.

Work on the improvement of nitroglycerine powder without a volatile solvent was aimed at the reduction of its content of nitroglycerine. By the selection of a suitable nitrocellulose and by the addition of non-volatile solvents ("gelatinizing agents"), of the so-called "centralite" type ("carbamite" according to English nomenclature) as in Claessen's [15] patents, a new type of nitroglycerine powder, the so-called RP-12 or RPC-12, was manufactured from 1912 onwards (p. 652). This powder was used extensively during World War I since it could be produced much more quickly than nitrocellulose powder. The manufacture of this powder contributed largely to the long resistance of the Central Powers in World War I.

The enormous consumption of smokeless powder during this war led to difficulties in producing a sufficient quantity of nitroglycerine. In Russia and Germany attempts were made to replace part of the nitroglycerine by aromatic nitro compounds such as DNT or "liquid TNT" (an oily mixture of DNT and TNT with isomers of TNT). This powder had several advantages. In comparison with nitroglycerine nitro compounds give a powder with a lower temperature of explosion that produces less erosion and flash. Powders containing nitro compounds with nitroglycerine were later adopted in the U.S.S.R.

Attempts to replace nitroglycerine partly or wholly by nitroglycol had little success due to the high vapour pressure of the latter which facilitates volatization and, consequently, reduces its ballistic stability (ballistic properties change as nitroglycol volatilizes). Later, diethylene glycol dinitrate was tried (nitrodiglycol, DGDN) and was shown to have great advantages over nitroglycerine. With nitroglycerine, good gelatinization of the nitrocellulose may be obtained if the ratio of nitroglycerine to nitrocellulose is not less than 60:40, whereas with nitrodiglycol this ratio may be much lower, viz. 20–45 nitrodiglycol to 80–55 nitrocellulose, since nitrodiglycol is a better solvent of nitrocellulose than nitroglycerine. This facilitates manufacture and, at the same time produces a more uniformly gelatinized mass. Various alterations may also be introduced in the composition of powder such as an increase in the content of nitrocellulose or on addition of insoluble ingredients, serving, for instance, to suppress flash.

Solventless powder without nitroglycerine (G powder, p. 660) has a lower heat of explosion, and consequently causes less wear on the bore.

Gallwitz [16] reports the following data on the influence of the heat of explosion upon the bore wear. With a nitroglycerine powder containing no solvent and giving a heat of explosion of 950 kcal, the barrel stands up to 1700 rounds while with a similar powder giving a heat of explosion of 820 kcal, it withstands 3500 rounds. The reduction of the calorific value of the powder by 130 kcal therefore doubles the useful life of the barrel.

Further reduction of the calorific value of nitroglycerine powder proved to be impossible. But by using nitrodiglycol instead of nitroglycerine, a powder was obtained with a heat of explosion of 690 kcal, which prolonged the life of the barrel considerably, i.e. to 15,000–17,000 rounds.

Nitroglycerine or nitrodiglycol powder was known in the U.S.A. as "double base powder".

A further development led to the invention of flashless powder. Tests carried out in various countries, included the addition of aromatic nitro compounds to nitrocellulose powders and of potassium salts to nitroglycerine powders. Nitrodiglycol powder with an addition of 2% K_2SO_4 produced a small flash. During World War II in Germany and Great Britain it was the custom to add a considerable amount of nitroguanidine to nitrodiglycol powders. In Germany this was called "gudol" powder (German Gudol Pulver).

Other attempts to improve nitrodiglycol powders were based on the introduction of substances such as penthrite (German Nipolit Pulver) and cyclonite. In both cases a powder with a high calorific value was obtained. The manufacture of these powders never went beyond the pilot plant scale.

PROPERTIES OF SMOKELESS POWDER

PHYSICAL PROPERTIES

The specific gravity of semicolloidal nitrocellulose powder with a mixture of ether and alcohol as a solvent usually ranges from 1.54–1.63, although the specific gravity of nitrocellulose itself is 1.66. This indicates a certain porosity of the powder. The pores are filled either with air or with traces of residual solvent. According to Brunswig [17] 100 g of nitrocellulose rifle flake powder contains 4–8 cm^3 of the air.

Nitroglycerine powder—completely or almost completely wholly colloidal—is less porous, therefore more difficult to ignite than nitrocellulose powder and requires a stronger priming.

The gravimetric density* of a powder depends upon the dimensions and shape of the grains. A suitably high gravimetric density may be obtained by polishing the grains and coating them with graphite. Its value determines the extent to which a cartridge case or powder chamber can be filled with powder. Generally, to make the most of the capacity of a cartridge case or powder chamber the gravimetric density should be as high as possible. E.g. by raising the value for smokeless powder from 0.770 to 0.830, the charge for a rifle was increased from 2.65 to 3.2 g and this led to an increase in muzzle velocity and range.

Occasionally it may happen that the gravimetric density of a powder is too high, in which case a considerably part of the chamber space or cartridge case remains empty. Then ignition may prove unreliable and burning not quite uniform. According to Brunswig [17], for instance, powder with a gravimetric density of 0.850 gave 0.07% misfires and 1.2% hangfires per 22,000 rounds, while a powder with a gravimetric density of 0.820 showed no such disadvantage.

Nitrocellulose powders (semicolloidal) are moderately hygroscopic; in an atmosphere saturated with water vapour they attain 2.0–2.5% moisture content. Nitroglycerine powders (colloidal) are virtually non-hygroscopic. (The hygroscopicity of nitrocellulose was discussed in fuller detail in Vol. II, p. 283.) This is accounted for by the fact that the nitrocellulose in the latter powders has a colloidal form of low hygroscopicity. By using such gelatinizing agents as DNT instead of nitroglycerine, the hygroscopicity of nitrocellulose powders was reduced. In the U.S.A. these powders were known under the name of NH-Powder (non-hygroscopic powder).

EXPLOSIVE PROPERTIES

Products of decomposition

The products of decomposition of smokeless powder resemble those formed by the decomposition of its ingredients, i.e. nitrocellulose or nitrocellulose with either nitroglycerine or dinitrodiglycol.

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* **Gravimetric density = the weight of the charge in a unit volume (e.g. kg in litre).**

In nitrocellulose powder the chief products of explosive decomposition are inflammable gases: CO, H_2 and CO_2, H_2O, N_2. In nitroglycerine powder the average composition of the gases is similar, but owing to the more advantageous oxygen balance the amounts of complete combustion products (CO_2 and H_2O) are higher. In the products of the decomposition of smokeless powder methane is also found in small amounts and sometimes also hydrogen cyanide or carbon.

The composition of the decomposition products of powder varies, depending on many factors, the most important of which is the pressure in the powder chamber and in the bore of the gun. The pressure, in turn, depends mainly upon the density of loading. Thus, for instance, the decomposition products obtained from the same powder vary according to the density of loading (Table 161): the amount of CO_2 and CH_4 increasing, and that of CO and H_2 decreasing as density increases.

TABLE 161

AMOUNTS OF DECOMPOSITION PRODUCTS OF POWDER IN RELATION TO DENSITY OF LOADING

Δ	Pressure kg/cm²	CO_2	CO	CH_4	H_2	N_2	H_2O
0.1	730	9.6	44.8	0.7	20.7	10.3	13.9
0.3	3200	16.4	38.4	5.5	13.2	13.3	13.2

This may be deduced from the following equation, which takes place with reduction in volume:

$$CO+3H_2 \rightleftarrows CH_4+H_2O+57.8\text{ kcal}$$

The reaction is exothermic, hence as the gases cool the reaction equilibrium is shifted to the right.

The decomposition products of a given powder differ at various distances from the muzzle since temperature and pressure decrease considerably with the movement of the projectile along the bore. Brunswig [17] reported the following figures for the German M/88 rifle (Table 162).

TABLE 162

Travel of the base of the projectile mm	Temperature of gases °C	Pressure kg/cm²
200	1426	1385
300	1202	834
400	1060	577
500	965	434
600	877	339
693 (muzzle)	818	280

In addition to the above reaction the following dissociation reactions also take place:

$$2CO_2 \rightleftarrows 2CO + O_2 - 135.2\ \text{kcal}$$

$$2H_2O \rightleftarrows 2H_2 + O_2 - 115.6\ \text{kcal}$$

Here rise in temperature favours the displacement of the equilibrium to the right, whereas increase of pressure displaces the equilibrium to the left.

Poppenberg and Stephan [18] showed that pressure affects the system more strongly than temperature, so that the content of CO_2 grows and that of CO falls as the projectile moves towards the muzzle. The ratio CO_2:CO at different positions along the bore varies as shown in Table 163.

TABLE 163

Travel of the projectile cm	18	28	50	70
$\frac{CO_2}{CO}$	0.298	0.324	0.362	0.393

Among the reactions which proceed inside the bore, the following is noteworthy:

$$CO + H_2O \rightleftarrows CO_2 + H_2$$

The reaction is exothermic and the equilibrium is displaced to the left as the temperature rises (Table 164).

TABLE 164

Temperature °C	$K = \frac{[CO][H_2O]}{[CO_2][H_2]}$
1600	4.24
1405	3.48
1086	2.04
886	1.19
686	0.52

The nitrogen present in the form of nitrate groups in the ingredients of the powder is almost completely transformed into molecular nitrogen N_2 in the final products of the reaction. A small amount of nitrogen, however, may remain in a form of nitrogen oxides, especially if the powder is burnt at a low pressure. Sometimes muzzle gases contain ammonia which is easy to detect by smell. Ammonia is formed by the reaction

$$N_2 + 3H_2 \rightleftarrows 2NH_3 + 22.0\ \text{kcal}$$

which proceeds while there is still considerable pressure as the gases cool. This reaction is promoted by the presence of iron particles in the propellant gases.

Diagrams (Fig. 184) show the effect of the density of loading of nitroglycerine and nitrocellulose powder upon the amount of CO_2, CO, H_2 and CH_4 evolved (according to Andrew Noble [19]) in the explosion products.

Nitroglycerine powder—cordite—gives a better proportion of more completely oxidized products.

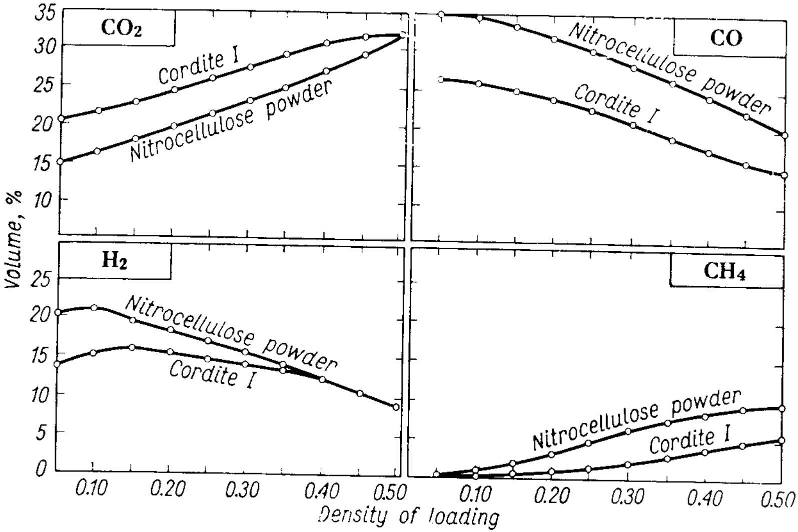


FIG. 184. Proportion of CO_2, CO, H_2 and CH_4 in products of explosion of cordite and nitrocellulose powder as a function of density, according to Brunswig [17].

Gases may escape from the barrel through the breech end after the breech block has been opened. They may be toxic to the gun detachment if the breech end is situated in a confined space (naval gun turret, concrete pillbox, tank etc.). A flow of air to remove them is therefore essential. Similar hazards arise due to backflash.

Knight and Walton [20] examined the products produced by burning powder in a confined space, simulating a naval gun turret. Ten seconds after the ignition of 32 kg of powder, the estimated composition of the gases in the test container (about 25 m^3 in capacity) was:

NO	1%
NO_2	7%
CO_2	17%
CO	28%
H_2	8%
CH_4	2%
N_2	37%

After 20 sec the powder had burnt completely and fresh air was introduced into the container. The hot combustion products exploded again on being mixed with air. The estimated composition of the products after the second explosion was:

NO_2	1%
CO_2	8%
CO	9%
O_2	12%
N_2	67%

Due to the presence of NO_2 and CO the gaseous products were very toxic to experimental animals.

Heat of explosion, volume of gases and temperature of the explosion products

The heat of explosion depends chiefly on the composition of the powder, e.g. in nitrocellulose powder on the content of nitrogen in the nitrocellulose and in nitroglycerine powder on the content of the nitroglycerine.

The effect of the composition of the powder, in particular of the content of nitroglycerine upon the volume of gases, heat and temperature of explosion is illustrated by the figures in Table 165 (according to Brunswig) and by the curves in Fig. 185 (on the basis of another series of experiments by the same author).

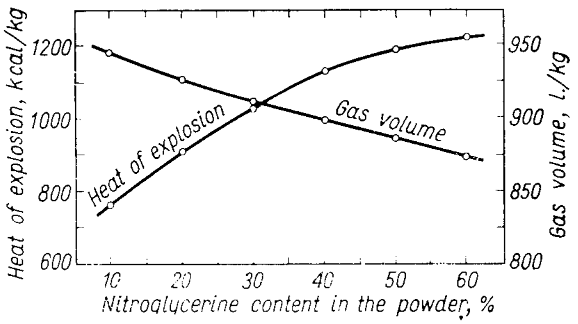


FIG. 185. Gas volume and heat of explosion of nitroglycerine powder as a function of the proportion of nitroglycerine in the powder [17].

TABLE 165

Composition of powder	1	2	3	4	5	6
Nitroglycerine	30	36	40	47	58	–
Nitrocellulose	65	52	50	53	37	100
Other non-explosive ingredients (centralite, vaseline etc.)	5	12	10	–	5	–
Volume of gases, V_0 (l./kg)	913	910	900	810	875	934
Heat of explosion (kcal/kg)	1030	935	1005	1090	1250	924
Temperature, t (°C)	2470	–	–	2850	2825	2230

Generally speaking, nitroglycerine powders give a higher heat of explosion, so that the temperature of their products is higher than that in nitrocellulose powders.

This means that nitroglycerine powders are more erosive (greater bore wear) (p. 548) and more flashy (p. 544).

Non-explosive substance (e.g. vaseline) are added to nitroglycerine powders to reduce the heat of explosion and the temperature of the flash. The addition of "cool" explosives such as nitroguanidine has the same effect.

The phenomenon of burning smokeless powder has been the subject of many investigations. Usually they are described in text-books on ballistics [21]. Here only a few essentials will be dealt with.

According to the Soviet authors Belayev and Zeldovich [22] the burning of colloidal or semicolloidal powder consists of the following stages:

(1) decomposition of the solid and formation of gases,

(2) reaction between the gases leading to a considerable increase of the temperature. The temperature of the solid surface remains relatively low.

This theory is diagrammatically represented by Fig. 186, according to Zeldovich [21]. The thickness is denoted by X.

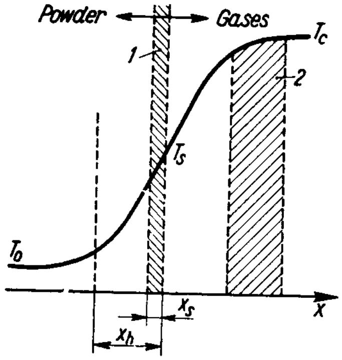


FIG. 186. Temperature distribution in a powder grain of thickness X, according to Zeldovich [21]; T_0—temperature inside the grain, T_s—temperature on the surface, T_c—temperature of the combustion flame.

The chemical reactions of gas formation occur in zone (*1*) of X_p thickness; reaction between the gases occurs in zone (*2*). The temperature inside the powder is T_0, in zones (*1*) and (*2*) is T_s and T_c respectively.

Inside the powder grain a superheated layer exists of thickness X_h. Here decomposition starts in the part denoted X_s.

The thickness of X_s is very small and forms only about 5% of the total thickness X_h. Heat is transmitted by conductivity, convection and radiation. The rate of burning of smokeless powders is determined by the rate of transmission of the energy from the products of combustion to the powder itself.

It is generally accepted that colloidal and semicolloidal powder burns in parallel layers. In fact this should be considered as an approximation as the burning surface is uneven and covered with pits products by the "hotter" spots.

Rideal and A. J. B. Robertson [23] suggest that initiation of the thermal explosion of nitrocellulose is preceded by liquefaction. Very likely the same would apply to nitrocellulose powder.

Huffington [24] studied the combustion of solventless cordite containing 56% nitrocellulose (12.2% N), 29% nitroglycerine, 4.5% carbamite and 10.5% dinitrotoluene plus 2.45% cryolite and 0.35% volatile matter.

He concluded that the burning of cordite is essentially an intermittent phenomenon in which periods of quiescence are followed by abnormally rapid burning. Under certain circumstances, there is a tendency towards the end of a rapid burning stage for the more stable components of the cordite (such as dinitrotoluene) to remain undecomposed or only partially decomposed relative to the other components.

These experiments appear to throw a new light on the structure of solventless cordite. It seems that nitroglycerine is present as minute globules and that the second type of intermittent burning is due to the non-thermal explosion of these globules.

A simple exponential equation proposed by Vieille [11] is very often used to denote the rate of burning (v) of colloidal and semicolloidal powders (i.e. powders burning approximately in parallel layers);

$$v = kp^n,$$

where k is a constant, p pressure, n an exponent.

For semicolloidal powder Vieille found $n=0.67$. Zabudskii [21] later established $n=0.93$.

Since smokeless powder burns by parallel layers the shape of the powder grains can have a decisive influence on the mode of burning: neutral (with an approximately constant burning surface), progressive (increasing surface), degressive (decreasing surface) (Fig. 187).

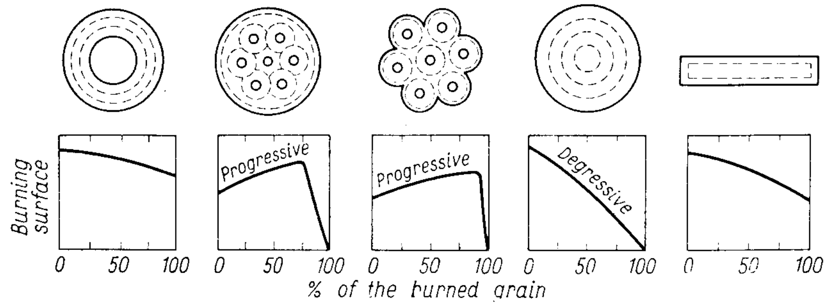


FIG. 187. Modes of burning of perforated grains and cords. The dotted lines represent approximately the positions of the inward and outward burning, according to [25].

The neutral and progressive types are most valuable.

Klein, Menster, Elbe and Lewis [26] recorded the flame temperature of burning smokeless powder using thermocouples and found in the vicinity of the burning surface layer about 0.6 mm in thickness in which there was a sudden jump in temperature to 1200°C at pressures 25–50 kg/cm^2. They calculated from the figures obtained that the temperature of the surface of the powder immediately before burning was 250°C.

The temperature of the explosion products of smokeless powder (flame temperature) is dependent on the density of loading, increasing as the density increases. This is illustrated by the diagram in Fig. 188. A particularly notable rise of temperature with density of loading is observed in nitrocellulose powders or those nitroglycerine powders which are poor in nitroglycerine and hence in oxygen.

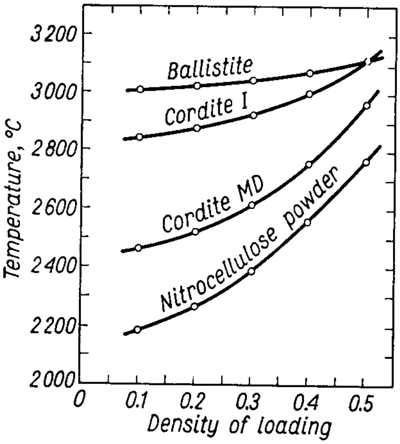


FIG. 188. Temperature of the explosion flame of powders as a function of density, according to Brunswig [17].

A knowledge of the heat of explosion of smokeless powder is of considerable practical importance since the muzzle velocity of the projectile depends largely on this factor. For this reason the heat of explosion of manufactured powder must be checked from time to time. If the heat of explosion of a given lot of powder deviates from the specified value, then the necessary size of charge should be calculated to match the standard muzzle velocity. For this the empirical formula

$$CQ = K$$

is used, where C denotes the charge of powder, Q — the heat of explosion of 1 kg of powder, K — a constant quantity for a given projectile and a given muzzle velocity, irrespective of the type of powder.

Thus, for instance a charge of 4.3 kg of powder with a heat of explosion equal to 820 kcal/kg gives the same muzzle velocity as a charge of 6.0 kg of powder with a heat of explosion equal to 590 kcal/kg.

J. Taylor [27] drew up the following table of the heat of explosive decomposition, the gas volume and rate of burning of British nitroglycerine (double base) and American nitrocellulose (single base) powders (Table 166).

TABLE 166

Nitrocellulose powders (U.S.A.)	Heat of explosive decomposition (water liquid) kcal/kg	Gas volume (water vapour) l./kg	Linear coefficient for rate of burning from one surface in./sec/in^2
Pyro Cannon Powder	875	955	0.40
NH Cannon Powder	765	978	0.38
FNH Cannon Powder	740	1005	0.355
Nitroglycerine powders (Great Britain)			
Cordite MD	1025	940	0.595
Cordite WM	1013	934	0.575
Cordite SC	970	957	0.50
Cordite NQ	880	1001	0.375
Cordite N	765	1058	0.315

In the German Army nitroglycerine powders (double base powders) possessed the following calorific values: 1250, 1150, 950 and 820 kcal/kg.

The diglycoldinitrate powders were characterized by calorific values: 930, 740, 690 kcal/kg (according to Gallwitz [16]).

Sensitiveness to impact and friction

Smokeless powders have low sensitiveness to impact and friction. They do not ignite when hit by rifle bullets and are thus fairly safe to handle in war-time. Nevertheless there have been accidents caused by the sudden ignition of nitrocellulose powder brought about by the violent friction between the sharp edge of a heavy bin and powder scattered on the floor.

Nitrocellulose powders is particularly sensitive to friction when hot. Accidents have been caused by the ignition of hot powder on removal from the drier, in all probability due to friction. Here electrification of the powder on drying also plays an important part (see below, pp. 542, 616) giving rise to the possibility of an electric discharge while it is being taken out. This had led to the regulation that the powder must not be taken out of the drier before it has been cooled.

Nitrocellulose powder is more sensitive to friction than nitroglycerine powder, although the latter is more sensitive to impact (due to the presence of nitroglycerine).

Sensitiveness to detonation

According to Kast [28] nitrocellulose powder does not detonate even when very strongly initiated (e.g. 50 g of picric acid or 100 g of tetryl), but may explode with a rate from 1000 to 1800 m/sec.

Conversely, T. Urbański and Galas [29] found that smokeless powder detonates with a rate from 3800 to 7000 m/sec when initiated by 20 g of picric acid, the rate of detonation depending either on the density of loading or, in wide strip powders, on whether the detonation wave travels perpendicularly or in parallel with the surface of the strips. The figures compiled in Table 167 are characteristic of the phenomenon observed (the powder was placed in iron pipes 26/33 mm dia., and 20 g of picric acid was used for initiation).

TABLE 167

Type of powder	Way of loading	Density	Rate of detonation m/sec
Nitrocellulose powder			
Rifle flake non-polished powder	loosely poured	0.79	3800
Rifle flake polished powder	loosely poured	0.93	5300
Cannon strip powder French type BC, 0.55 mm thick	circles laid perpendicularly to the tube axis	1.45	7010
Nitroglycerine powder			
Ballistite, 1.3 mm thick	circles laid perpendicularly to the tube axis	1.53	7445–7615
Ballistite, 3 mm thick	circles laid perpendicularly to the tube axis	1.52	7720–7125

If powder strips or tubes are laid along the axis of the bore the powder is much more difficult to detonate. A stronger initiator is required and not infrequently explosion occurs with a rate of about 1500 m/sec, instead of a detonation. The figures listed in Table 168 refer to the same conditions of initiation (20 g of picric acid) in a pipe 26/33 mm.

Médard [30] also described experiments which were carried out in France by Vieille as early as 1906, Dautriche (1913), Burlot (1920–26) and by himself in 1938. Dautriche found that nitrocellulose powder BM 17 D2 in bands of thickness *ca.* 44 mm detonated at the rate of 6560–7200 m/sec when initiated by 50 g of picric acid.

Burlot found similar figures. He also examined the effect of the impact of a falling weight or of a rifle bullet. Only deflagration occurred — there was no detonation. However in his later experiments Burlot [31] has found that nitrocellulose powder (poudre BM9—in strips) can detonate under the shock produced by a rifle bullet "D" (caliber 8 mm, 7.5 g) having a velocity above 1200 m/sec (e.g. 1266 m/sec).

Ignitability

The ignition temperature of nitroglycerine smokeless powder is approximately 180°C and that of nitrocellulose powder about 200°C. Ignition with a direct flame, especially of nitroglycerine powder, is rather difficult. In practice an indirect priming of blackpowder is used, the latter being ignited with a priming cap.

It has long been known that smokeless powder is readily electrified and that an electric discharge may cause its ignition. When dried it is particularly readily electrified by the frictions produced by the current of warm, dry air. The powder is also subject to very strong electrification when polished due to friction of the grains against each other and against the wooden balls.

TABLE 168

Type of powder	Way of loading	Density	Rate of detonation m/sec
Nitrocellulose powder			
BC strip powder 0.55 mm thick	strips laid along the bore	0.95	1495–1150 (explosion)
Nitroglycerine powder			
Ballistite 1.3 mm thick	strips laid along the bore	1.23	no detonation
Ballistite 3 mm thick	strips laid along the bore	1.24	2250–1965

According to Nash's [32] studies, nitrocellulose EC powder is electrified under the effect of an air current at a temperature of 65°C. The drier the powder, the more it is electrified. The dependence of voltage on the moisture content of the powder is shown in the diagram (Fig. 189). As can be seen, powder with a moisture of over 1% cannot easily be electrified. Dry EC powder can be electrified up to 300 V. Colloidal powder is electrified even more strongly. E.g. pyrocellulose powder gelatinized with a mixture of alcohol and ether, when heated to 50°C, can be charged up to 3200 V under the influence of a warm air current. After being cooled to 15°C

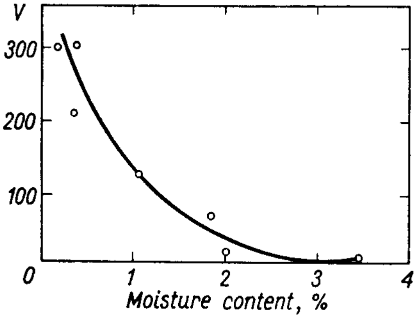


FIG. 189. Electric (static) charge of nitrocellulose powder as a function of moisture content, according to Nash [32].

and subjected to a cold air stream the voltage falls in 5 min to 2200 V, and after 20 min to 900 V, after which the latter voltage remains constant. Powder electrified to 2300 V maintains a charge of this voltage for a long time if not subjected to a cold air stream.

Nash proved experimentally that a discharge of accumulated electricity may cause EC powder to ignite if the voltage reaches 20,000 V. On this basis he came to the conclusion that EC powder cannot take fire in the drier under the influence of electric discharges since for its ignition a charge of higher potential is needed than that to which it can be charged on drying. Nevertheless the many accidents which have occurred by the ignition of hot powder when taken out of the drier appear have been caused by the discharges of static electricity (sensitization of the powder to friction due to heating may also be possible here, as mentioned above, p. 540).

A number of explosions of smokeless powder during polishing are also attributable to electrification and subsequent discharge of electricity. In practice the careful earthing of the drums used for polishing is a sufficient safeguard. A danger can also be produced if the solvent (particularly ether) is charged with static electricity and then discharged with sparking. This is dealt with later on p. 589.

Langevin and Biquard [33] showed that the evaportion of a liquid (alcohol, ether, benzene) does not electrify the residual solvent. Hence evaporation of the solvent in driers cannot lead to electrification of the powder. In the opinion of these authors nitrocellulose powder may be ignited by the discharge of the condenser at a voltage of 3000 V, if the condenser charge is greater than 0.3 μF.

According to the work of Brown, Kusler and Gibson [34] dry nitrocellulose can be ignited by a discharge of 0.062 J energy, nitrocellulose smokeless powder may be ignited by a discharge of 4.7 J energy whereas graphitized powder is much more difficult to ignite, requiring an energy of over 12.5 J. English authors (Morris [35]) believe these figures should be considerably lower: 0.3–0.6 J.

The French Comité Scientifique des Poudres [36] collected statistical data indicating that 75% of the accidents involving ignition occurred with completely dried powder; of these 41% were caused by the electrification of the powder by friction, and 34% by other, undefined reasons (e.g. insufficient chemical stability of powder). The remaining 25% of all accidents involving ignition were caused by the fact that the powder contained a considerable amount of solvent. Of these cases, 19.5% arose from electrification of the powder itself by friction, and 5.5% by electrification of the solvent. Generally speaking, electrification proved to be the source of 60% of the accidents in which the powder ignited.

MECHANICAL PROPERTIES

Mechanical properties of double base powders mainly for large rockets will be discussed later (pp. 675 and 678).

FLASH AND METHODS FOR SUPPRESSING IT

The discharge of a gun is almost always accompanied by a glaring flash which at night discloses its position. Experiments, particularly using cine-films, give the following picture of how flashes arise.

The "primary flame" in the form of a dark-red taper is created by inflammable gases escaping from the bore. These gases mix with the air to form an inflammable mixture. If the temperature of the mixture is sufficiently high, it ignites at the end furthest from the muzzle (Fig. 190).

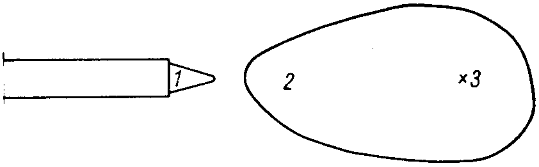


FIG. 190. Muzzle flame: *1*—primary flame, *2*—secondary flame, *3*—initiation of the secondary flame.

The burning of the mixture may end with an explosion (detonation) if its composition is suitable. The explosion of the gas mixture is accompanied by a bright flame. This "secondary flame" is elliptical and visible for a great distance. The dimensions of the flame and the intensity of the flash depend to a great extent on the calibre of the gun; e.g. a shot from a 30 cm naval gun gives a secondary flame up to 50 m long, visible for a distance of 50 km.

The following circumstances favour the formation of a secondary flame:

(1) The presence of gases that form inflammable mixtures in the gaseous products formed by the explosion of the charge (in the muzzle gases).

(2) High temperature of the muzzle gases.

On the other hand the presence among the products of explosion of substances that prevent the explosion of the gas mixtures reduces the possibility of the secondary flame.

The most important inflammable components are hydrogen, carbon monoxide and methane, which form explosive mixtures with air. Gas composition has been discussed earlier in this chapter (p. 532).

According to Roszkowski [37] the explosive limits for these gases with air are:

Hydrogen	9.2–68.5%
Carbon monoxide	13.0–77.6%
Methane	5.5–13.2%

Methane has the narrowest limits so that a shot in which a large amount of this gas is generated is unlikely to produce a secondary flame. A high pressure in the bore favours the formation of a large proportion of methane (p. 533), hence a high charge density reduces the probability of the secondary flame.

Another factor in reducing the likelihood of a secondary flame is an increase in the concentration of non-flammable gases (CO_2 and N_2) in the products formed by explosive decomposition of the powder. Since the nitrogen content in these products is limited by the nitrogen content of the powder, the only factor that can be varied to any extent is the content of carbon dioxide. High pressure and low temperature promote reactions for the formation of CO_2 (p. 534). Coward and Hartwell [38] claim that the explosive limits of a methane–air mixture are narrowed by adding CO_2 or N_2 (Fig. 191). Methane–air mixtures containing about 50% CO_2 are non-explosive.

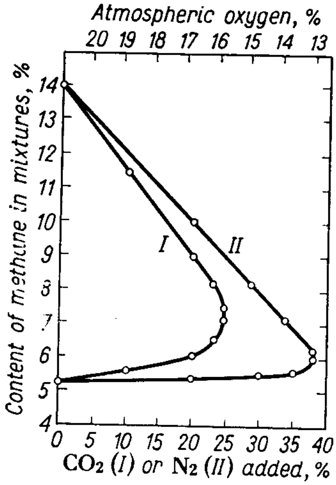


FIG. 191. Change of limits of explosibility of methane–air mixtures under the influence of added CO_2 (curve *I*) and N_2 (curve *II*) according to Coward and Hartwell [38].

The presence of water vapour in a methane–air mixture may exert the same effect as the presence of CO_2, but small amounts of water vapour increase the possibility that the gas mixture will explode. This accounts for the observation that the secondary flame develops much more easily when the firing takes place in a moist atmosphere.

Another component favouring explosion in gas mixtures is nitrogen dioxide which may occur in small amounts as a result of incomplete decomposition of the powder.

The temperature of the propellent gases depends on the heat of explosion and on the gas composition. The greater the heat of explosion, and hence the temperature of gases, the more readily the secondary flame arises. Powders of a low calorific value may therefore give no secondary flame if the temperature of the gas mixture is lower than the temperature of ignition.

The ignition temperatures of the most important gaseous components of the explosion products (H_2, CO and CH_4) in methane–air mixtures lie within the following limits:

Hydrogen	390–620°C
Carbon monoxide	610–725°C
Methane	730–790°C

This shows clearly the advantage of shifting the equilibrium towards the formation of a larger proportion of methane.

From a large number of practical data, it has been deduced that a powder will be flashless if on decomposition the heat emitted is below a certain limiting value. The heat effect of the explosion depends on the type of ordnance, i.e. on the calibre and length of the barrel, ranging from 800 kcal/kg for big guns to 1000 kcal/kg for smaller ones. "Flashlessness" can therefore be achieved either by adding active (explosive) components that lower the heat of explosion, (e.g. nitroguanidine, DNT) or inert (non-explosive) ones such as vaseline, centralite etc., to the propellant.

Substances inhibiting the development of the secondary flame are those which inhibit burning reactions. The strongest of the substances known to possess this property is the potassium ion. Its ability to prevent the development of a secondary flame was demonstrated by Dautriche [39] as early as 1908. Since then potassium nitrate has been employed in the manufacture of flash-reducing charges added to the charges of ordinary propellant.

Fauveau and Le Paire [40] proved that the addition of substances such as chlorides of alkali metals and alkaline earths to the charge reduces their tendency to develop a secondary flame; here the result is achieved by inhibiting the reaction of explosion, not by reducing the temperature of the gases. This is proved by the fact that salts of alkaline earths (e.g. $CaCl_2$) and of metals which have a high heat of evaporation and a considerable heat of decomposition at a high temperature, do not prevent the formation of secondary flame. Conversely, a typical inhibitor of gas explosions is potassium chloride which has neither a high heat of evaporation nor dissociates at temperatures reached within the barrel.

TABLE 169

EFFECT OF KCl ON THE IGNITION TEMPERATURE OF MIXTURES OF CO WITH AIR

Content of KCl in mg per litre in the gas mixture	Ignition temperature (°C) of the mixture with air containing		
	24.8% CO	44.1% CO	67.3% CO
0	656	657	680
0.4	–	750	800
0.5	730	–	820
0.7	–	810	900
1.0	790	850	1020
1.3	810	–	–
2.0	890	950	–
2.5	–	1000	–
3.0	970	–	–
3.5	1010	–	–

Prettre [41] found that potassium chloride sprayed in a mixture of carbon monoxide and air considerably raises the ignition temperature of these mixtures (Table

169), but it does not affect the ignition temperature of mixtures of hydrogen with air.

It has been shown that potassium chloride lengthens the induction period (the interval between the time the heating of gas mixture begins and the moment of explosion). Pease [42] found that in a vessel with walls coated internally with potassium chloride, the reaction of hydrogen with oxygen undergoes considerable inhibition, the induction period being lengthened one thousand times. The action of potassium ions is now explained by their capacity to initiate the combination of free H and O atoms and OH radicals into inert molecules, thus breaking chain reactions.

Free atoms of hydrogen and oxygen and OH radicals arise as a result of the following chain reactions:

$$\begin{aligned} H_2+O_2 &\rightarrow 2OH \\ OH+H_2 &\rightarrow H_2O+H \\ H+O_2 &\rightarrow OH+O \\ O+H_2 &\rightarrow OH+H \\ CO+OH &\rightarrow CO_2+H \end{aligned}$$

Examination of the flame spectrum of a mixture of hydrogen and oxygen does indeed point to the fact that hydrogen atoms and hydroxyl radicals take part in this reaction. The presence of OH radicals as intermediate products of the reaction between hydrogen and oxygen was demonstrated by an examination of the absorption spectrum of a mixture of these gases heated to a high temperature (over 1000°C) and by an examination of the absorption spectrum of water vapour at a temperature of 1500°C and higher (Bonhoeffer and Reichardt [43]; Avramenko and Kondratyev [44, 45]; Dwyer and Oldenberg [46]). Examination of the course of gaseous explosive reactions by kinetic absorption spectroscopy, invented by Norrish and Porter [47] is particularly noteworthy. By this method Norrish *et al.* [47–49] established the presence of the OH radical as an intermediate product in the reaction of hydrogen with oxygen, in the burning of hydrocarbons in an atmosphere of oxygen and in the other reactions in which water is one of the final products. Potassium ions promote the following chain-breaking reactions:

$$\begin{aligned} H+H &\rightarrow H_2 \\ H+OH &\rightarrow H_2O \\ O+O &\rightarrow O_2 \\ CO+O &\rightarrow CO_2 \end{aligned}$$

Investigations showed that the salts of other alkali metals are not so efficient in suppressing secondary flame as potassium salts. Fairly numerous experiments were carried out to clear up whether or not known antiknock substances, such as tetraethyl lead or nickel carbonyl prevent the development of a secondary flame. They proved to have no effect on its development. In practice, two methods for removing gun-flash may be employed, i.e. either a special flashless powder is produced, containing nitroguanidine or DNT and a small admixture of potassium sulphate, or special flash-reducing charges containing potassium salts are added to the charges of smokeless powder. Potassium salts are often mixed with a weakly explosive substance (e.g. DNT) to facilitate the dispersion of potassium salt in the mixture of gases. The majority of the methods for removing flash, however, lead to an increase in smoke. The best results, in this respect, are obtained by the addition of nitroguanidine to the propellant. This either does not increase the smoke at all, or increases it only to an insignificant extent (smoke formation will be discussed later).

The combustible ingredients in the products formed when a propellant charge explodes give rise to backflash. This may arise when the breech-block of the gun is opened due to the air-current which is then created in the barrel. This air-current may be intensified by wind blowing in the direction opposite to the direction of fire. Then ignition of the hot gases mixed with air often results from the smouldering residue in the barrel (smouldering remainder of the cartridge bag, glowing soot). Sometimes the gases do not stop burning after a shot and continue to burn after the opening of the breech-block. Backflash creates a great danger for the gun crew since it may cause the ignition of the charges of powder prepared for subsequent shots or introduced into the barrel.

As with secondary flame, the addition of potassium salts to the powder prevents the development of backflash. In modern guns of heavy calibre the development of backflash is prevented by blowing either air, or a stream of water through the barrel, immediately after each shot.

SMOKE FORMATION

Nitrocellulose and nitroglycerine powders should properly be called "slightly smoky"; the name "smokeless" is inexact. The smoke from nitrocellulose and nitroglycerine powders is composed chiefly of water vapour. Shots from small arms or cannons of small calibre are slightly smoky or almost smokeless. Conversely guns of heavy calibre often give a considerable amount of smoke. The presence of metal torn off from inside the barrel and from the driving band in the products of combustion of the propellant is a partial cause of smoke.

It has been observed that the majority of remedies for preventing the development of flash lead to an increase of smoke (e.g. potassium salts give white smoke, aromatic nitro compounds give black-grey smoke due to the presence of unburnt carbon). Nitroguanidine is the only additive that does not appreciably increase smokiness. The burning of blackpowder in the primer produces an insignificant amount of smoke.

EROSIVENESS OF SMOKELESS POWDER

Every powder produces erosion or bore wear to some extent. After a large number of shots the wear may be considerable, especially in large guns, and this reduces their accuracy. The erosiveness of a given powder depends, first of all, on its flame temperature. Nitroglycerine powders cause particularly severe erosion due to their high heat of explosion; they have a higher flame temperature than nitrocellulose powders. Attempts to reduce the heat of explosion of nitroglycerine powder by the addition of explosively inert substances (vaseline, centralite) or active substances of a lower heat of explosion (DNT) were primarily intended to decrease erosion.

Vieille [11] conducted extensive experiments on erosion in a manometric bomb, closed except for a small orifice, about 1.3 mm dia. in a metal plug (Fig. 192). Hot gases escaping through the orifice, eroded it to an extent determined by weighing the plug before and after each experiment: the loss of weight was taken as a measure of the erosiveness of the powder. Vieille showed that pressure lower than 1000 kg/cm² had little effect on erosion. Erosion increased with pressure over the range from 1000 to 2000 kg/cm² after which a further increase of pressure from 2000 to 4000 kg/cm² had no effect.

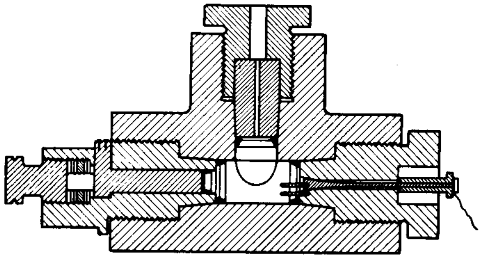


FIG. 192. Erosion bomb of Vieille [11].

The erosion of metals varied depending largely on the melting point. For various metals erosion expressed in mm³ of metal removed from the orifice per 1 g of powder was:

Platinum	59 mm³
Platinum–iridium	74 mm³
Brass	326 mm³
Zinc	1018 mm³

Vieille considered that erosion is caused by fusion of the metal and subsequent expulsion of the molten substance. The results of Vieille's experiments are summarized in Table 170. The weak erosive action of nitroguanidine, attributable to its low temperature of explosion, is noteworthy.

Apart from physical agents such as temperature and the mechanical action of gases, chemical agents also cause the erosion. Monni [50] noticed that the erosiveness of smokeless powder decreases with the addition of charcoal, probably because the additional quantity of carbon thus introduced serves to carbonize the steel which may undergo decarbonization under the influence of CO_2 at a high temperature, according to the reaction:

$$CO_2 + C \rightarrow 2CO$$

TABLE 170

EROSIVENESS OF VARIOUS POWDERS ACCORDING TO VIEILLE [11]

Type of powder	Charge	Pressure kg/cm2	Calculated temperature °C	Erosion mm3/g
Nitrocellulose powders				
Pistol T	3.55	2500	2675	7.4
Rifle BF	3.55	2200	2675	6.4
Nitroglycerine powders				
Ballistite 50% NG	3.55	2360–2540	3385	24.3
Cordite 38% NG	3.55	2500	—	18.1
Blackpowder				
Sporting (78% KNO_3)	8.88	1960	3530	4.5
Rifle (75% KNO_3)	10.00	2165	2910	2.2
Various explosives				
Blasting gelatine (94% nitroglycerine)	3.35	2460	3545	31.4
Nitroguanidine	3.90	2020	970	2.3

The decarbonization of steel increases the porosity of the metal. The adsorption of gases in the pores may intensify the erosive action; since the gases enter the pores at high pressures and temperatures and then expand, they "blow up" the pores.

The following factors reduce erosion:

(1) Low maximum pressure;

(2) Low temperature of explosion;

(3) Uniform ignition of powder, uniform burning and complete combustion;

(4) The largest possible content of H_2 and the smallest possible content of CO_2 and CO in the explosion products.

To minimize erosion it is desirable to use powders which give a heat of explosion of about 700 kcal/kg and a temperature of about 2100°C. The effect of the heat of explosion on the lifetime of the barrel has been dealt with earlier (p. 531).

STABILITY OF SMOKELESS POWDER

Soon after the manufacture of nitrocellulose smokeless powder began it was established that the powder obtained by the partial dissolution of nitrocellulose in a mixture of alcohol and ether (partly colloidal powder) has a chemical stability inferior to that of the nitrocellulose from which it derived. Thus Vieille [11] reports that on heating to a temperature of 110°C CP_1 guncotton undergoes denitration with the evolution of 0.04 cm^3 NO/hr/gramme whereas the powder obtained from these substances without a stabilizer undergoes denitration at more than twice the rate, namely 0.10–0.15 cm^3 NO/hr/gramme of substance.

Originally, the cause of this phenomenon was unknown. In all the countries producing smokeless powder methods for improving the stability of the powder were sought. Similar research was also initiated by Vieille but in spite of systematic experiments he arrived at the wrong answer. Vieille examined powders which had been stored for a long time and in which it was assumed that decomposition had started. He noticed that these powders contained less residual solvent than fresh powders, i.e. freshly manufactured powders contained approximately 1% of residual solvent (mainly less volatile ethyl alcohol) whereas the old powders contained considerably less than 1%. He therefore concluded than the stability of powder is lowered by the loss of residual solvent and its stability may be improved by adding a less volatile substance, chemically similar to the solvent. Indeed an improvement in stability was achieved (1896) by adding 2% amyl alcohol (the proportion being referred to the dry weight of the nitrocellulose). Ten years later, however (1906) it was noticed that these powders showed signs of decomposition, so the amount of alcohol added was increased to 8%. These powders were marked with the letters AM and a number indicating the content of amyl alcohol, thus AM 2, AM 8.

In 1905, on the Japanese battleship "Mikasa" some English nitroglycerine powder containing a certain amount of mercuric chloride, exploded. This substance interferes with the heat test (Vol. II, p. 23) and makes it impossible to detect the begining of decomposition in the powder. (Mercuric chloride inhibits the darkening of the potassium iodide–starch test paper in the presence of N_2O_4.) Next, in 1907, a disaster occurred which aroused public protest all over the world, especially in France. This was the explosion of the ammunition store on the French battleship "Jena". The investigation into the cause of this explosion was still in progress when, in 1911, another similar catastrophe occurred when some powder manufactured in 1906 containing 8% amyl alcohol blew up on the battleship "Liberté". It became plain that the decomposition of smokeless powder during storage was caused by some process other than the volatilization of residual solvent (Buisson [51]).

The accidents described above showed that nitrocellulose cannot be considered wholly safe even when carefully purified, if it is partly or wholly colloidal in form.

Subsequent investigations have shown that the stability of powder at temperatures higher than room temperature depends upon many factors. Thus, an examination of the effect of the web thickness of flakes or tubes upon the stability of powder at temperatures of 75–80°C showed that the larger the web thickness the higher the stability. This relationship is shown in Brunswig's [17] diagram (Fig. 193). Curve *I* shows losses in weight (in %) of the fine tubular powder (for a 3.7 cm cannon), curve *II* refers to a somewhat thicker powder (for a 7.5 cm gun), curve *III* refers to a thicker powder (for a 15 cm gun), curve *IV* refers to a very thick powder (for a 20 cm gun), curve *V* to the thickest powder of all (for a 30 cm gun). A loss of 25% weight occurred in the finest powder after 2¼ months. In the thicker powders it occurred after about 4, 9, 10¾ and 12¾ months, respectively.

The lower stability of smokeless powder in comparison with that of nitrocellulose is accounted for by its content of residual solvent and of the oxidation products of this solvent. Since in a finer powder the ratio of the surface to weight is high, the oxidation processes are more intense. A larger amount of decomposition products of residual solvent is formed by oxidation, and their destructive effect on nitric esters (nitrocellulose, nitroglycerine) in the powder is more severe.

The following findings point to the harmful effect of air on the stability of "green" nitrocellulose powder, i.e. freshly pressed and containing a considerable quantity of solvent (alcohol and ether) (Table 171).

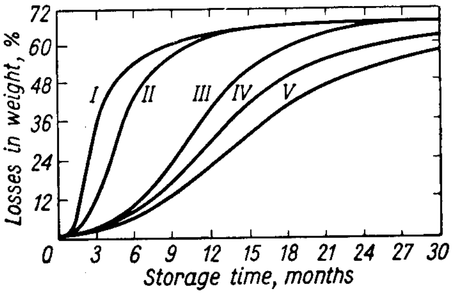


FIG. 193. Stability of tubular nitrocellulose powder at 75–80°C as a function of the web thickness of the tubes, according to Brunswig [17].

TABLE 171

THE EFFECT OF AIR ON THE STABILITY OF NITROCELLULOSE POWDER

Method of drying the powder	Stability, min	
	at a temperature of 110°C (for reddening of litmus paper)	at a temperature of 135°C (for appearance of first brown fumes)
Dried in the air	285	50
5 days in absence of air	570	110
7.5 days in absence of air	825	180
10 days in absence of air, then in the open	1020	190

When the powder is freed from most of the solvent in absence of air, subsequent drying in the open is not detrimental, since the amount of solvent is too insignificant to form oxidation products in a quantity which might impair stability.

The experiments of Świętosławski, T. Urbański, Całus and Rosiński [52] showed that "green" flake powder containing about 15% solvent emits a certain amount of heat which is very small but which may be detected in Świętosławski's [53] microcalorimeter. The heat effect fades after the green powder has been stored for a certain time in a sealed calorimetric vessel but reappears if oxygen is added, hence it may be assumed that this heat effect is caused by oxidation reactions between the residual and atmospheric oxygen. A powder containing very little solvent (soaked and dried) gives no such heat effect.

This means that the presence of a substance of very low volatility such as amyl alcohol may under certain circumstances prove detrimental to the powder's stability.

Indeed, it was found that amyl alcohol is converted into amyl nitrite and nitrate by the action of nitric oxides resulting from the decomposition of nitrocellulose. These substances are then oxidized to form valeric acid and amyl valerate products distinguishable by their characteristic smell.

There are many factors which affect the decomposition of powder during storage, the most important of which is temperature.

The decomposition of powder at an elevated temperature does not differ greatly from that of the nitric esters themselves, i.e. nitrocellulose and nitroglycerine (the decomposition of nitrocellulose at various temperatures was discussed earlier in Vol. II, p. 310). The higher the temperature, the more actively the decomposition of the powder proceeds, with total loss of nitrogen, as NO and NO_2, and carbon as CO and CO_2. Hydrogen is evolved chiefly as water, the amount of water decreasing with increase in the temperature of decomposition of the powder (Sapozhnikov's investigations).

The course of the decomposition reaction is different when the powder is stored at or just above room temperature. A marked oxidation then occurs. It is chiefly an internal oxidation with the ONO_2 groups acting as an oxidizer, but also involves atmospheric oxygen, and the residual solvent.

Powder for use in a tropical climate requires higher stability than that in a temperate climate. Powder for the navy must also have a high stability, since it may be transported into a tropical zone.

Atmospheric humidity has a deleterious effect on the stability of powder. Storm [54] reports that a good nitrocellulose powder, which withstood heating at a temperature of 65.5°C for 400 days without marked decomposition, showed evident decomposition in 175 days when stored at the same temperature in an atmosphere saturated with water vapour. Powder which passed the first test subsequently withstood heating for 5 hr at a temperature of 135°C without explosion, whereas powder from the second test exploded at the same temperature after 10 min.

The ease of decomposition by moisture is particularly pronounced in nitrocellulose powders, which are hygroscopic but is much less in those with a lower hygroscopicity i.e. in nitroglycerine powders. According to Brunswig [17] nitroglycerine tubular powder lost the same amount of weight at a temperature of 46°C in both a dry and a damp atmosphere, when stored for a period of 6 months. Nitroglycerine powder of the cordite type, containing vaseline, i.e. a moisture-proofing agent, is also noteworthy, its stability in a damp atmosphere being the same as that in a dry one. In Brunswig's opinion the addition of 3% vaseline to nitroglycerine powder protects it against the harmful effect of moisture. This powder when stored in a damp atmosphere, at a temperature of 46°C showed no loss of weight over 6 months, while common nitrocellulose powder, stored under the same conditions, for comparison, showed a loss of weight of 7.1%. The nitrocellulose powder with added vaseline is however unacceptable ballistically, so that proofing of this kind has no practical significance for nitrocellulose powders.

Nitric oxides exert a very detrimental effect upon the stability of powder, inducing rapid denitration. Vieille [11] gives the following figures for nitrocellulose powder maintained at a temperature of 40°C, in an atmosphere containing nitrogen dioxide (Table 172).

TABLE 172

THE EFFECT OF NITRIC OXIDES ON THE STABILITY OF NITROCELLULOSE POWDER

Duration of test, days	Powder without stabilizer	Powder with an addition of 7% amyl alcohol	Powder with an addition of 1% diphenylamine
	Nitrogen content of powder (%)		
0	12.10	12.40	12.50
7	11.05	11.0	11.20
13	10.68	9.85	9.60
21	9.18	9.40	9.41

On the basis of extensive investigations into the stability of powder de Bruin and de Pauw [55] proved that the gaseous products of the decomposition of smokeless powder, in particular nitric oxides and water, increase the rate of the decomposition of powder at a temperature of 110°C. This is confirmed by the fact that when absorbents that take up the gaseous products are introduced into the test room, the duration of the test is extended. Figure 194 shows a number of curves for the stability of nitrocellulose powder at a temperature of 110°C in the presence of various substances absorbing the gaseous products of decomposition. The sample of powder tested without an absorbent decomposed most rapidly (curve *VIII*). The substances which inhibit the decomposition of powder most efficiently are: phosphoric anhydride (combining with water) (curve *I*), calcium oxide (combining with water and NO_2) (curve *II*), carbamite (centralite) (combining with NO_2) (curve *III*), activated carbon (absorbing water and NO_2) (curve *IV*). Sodium carbonate (combining with water and NO_2 but evolving CO_2) (curve *V*), vaseline, absorbing nitric oxides (curve *VI*) and anhydrous cupric sulphate combining with water (curve *VII*) were less efficient. Thus, when the decomposition of powder involved the isolation of nitric oxides its denitration occurred rapidly both in powders with and without a stabilizer.

Other acid substances, e.g. hydrogen chloride or vapours of sulphuric acid, affect the powder in a similar deleterious way.

If a powder which decomposes and forms acid products is mixed with a "healthy" powder it causes the latter to decompose. The products of decompostion of smokeless powder were found to contain formic acid, hydroxypyruvic acid $CH_2OH\cdot\cdot CO\cdot COOH$, hydroxyisobutyric acid $(CH_3)_2C(OH)COOH$ and oxalic acid. All these acids except oxalic acid are hygroscopic, hence by increasing the moisture content in the powder, they hasten its decomposition. Acid products react with alkaline stabilizing components.

Brunswig [17] describes the following experiment. 30 g of flake powder was poured into a flat glass vessel. In the middle of this charge was placed a piece of tubular powder in a state of decomposition, containing acid products. The vessel was covered with a watchglass and put into an atmosphere saturated with water vapour. In a few days the tubular powder had changed into a greasy substance. In a few weeks the flake powder gradually underwent a similar transformation with pronounced decomposition progressing from the tubular powder in concentric rings. The flake powder became soft so that it could be rubbed through the fingers.

It is a practice in some countries to add a small amount of sodium hydrogen carbonate to the powder dough, to neutralize dinitrogen tetroxide evolved during the decomposition of the powder. This would lead to formation of sodium nitrate and nitrite. Angeli and Jolles [56] established a colorimetric method for determining the quantity of sodium nitrite in powder (by extracting it with water, diazotizing aniline and coupling with dimethylaniline). They suggested it as a method for estimating the degree of decomposition of the powder. The quantity of nitrites (calculated as nitrous acid) varied form 0 to 145 mg in 100 g of the powder.

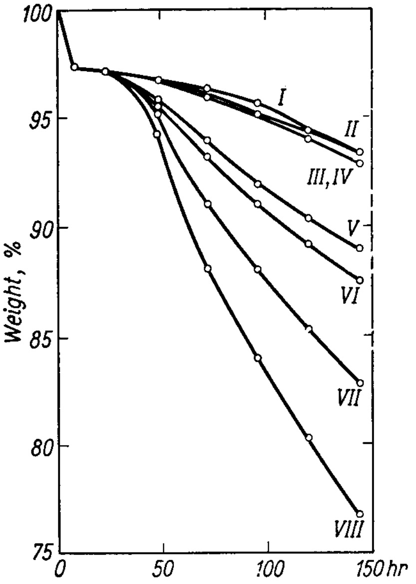


FIG. 194. Stability of nitrocellulose powder at 110°C (measured as a reduction of weight) in presence of substances absorbing gaseous products of decomposition (H_2O, NO_2).

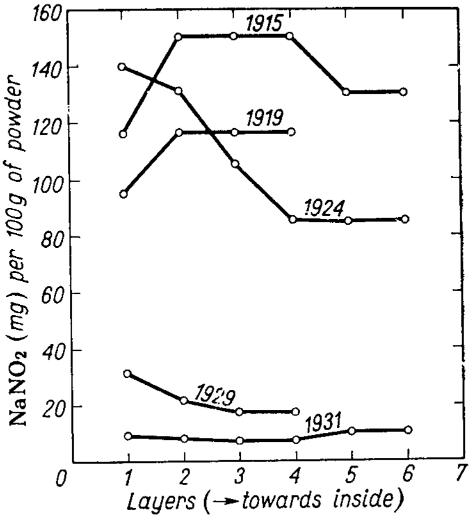


FIG. 195. Quantity of sodium nitrite in various layers of Italian powder (Polvere C) at various times of manufacture [57].

Jolles and Socci [57] also examined the distribution of sodium nitrite in various layers of an Italian tubular double base powder (Polvere C). According to their estimation the distribution of sodium nitrite along the tubes is practically the same whether on the surface or in an internal layer. The distribution varies from the surface to the inside of the tube. In "young" powders the quantity of nitrite on the surface is higher than inside. With time this may be reversed and in "old" powders the internal layers may be richer in nitrite. This is shown in the diagram (Fig. 195) which gives the results of an examination of "young" (e.g. 1931) and "old" (e.g. 1915) powders.

Decomposing powder which on heating emits visible nitric oxides ($N_2O_4 \rightleftarrows 2NO_2$) also emits a small amount of heat at room temperature. This was ascertained (Świętosławski, T. Urbański, Całus and Rosiński [52]) in Świętosławski's microcalorimeter. Immediately before this stage of decomposition, however, powder which has not yet started to emit nitric oxides abundantly shows no positive heat effect at room temperature.

These results do not conform to those of the "silvered vessel test". This test determines the time necessary to produce pronounced exothermic reaction in a sample of powder heated to a temperature of 80°C. This reaction causes a rise of temperature by 2°C above the ambient temperature. The relatively high temperature (80°C) may account for the different results. It may well be that the exothermic reaction recorded here is a reaction between the acid products of the decomposition of the powder and the basic ingredients of the glass of the vessel at the relatively high temperature.

A good powder should withstand this test for at least 500 hr. Immediately before the rise of temperature up to 82°C, or just after this rise, nitric and nitrous acids are evolved from the powder. Sometimes, shortly after a temperature of 82°C has been achieved, explosion follows.

On heating nitroglycerine powder of a ballistite type to a temperature of 95°C in a Dewar vessel without a stabilizer, de Bruin [58] obtained the following data on temperature rise:

after a lapse of 48 hr	95°C
after a lapse of 72 hr	95.2°C
after a lapse of 96 hr	95.2°C
after a lapse of 108 hr	96.4°C
after a lapse of 119 hr	97.9°C
after a lapse of 120 hr	98.6°C
after a lapse of $120\frac{1}{2}$ hr	102.6°C
after a lapse of $120\frac{3}{4}$ hr	explosion

When the powder used for this test was mixed with Centralite II, the temperature first rose to 97.2°C during 26 days of heating (an increment by 2.2°C) followed by a gradual drop.

Strong bases have an adverse effect on the stability of smokeless powder as described above. Moreover, Angeli [59] found that pyridine and its homologues cause decomposition of nitrocellulose. (On the action of pyridine on other nitric esters see Vol. II.) At an elevated temperature (e.g. 110°C) pyridine can produce an intense denitration of esters which may even lead to an explosion.

After World War I the influence of sea water on the stability of smokeless powder was examined. It was found that nitrocellulose powder submerged in the sea during military activities did not suffer any perceptible deterioration as a result of immersion in sea water for several years, neither in its colloidal properties nor in its stability.

In all probability this may be partly accounted for by the low temperature of sea water at a certain depth.

Sunlight is a factor which hastens the decomposition of smokeless powder. Experiments carried out by D. Berthelot and Gaudechon [60] showed that powders containing various types of stabilizers behave in different ways towards light. E.g. powder stabilized with amyl alcohol proved to be more resistant to sunlight than that containing diphenylamine. The latter darkens very rapidly under the influence of light, which no doubt accelerates the decomposition of diphenylamine.

Whatever its behaviour in sunlight, powder should not be exposed to direct sunshine at any stage of manufacture; all the windows of the plant should face north and any that do not should be covered with a layer of blue or yellow varnish, to cut off the rays of shorter wavelength.

STABILITY TESTS

The majority of the stability tests for smokeless powder are much the same as the methods used to determine the stability of nitric esters, in particular nitrocellulose (Vol. II). They are based on heating samples of the powder, thus starting decomposition processes or hastening processes already initiated within the powder. The value of such methods is comparative, since at an elevated temperature different reactions occur than those which would arise under normal conditions of storage. Nevertheless experiments over many years have shown that certain interrelations may be established for the stability of powder at various temperatures. Vieille [61] reports that the heating of a sample of powder for 1 hr at a temperature of 110°C involves approximately the same decomposition as:

24 hr of heating at a temperature of 75°C
7 days of heating at a temperature of 60°C
30 days of heating at a temperature of 40°C

In addition to the testing methods common to nitric esters (nitrocellulose, nitroglycerine) and smokeless powder there are also methods used exclusively for testing the stability of smokeless powders.

One of the inspection methods employed in smokeless powder factories consists in taking samples (about 500 g) from each lot of powder and placing them in hermetically closed jars. The jars are kept in thermostatic premises where a temperature of 30–50°C is maintained. A methyl violet reagent-paper (a paper tinted with crystal violet and rosaniline) is placed in each jar above the surface of the powder. If oxides of nitrogen are evolved by the powder, the paper gradually loses colour. A change in the colour of paper is therefore a sign that particular attention should be paid to this lot of powder, which should be subjected to detailed testing. This method may also be used in powder magazines.

Another method of checking stability consists of placing the powder into boxes of special design connected with an exhaust valve and a tube that leads any gases formed inside the box to a vessel containing a solution of potassium iodide and starch. Any traces of nitrogen dioxide given off by the powder are detected immediately since they produce a coloration of the solution.

In addition to the above methods which are designed to detect active decomposition periodical sampling and stability testing by one of the known methods is absolutely indispensable. The simplest of these methods are:

(1) The Abel heat test (heating at a temperature of 75–80°C in the presence of standard potassium iodide–starch paper).

(2) The stability test for nitrocellulose powder at a temperature of 134.5°C; the sample will not be considered serviceable unless the time necessary to produce the evolution of nitrogen oxides is at least 45 min and the powder withstands this temperature without exploding for 5 hr. The test can be combined with methyl violet test: decoloration of the test paper should not occur before 30 min or longer according to particular specifications.

(3) The test for nitroglycerine powders at a temperature of 120°C (nitroglycerine powders cannot withstand higher temperatures); here the same conditions apply as in the test for nitrocellulose powders, viz. appearance of the nitrogen oxides after a lapse of at least 45 min and no explosion for 5 hr. The same test can be carried out in the presence of methyl violet test papers. Decoloration of the paper should not occur before 30 min.

(4) The reduced heating test at a temperature of 110°C in the presence of a blue litmus paper, which should not redden in less than 10 hr.

(5) The Vieille test at a temperature of 110°C (Vieille [61]). For this a sample of powder is heated daily for 10 hr or until the litmus paper has assumed a standard red tint. The sample is then aerated for 14 hr and the procedure is repeated each day until the litmus paper reddens in one hour or less. The course of the test can be seen from a following example:

1st day	10 hr	together the first reddening after 19 hr
2nd day	9 hr	
3rd day	7.5 hr	
4th day	7.5 hr	
*n*th day	1 hr (or less)	
Together	x hr	

The value of x for good powders should not be less than 70 hr.

Quantitative tests are rarely conducted in magazines and for production inspection purposes except for a test devised by Bergmann and Junk [62] in which the quantity of acid products (calculated as NO) evolved by the powder is determined by titration. The quantity of NO evolved on heating for 2 hr at a temperature of 132°C should not exceed 2.5 cm^3 NO per 1 g of powder. (For more details see Vol. II p. 26.) Other quantitative tests are usually employed in research.

According to Jolles *et al.* [56, 57] the colorimetric determination of the quantity of sodium nitrite in powder (p. 555) can be an auxiliary method of estimating the stability of powders. Results agree well with the results of the heat test.

Tonegutti and Debenedetti [63] found that this test also agrees well with the methyl violet test at 120°C.

Jolles and Socci [57] give the following figures confirming the findings of Tonegutti and Debenedetti (Table 173).

TABLE 173

COMPARISON OF SODIUM NITRITE CONTENT AND THE METHYL VIOLET TEST OF ITALIAN DOUBLE BASE POWDER (POLVERE C)

Sample	Date of manufacture	$NaNO_2$ in mg %	Decoloration of methyl violet test paper at 120°C after min
1	1915	150.0	45
2	1919	116.0	50–55
3	1924	80.0	70–75
4	1929	16.0	100–105
5	1931	7.0	105–110

STABILIZATION OF SMOKELESS POWDER

STABILIZATION WITH DIPHENYLAMINE

An important advance in the stabilization of nitrocellulose powder was the addition of diphenylamine to the powder cake, suggested by Alfred Nobel in 1889 [64] and introduced into practice in Germany. According to Gorst [65] diphenylamine was also used in Russia at the end of the nineteenth century on the suggestion of Nikolskii. The application of diphenylamine to the powder in Germany was kept a profound secret, but as early as 1896 it was known in France that German nitrocellulose powder contained 2% diphenylamine. However it was believed in France that diphenylamine was too basic, and liable to hydrolyse nitrocellulose. Nevertheless, in view of the disaster on the battleship Liberté, the use of diphenylamine as a stabilizer for nitrocellulose powder was approved in 1911. Comparison of the stability of powders without stabilizer, with amyl alcohol and with diphenylamine gave *inter alia* the following results:

At a temperature of 75°C in a dry atmosphere, a powder with an admixture of 2% diphenylamine gave off only about one quarter the amount of gases evolved by a powder with an admixture of 8% amyl alcohol heated for the same period of time. At a temperature of 110°C the stability of the powder containing diphenylamine proved to be 2.5 times greater than that containing amyl alcohol.

A powder with an admixture of 1.5% diphenylamine, when heated at a temperature of 75°C in a dry atmosphere showed signs of decomposition only after 512 days, whereas powder containing 2% amyl alcohol began to decompose after 122 days. In a damp atmosphere at a temperature of 75°C a powder containing

2% diphenylamine decomposed much more slowly (at least four times more slowly) than the powder containing 8% amyl alcohol.

Berger [66] defined the degree of decomposition of powder at temperatures of 40–110°C, by determining the amounts of heat emitted by the fresh powder on burning and by partly decomposed powder. From this difference he calculated the amount of heat emitted on decomposition. Berger thus examined the behaviour of powder without a stabilizer (AT), powder with amyl alcohol (AM) and D powder with diphenylamine; he obtained curves (Fig. 196), the shapes of which are characteristic for the transition from slow to fast decomposition of powder. In the author's opinion violent decomposition coincides with the sharp inflection in the curve that occurs after an initial period characteristic of a resistance to decomposition that varies with the type of stabilizer added.

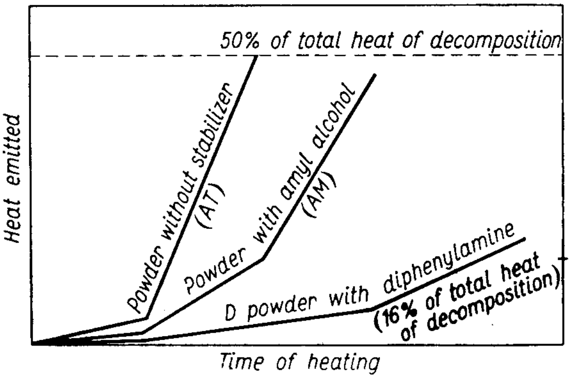


FIG. 196. Effect of the addition of amyl alcohol and diphenylamine on the stability of nitrocellulose powder, according to Berger [66].

Investigations have shown that the basic properties of diphenylamine are so weak that it cannot hydrolyse nitrocellulose, but they are sufficiently strong to neutralize any acid product arising either from the decomposition of impurities in the nitrocellulose, from the oxidation of residual solvent or even from decomposition of the nitrocellulose itself. It was also demonstrated that the basic properties of diphenylamine may have a deleterious effect on the powder if the diphenylamine content exceeds 5%. The best stabilizing results are achieved by using 1.0–2.5% diphenylamine.

The results of extensive investigations into the influence of the content of diphenylamine and other stabilizers on the stability of powder are tabulated below.

More recently Demougin and Landon [67] examined the stability of nitrocellulose powder containing 1.02–7.8% diphenylamine at a temperature of 110°C. After 160 hr of heating they determined the nitrogen content in nitrocellulose isolated from powder (Table 174.). The initial content of diphenylamine in the sample was 7.8%; on heating for 180 hr at a temperature of 110°C it was reduced to 1%.

TABLE 174

THE INFLUENCE OF DIPHENYLAMINE CONTENT ON THE STABILITY OF NITROCELLULOSE POWDER

Time of heating at a temperature of 100°C	Content of diphenylamine			
	1.02	2.2	3.75	7.8
	Content of nitrogen in nitrocellulose, %			
0 hr (fresh powder)	12.82	12.89	12.76	12.58
160 hr	11.89	13.01	11.14	10.13

A large content of diphenylamine may be particularly detrimental to the ballistic properties in fine-grain (rifle) powders. That is why 0.5–1.0% diphenylamine is used in these powders whereas in slower burning cannon powders 1.5–2.0% is used.

Diphenylamine is not used for stabilizing powders containing nitroglycerine since it hydrolyses this ester. Diphenylamine also causes the decomposition of higher nitrated aromatic compounds and therefore should not be used in powders containing such compounds.

In wartime the content of diphenylamine was reduced to 0.5% and even to 0.25% in expectation of the rapid utilization of the powders. Such powders should be labelled, e.g. by the addition of red dye, so that after hostilities they can be re-checked and used up quickly or destroyed. After World War I the storage of such powders caused a number of catastrophes; e.g. in Poland there were explosions of the magazines in the Warsaw citadel (1924) and at Witkowice (1927) and in France at Bergerac (1928).

Diphenylamine behaves not only as a stabilizer, but also as an indicator of the oxidation and decomposition processes which occur in powders. It was noticed long ago that powders containing diphenylamine assume under certain conditions colours ranging from greenish or bluish shades to dark blue or almost black and sometimes to yellow or brown, i.e.:

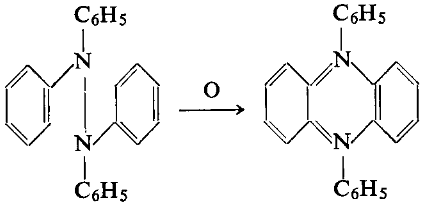
(1) The powder turns dark blue if it contains a large quantity of solvent and if it is exposed to the action of hot air, e.g. on drying at a temperature of 50–60°C. The investigations of Desmaroux [68], Marqueyrol and Muraour [69] and of Marqueyrol and Loriette [70] showed that this is due to the oxidation of diphenylamine produced by peroxides formed from residual ether and atmospheric oxygen.

(2) The powder turns blue if it contains traces of metals or if it is in contact with such metals as iron, copper, zinc, etc. Traces of metals present in powder sometimes cause the formation of blue stains around the metallic particles. A blue coloration appears sometimes at the points where the powder is in contact with metal on the inner surface of cases lined with metal.

Dark coloration of the powder need not necessarily signify decomposition, but it proves that some of the diphenylamine has undergone changes and has been consumed to form new products. This might reduce the stability of the powder and, as a rule, it is no longer serviceable for military purposes.

Much research has been devoted to finding the mechanism of the changes which diphenylamine undergoes in powder. Marqueyrol and Loriette [70] report that under the action of oxidizing agents, particularly of peroxide formed from ether, diphenylamine undergoes the following reactions to produce tetraphenylhydrazine (I) and diphenylphenazine (II):

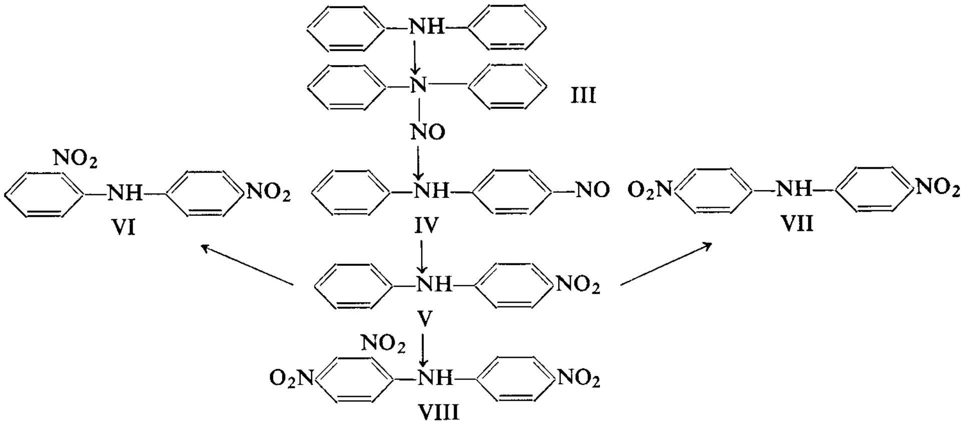
$$2(C_6H_5)_2NH \rightarrow \underset{\text{I}}{(C_6H_5)_2N{-}N(C_6H_5)_2}$$



I II

In these authors' opinion phenazine (II) causes powders to darken.

Davis and Ashdown [71] report that diphenylamine in powder undergoes the following reactions:



N-Nitrosodiphenylamine (III) which is formed first, has been proved experimentally to be nearly as good a stabilizer as diphenylamine itself. Neither of the above substances gives powders an intense coloration.

Davis and Ashdown devised methods for detecting these substances in powder. If the alcoholic extract from powder contains diphenylamine it forms a blue colour with ammonium persulphate; N-nitrosodiphenylamine gives no coloration with this reagent. The intensity of the colour developed by a mixture of both substances evidently depends upon the concentration of diphenylamine. On the other hand N-nitrosodiphenylamine gives an intense blue coloration to concentrated sulphuric acid.

Another test for N-nitrosodiphenylamine is based on the treatment of an alcoholic solution of this substance with a 1% alcoholic solution of α-naphthylamine followed by heating, when it turns orange.

With mineral acids, including nitric acid produced by the decomposition of powder, the N-nitroso compound undergoes rearrangement to form *p*-nitrosodiphenylamine (IV). This substance is readily oxidized to *p*-nitrodiphenylamine (V). Furthermore, the higher nitrated products, i.e. dinitro derivatives (VI) and (VII) and trinitro derivatives (VIII) may be formed in powder. Davis and Ashdown isolated 2,4,4′-trinitrodiphenylamine from American pyrocollodion powder by heating a sample in a closed vessel for 240 days at a temperature of 65°C. At the end of the heating period brown nitric oxides were given off by the powder.

It is generally agreed that powder in which diphenylamine is completely converted into N-nitrosodiphenylamine is suitable for storage. However, on the disappearance of N-nitrosodiphenylamine and its conversion into nitro compounds, the powder should be considered unsuitable for storage since it then lacks a stabilizer.

Powder in which nitro derivatives of diphenylamine have been formed is coloured reddish-yellow or brown.

According to Schroeder *et al.* [72] the chromatographic analysis on silica of the conversion products of diphenylamine in nitrocellulose powder indicates that diphenylamine may be converted into hexanitrodiphenylamine. From $\frac{1}{2}$ to $\frac{2}{3}$ of diphenylamine is converted into nitro derivatives if the powder is kept at a temperature of 71°C for 258 days.

Stabilizers which had or still have practical application are classified into inorganic and organic.

INORGANIC STABILIZERS

As early as 1867 Abel [73] realized that nitrocellulose tends to decompose in an acid medium, and suggested that sodium carbonate should be added to it to neutralize the acid products of the decomposition of the impurities in the powder or of nitrocellulose and nitroglycerine *per se*. However more than 2% sodium carbonate in the powder proved detrimental—due to its strongly alkaline reaction it impairs the stability of the powder.

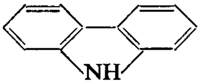
Accordingly, attempts were made to use the less alkaline sodium hydrogen carbonate ($NaHCO_3$). It was shown that 1% of the latter has no marked effect, either positive or negative, on the stability of nitrocellulose powder, but with nitroglycerine powder containing vaseline, its influence is decidedly helpful. Brunswig [17] describes cases in which nitroglycerine powder with vaseline and $NaHCO_3$ withstood storage for 20 years without any signs of decomposition whereas the same powder without $NaHCO_3$ showed a pronounced decomposition, several times ending in self-ignition after a lapse of 5 years.

Calcium carbonate, often added to nitrocellulose at the end of stabilization, affects the stability of powder beneficially, its influence, however, becomes strongly marked only when used in large quantities. Brunswig reports that powder containing 0.1% of $CaCO_3$ withstands heating at a temperature of 94°C in a closed vessel for 4.5 hr; nitric oxides are then given off and after 20 hr its loss of weight amounts to 19.7%. If the same powder contains 6% of $CaCO_3$ the loss of weight on heating at a temperature of 94°C for 200 hr does not exceed 0.4%. Nevertheless, it is inadvisable to introduce large amounts of a non-explosive substance to the powder mass lest its ballistic properties should be impaired. Magnesium carbonate acts similarly to calcium carbonate.

Magnesium oxide was added to the newest German nitroglycerine powders used during World War II. A content of 0.25% MgO considerably improved their stability and, in addition, facilitated pressing the powder paste. In all probability this is the most efficient inorganic stabilizer.

ORGANIC STABILIZERS

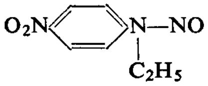
Apart from diphenylamine a number of other organic bases were tested for use as stabilizers. Some of them, e.g. aniline, were used only temporarily, chiefly during World War I when diphenylamine was in short supply. The basic properties of aniline are too marked and this is detrimental to stability. On the other hand, relatively good results have been obtained with carbazole which resembles diphenylamine in its structure:



Marqueyrol [74] reported experiments carried out in France over a period of 15 years to compare the efficiency of various stabilizers. The results are shown in Table 175. In addition to amyl alcohol and diphenylamine, the action of N-nitrosodiphenylamine (diphenylnitrosamine), carbazole, diphenylbenzamide, nitronaphthalene and naphthalene was also tested. The powder was stored at temperatures of 40, 60 or 75°C. The experiments were stopped when the powder showed signs of intense decomposition, giving off nitric oxides. This was also manifested by a sudden fall of the nitrogen content in nitrocellulose isolated from the samples.

Non-volatile solvents ("gelatinizers") such as camphor and butyl phthalate have also a definite stabilizing effect on powder. This applies especially to those which contain nitrogen: urea substitution derivatives (centralites or carbamites, acardit) and urethane substitution derivatives (see p. 645). It was found that on decomposition of the powder the centralites are nitrated and their nitro derivatives are formed. Nitro groups are obviously introduced into aromatic rings. Lecorché and Jovinet [75] ascertained that the centralite (carbamite) in solventless nitroglycerine powder is converted into substances volatile and non-volatile with steam.

The volatile fraction consists chiefly of *p*-nitrophenylethylnitrosamine (I) and the non-volatile fraction of dinitrocentralite (II):



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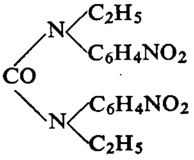

II

TABLE 175

THE EFFICIENCY OF VARIOUS ORGANIC STABILIZERS

Time (days) of storage at a temperature of 40°C	0	387	843	1174	2991	3945	4016
Stabilizer	Nitrogen content in the nitrocellulose, %						
No stabilizer	12.63	–	12.48	9.25	–	–	–
2% amyl alcohol	12.65	–	12.43	12.55	12.46	–	10.81
8% amyl alcohol	12.60	–	12.46	12.57	12.44	–	12.40
1% diphenylamine	12.60	–	12.48	12.58	12.57	–	12.58
2% diphenylamine	12.48	–	12.40	12.46	12.47	–	12.52
5% diphenylamine	12.52	12.59	–	–	–	12.36	–
10% diphenylamine	12.52	12.45	12.40	–	–	–	–
Time (days) of storage at a temperature of 60°C	0	146	295	347	1059	2267	3935
Stabilizer	Nitrogen content in the nitrocellulose, %						
No stabilizer	12.65	9.15	–	–	–	–	–
2% amyl alcohol	12.65	12.35	–	9.2	–	–	–
8% amyl alcohol	12.60	12.34	–	12.41	10.0	–	–
1% diphenylamine	12.60	12.36	–	12.51	–	–	–
2% diphenylamine	12.48	12.27	–	12.41	–	–	–
5% diphenylamine	12.52	–	12.26	–	–	–	11.62
10% diphenylamine	12.52	–	12.03	–	–	–	10.82
Time (days) of storage at a temperature of 75°C	0	86	231	312	516	652	667
Stabilizer	Nitrogen content in the nitrocellulose, %						
2% amyl alcohol	12.71	11.97	–	–	–	–	–
1% diphenylamine	12.60	12.26	–	12.39	11.94	–	–
2% diphenylamine	12.48	12.18	–	12.40	–	12.02	–
5% diphenylamine	12.52	–	12.06	–	–	–	11.65
10% diphenylamine	12.52	–	11.52	–	–	–	11.00
Time (days) of storage at a temperature of 75°C	0	55	146	312	419	493	–
Stabilizer	Nitrogen content in the nitrocellulose, %						
1% diphenylamine	12.54	12.38	12.41	12.46	12.36	12.40	12.14
2% diphenylamine	12.51	12.61	12.41	12.42	12.36	10.73	–
10% diphenylamine	12.61	12.22	12.15	12.07	11.93	11.72	11.53

TABLE 175 (CONTD.)

Time (days) of storage at a temperature of 75°C	0	60	85	108	197	377	633
Stabilizer	Nitrogen content in the nitrocellulose, %						
2% amyl alcohol	12.57	12.44	12.31	–	–	–	–
1.25% carbazole	12.55	12.47	–	12.46	11.44	–	–
10% carbazole	12.53	12.43	–	12.37	12.40	12.07	11.90
Time (days) of storage at a temperature of 75°C	0	31	50	62	87	227	556
Stabilizer	Nitrogen content in the nitrocellulose, %						
1.5% diphenylbenzamide	12.52	12.47	11.65	–	–	–	–
10% diphenylbenzamide	12.52	12.40	–	–	12.53	–	–
1.5% mononitronaphthalene	12.66	12.50	–	–	–	–	–
10% mononitronaphthalene	12.64	12.40	–	12.07	–	–	–
1.5% naphthalene	12.66	12.52	12.19	–	–	–	–
10% naphthalene	12.63	12.46	–	–	–	12.46	12.52

Such substances as vaseline (added to nitroglycerine powders of the cordite type), castor oil and rosin are also capable of stabilizing powder.

Brunswig [17] gives the following comparative figures based on the weight loss coefficient, i.e. the loss of the weight of powder in a unit of time $\frac{\Delta m}{\Delta t}$, as a criterion of stability. The values of the weight loss coefficient have been found for powder consisting of 10 parts of guncotton and 8 parts of nitroglycerine, obtained with the use of acetone as a solvent. They are summarized in Table 176.

TABLE 176

Type of stabilizer	Amount of stabilizer	$\frac{\Delta m}{\Delta t}$
No stabilizer	–	0.77–1.05
Vaseline	0.8 pt.	0.31
Rosin	0.8 pt.	0.30
Centralite	0.8 pt.	0.28

The systematic studies of T. Urbański, Kwiatkowski and Miładowski [76] proved that the addition of an aromatic nitro compound distinctly enhances the stability of nitrocellulose and nitrocellulose powder. Thus, nitrocellulose containing 13.4% N which on heating for 5 hr at 120°C had pH=2.28 showed pH=2.89 on addition of 9.1% *p*-nitrotoluene, pH=3.17 on addition of 9.1% 2,4-dinitrotoluene and pH=3.34 on addition of the same amount of α-trinitrotoluene. The same samples when heated in a constant volume (Tagliani test) gave at 134.5°C a pressure of decomposition products of 109 mm Hg after 32.5 min with pure nitrocellulose, after 44.5 min with nitrocellulose and the addition of 9.1% *p*-nitrotoluene, after 48.5 min with nitrocellulose and the addition of 9.1% 2,4-dinitrotoluene and after 52.5 min with nitrocellulose and the addition of 9.1% α-trinitrotoluene. The same nitro compounds do not influence the stability of nitroglycerine.

The experiments summarized in Table 175 show the stabilizing action of nitronaphthalene. Dinitro- and trinitronaphthalene also act in a stabilizing manner. On the other hand mixed nitramines such as tetryl are detrimental to stability.

APPARENT STABILIZERS

There are substances which appear to stabilize a powder by masking the results of stability tests. One of them is mercuric chloride (corrosive sublimate). Sell [77] originally suggested the addition of sublimate to nitrocellulose to prevent the development of mould on moist nitrocellulose. A test of the purity and accuracy of the stabilization of nitrocellulose containing sublimate led to an unexpected result, i.e. even the worst stabilized nitrocellulose gave no coloration to the standard test paper in the Abel heat test. For a certain time sublimate was added to the powder mass in an amount of 0.02–0.03% and to powder earmarked for tropical countries in an amount of 0.05%. This greatly hindered research on genuine stabilizers. It was later shown that mercuric chloride is partly reduced under the influence of nitrocellulose and during the heat test mercury volatilizes (usually at 65–82°C) and combines on the test paper with iodide formed by nitric oxides, to form colourless mercuric iodide.

Experiments showed that minute amounts of mercury vapour in the atmosphere are sufficient to discolour a blue iodide–starch paper, e.g. on heating a mixture of 0.2 g of barium nitrate with 0.8 mg of mercury to a temperature of 80°C there is immediate discoloration of the paper.

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CHAPTER VIII

THE MANUFACTURE OF SMOKELESS POWDER

INTRODUCTION

THE present chapter does not deal comprehensively with all the existing methods of powder manufacture. The manufacturing processes for smokeless powders described below should be regarded only as typical of some of the methods which were or still are used but which are often liable to very considerable variation. It should be borne in mind that some of the more recent methods are kept secret. The author has accentuated, as far as possible, the differences existing between the methods adopted in various countries.

Nitrocellulose powders can be classified into semicolloidal powders made of two kinds of nitrocellulose (insoluble and soluble in the solvent—ether and alcohol), almost fully colloidal, made of pyrocollodion cotton (highly soluble in ether–alcohol) and Schultze type powders with a very low content of colloidal nitrocellulose and containing inorganic salts. The Schultze nitrocellulose powders are now of little significance and very little used, so they will be discussed only briefly.

Nitrocellulose powders completely gelatinized with such solvents as acetone, ethyl acetate etc. were also known and manufactured for some time in various countries. They were of passing interest only because they possessed a number of disadvantages: the high cost of the solvents, the difficulty of igniting the powder and a number of difficulties in the course of manufacture produced by the high viscosity of the dough and its ready adhesion to metallic surface which made extrusion or rolling difficult.

Ball-grain powder is an example of a modern powder approaching fully colloidal structure through the use of ethyl acetate.

Another type of nitrocellulose powder used for some time which eventually disappeared from the market was a semi-colloidal nitrocellulose powder containing inorganic salts such as potassium or barium nitrate (e.g. Poudre T in France, with 2% potassium nitrate) or with dichromates (e.g. Poudre J in France with 14% ammonium dichromate and 3% potassium dichromate). The dichromate powder was very sensitive to friction and its dust contained toxic dichromates.

Nitroglycerine powders can be classified into two groups: with and without a volatile solvent. Semi-colloidal nitrocellulose powders and nitroglycerine solventless powders are the most important types of smokeless powder.

NITROCELLULOSE POWDER

NOMENCLATURE

The semi-colloidal powders are designated in every country according to the purpose for which they are intended. In the U.S.S.R. (Gorst [1]) rifle powders were formerly given the letter B (Russian V from the word "vintovka" i.e. rifle) followed by another letter denoting the type of projectile to be used, thus BΛ (Russian VL) for powder for light projectiles, BT (Russian VT), for powder for heavy projectiles.

Tubular and multiperforated powders for field artillery are, in addition, designated by a fraction, in which the numerator shows the web thickness in tenths of millimetres, and the denominator the number of perforations. The letters TP (Russian TR) following these figures mean that the powder in question is a tubular one. Thus $\frac{10}{1}$ TP denotes a single-perforated tubular powder with a web thickness of 1 mm. Similarly $\frac{9}{7}$ TP denotes a multiperforated tabular powder (7 perforations) with a web thickness of 0.9 mm.

Naval and coastal artillery powders are also designated by fractions, but for these the numerator signifies the calibre of the gun in millimetres, while the denominator shows the length of bore in calibres. Thus 75/50 signifies a powder for 75 mm guns, 50 calibres long.

The number of the lot of the powder, and the date and place of manufacture are given at the end, e.g. 2/49Φ is a powder forming part of the 2nd lot of 1949 produced at Φ (Russian F).

In Anglo-Saxon countries nitrocellulose powders are known as single base powders, i.e. made of only one explosive component.

In France nitrocellulose flake (strip) powder is shown by the letter B followed by further letters indicating its purpose. E.g. BF denotes rifle powder (fusil), BnF—newer (nouveau) rifle powder, BFP—progressive rifle powder, BC—powder for field (campagne) guns, BSP—powder for siege howitzers (siège et place) used mainly in 75 mm field guns. Recently, powders for the larger military guns were given letters BGC (gros calibre) with a subscript showing the calibre, e.g. BGC_4, BGC_5 etc. or simply BG_4, BG_5 etc. Powders for naval ordnance have the letters BM (marine) also with a subscript denoting the calibre:

Powders	Calibres
BM_5 to BM_7	100 and 138.6 mm
BM_5 to BM_9	164.7 mm
BM_9 to BM_{10}	194 mm
BM_7 to BM_{13}	240 and 274.4 mm
BM_{13} to BM_{17}	305 mm
BM_{13} to BM_{19}	340 mm

Other letters and subscripts show the stabilizer used and its amount, thus BM_7AM_8 means a powder BM_7 stabilized with an addition of 8% amyl alcohol. BSP D1.5 is a powder for siege howitzers stabilized with an addition of 1.5% diphenylamine. BM_5 powder is thin since it is extruded through a die of about 2.3 mm, and BM_{17} powder through a die of about 7.5 mm.

In Germany, the following nomenclature of nitrocellulose powder was in use:

SP—flake powder for rifle;
Gesch. Bl. P. (Geschütz Blättchenpulver)—flake powder for 8.8 cm guns;
Gr. Bl. P. 03 (Grobes Blättchenpulver)—large flake powder for 15 cm and 21 cm guns;
RG 96 } RP 05 } tubular powders for 96 n/a (127 mm long);
RP 97 and 99 (Röhrenpulver)—tubular powders for 10 cm guns;
RP 07—tubular powder for 13 cm guns;
Man RP (Manöver-Ringpulver)—blank ring powder for field guns.

According to Gallwitz [2] more recent German coding used during World War II also indicated dimensions, composition etc. The dimensions of the dies used for the extrusion of tubular or strip powder were given in millimeters. They differ from the actual grain dimensions. All powders containing volatile solvents shrink in the course of drying and their dimensions are therefore smaller than indicated by the code name.

All the German nitrocellulose powders are marked with the letters Nz. This designation is followed by letters indicating the shape of the grain and its dimensions.

RP.—(Röhrenpulver) tubular powder followed by figures (in brackets) indicating the length of the tubes, and the outer and inner diameter, e.g. RP (150·2·1) means a tubular powder 150 mm long outer diameter 2 mm, inner diameter 1 mm.

St. P.—(Streifenpulver) indicates strip powder: e.g. St. P. 150·15·1 means strip 150 mm long, 15 mm wide, 1 mm thick.

Bl. P. (Blättchenpulver) indicates square plate powder, followed by dimensions as above, e.g. Bl. P. (4·4·1).

Rg. P. (Ringpulver) is ring powder—and the figures indicate its dimensions: (thickness, outer diameter, inner diameter) e.g. Rg. P. (3.25/5).

Pl. P. (Plattenpulver) is plate or disk having diameter, thickness as indicated, e.g. Pl. P. (50·0,2).

N. P. (Nudelpulver) is cylindrical (macaroni) powder of the length and diameter, indicated e.g. N. P. (1,5·1,5).

German double base powders are also marked with figures or letters indicating their calorific values. Nitrocellulose powders had no such marks, as their calorific value is approximately the same in all types of powder.

The German nomenclature for double base powder is given in the appropriate chapter – p. 660.

MANUFACTURE OF NITROCELLULOSE POWDER

THE DEHYDRATION OF NITROCELLULOSE

For safety purposes nitrocellulose is delivered to the factory in a wet state and before it is partially dissolved in a mixture of alcohol and ether the water must be removed since this prevents the process of swelling and dissolution.

Formerly the water was removed by drying the nitrocellulose. This operation is dangerous due to the high sensitiveness of the dry nitrocellulose to friction, impact and static electricity. The dust of dry nitrocellulose either suspended in the air or spilled on the floor, or on radiators etc. is particularly dangerous, hence the drying of wet nitrocellulose has caused many accidents.

In the manufacture of nitrocellulose powders the water is displaced with alcohol. This method was proposed by Lundholm and Sayers [3] and widely used in many countries [4, 5]. Despite the simplicity of the idea the dehydration process is rather complicated. It is influenced by such factors as the solubility of nitrocellulose in alcohol and the ability of nitrocellulose to swell under the influence of alcohol: the lower the solubility of nitrocellulose in alcohol, the more easy dehydrated with alcohol. Since, however, the solubility of nitrocellulose depends primarily on its nitrogen content dehydration is easier with the higher nitrated types of nitrocellulose.

The advantage of dehydrating nitrocellulose with alcohol lies in the fact that any residual alcohol may be subsequently included in the solvent. The amount of residual alcohol in nitrocellulose depends not only upon the pressure applied in the dehydration press, but also on the type of nitrocellulose, i.e. it is somewhat larger in more highly nitrated nitrocellulose. Nitrocellulose made from wood cellulose swells in alcohol more readily than that made from cotton which is why the former retains more alcohol and more water.

The dehydration process is based primarily on the ability of alcohol to displace water. Since, however, the water is not always perfectly displaced the alcohol becomes partly mixed with water. In addition, some of the water is adsorbed by the nitrocellulose and cannot readily be removed, which causes a further dilution of the alcohol. The subsequent portions of fresh alcohol displace the dilute alcohol, the residual alcohol adsorbed by nitrocellulose is mixed with concentrated alcohol, the latter is displaced by fresh alcohol etc. This course of the operation is illustrated by variations in the concentration of alcohol in the liquid flowing out of the dehydration apparatus (Figs. 203–205).

It has been shown that washing out nitrocellulose with alcohol also serves another purpose; it dissolves and removes from the nitrocellulose degradation products which for the most part are known to be of low stability (Berl and Delpy [6]). Thus, the removal of water from nitrocellulose by displacement may be considered as an additional stabilization process.

The accuracy of the process, its duration, and the variation in the concentration of alcohol, depend to a great extent on the apparatus used for dehydration. The yield of the recovered alcohol also depends upon the apparatus and the particular process used.

Dehydration with centrifuges

The simplest method of dehydration is by centrifuging. Various types may be used e.g. power driven centrifuges usually with a capacity of 30 kg of nitrocellulose (calculated on the weight of the dry substance). Power drive, however, is somewhat risky if the nitrocellulose is moistened only with alcohol, since it very quickly dries up and can penetrate into the driving gear. For this reason a special centrifuge driven by means of a water turbine was designed (Figs. 197 and 198). The basket of this centrifuge can rotate at two speeds: 1000–1200 r.p.m. and 500–600 r.p.m. The rate of rotation should be reduced when introducing alcohol, after which it is increased to remove the liquid. Some centrifuge baskets have a double wall of perforated sheet (Fig. 198), the annular space between the two walls being lined with a strong filter cloth. The basket is loaded with 60 kg (dry substance) of wet nitrocellulose. The cloth acts as a filter and retains the nitrocellulose in the basket.

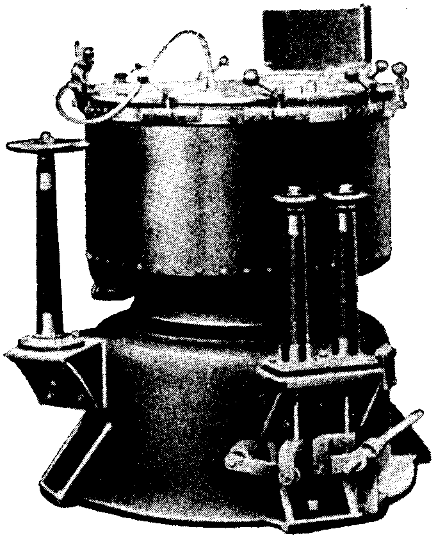

FIG. 197. Centrifuge for dehydration of nitrocellulose with alcohol, according to Brunswig [7].

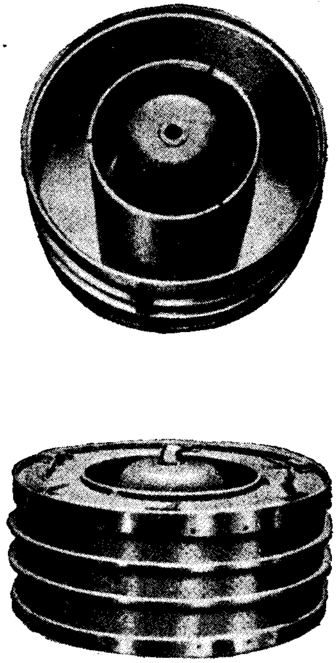

FIG. 198. Basket of a dehydration centrifuge, according to Brunswig [7].

After the centrifuge has been loaded it is closed with a lid fixed with clamps. The basket of the centrifuge is set in slow motion and a pipe that injects alcohol into the space between the shaft and the outer wall of the basket is introduced through a special hole in the lid. The pipe has numerous delivery nozzles facing the outer wall of the basket. At first 80% alcohol from the previous dehydration is introduced and the motion of the basket is speeded up to drain away a part of the water and alcohol. Further alcohol is added in several portions, the centrifuge being slowed down and then speeded up after each injection. When the content of alcohol in the drained liquid reaches about 60%, fresh 96% alcohol is introduced. This operation is repeated 2–3 times as described above until the concentration of alcohol flowing out of the centrifuge reaches 92%. The amount of alcohol supplied each time is established experimentally for a given centrifuge.

When operating the centrifuge described above with a load of 60 kg of nitrocellulose the alcohol is usually injected in four portions:

I *ca.* 40 l. of 80% alcohol
II *ca.* 40 l. of 80% alcohol
III *ca.* 30 l. of 95% alcohol
IV *ca.* 30 l. of 95% alcohol

The nitrocellulose is then centrifuged to a definite alcohol content. The dehydration of one batch of nitrocellulose requires approximately 1 hr.

The best method for recovering the alcohol is to collect the 60–70% alcohol and rectify it and to collect the 80% alcohol separately and use it for the dehydration of the next batch of nitrocellulose. 125 l. of 95% alcohol is consumed per 100 kg of dehydrated nitrocellulose; of this 30–35 l. remain in the nitrocellulose and about 90 l. are recovered by rectification.

After dehydration 30–35% alcohol remains in the nitrocellulose and is subsequently utilized as a part of the solvent. The final centrifuging should last until the content of residual alcohol remains constant. It is found that with certain forms of nitrocellulose (e.g. those made from wood cellulose) the removal of excess alcohol by centrifuging is difficult. In such cases centrifuging should last somewhat longer. If the content of alcohol in the nitrocellulose is too high, more solvent will be put at a later stage of dilution, or its composition is altered to increase the content of alcohol in it.

The centrifuged nitrocellulose is taken out of the centrifuge together with the cloth. Since the cloth and its charge adheres strongly to the wall of the basket, it may be necessary to use aluminium spades to separate it. The unloaded nitrocellulose is weighed. This gives the content of alcohol, the weight of the dry substance being known. The alcohol-damp nitrocellulose is broken up into lumps and loaded into cylindrical cans made of strong galvanized iron, hermetically sealed. Each can contains approximately 20 kg of nitrocellulose (calculated as dry substance).

The nitrocellulose to be loaded into the centrifuge may be in lump form or compressed (taken directly from the transportation cases). To attain uniformity in the operation of the centrifuge it is recommended that before loading the nitrocellulose is rubbed through a 1–2 cm mesh sieve either manually or mechanically. Manual rubbing may be carried out either by hand or with wooden paddles. For mechanical rubbing Nussbaumer's [8] apparatus (Fig. 199) may be used, in which bronze scrapers fixed on horizontal shafts (*1*) rotating around a vertical shaft are clamped down to screen (*2*) made of brass or aluminium wire. Swivel dampers (*3*) are used to load the rubbed nitrocellulose into sacks.

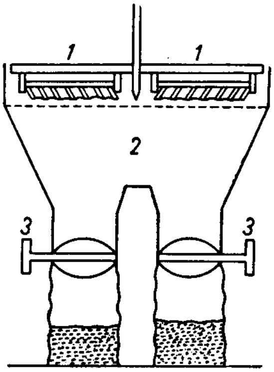

FIG. 199. Schematic view of Nussbaumer's apparatus for rubbing nitrocellulose before dehydration.

Dehydration in presses

Another method for dehydrating nitrocellulose is based on the use of pneumatic or hydraulic presses. Dehydration in pneumatic presses (diffusers) (Fig. 200) consists of filling the cylinder of the press with wet guncotton squeezed out of the tank under

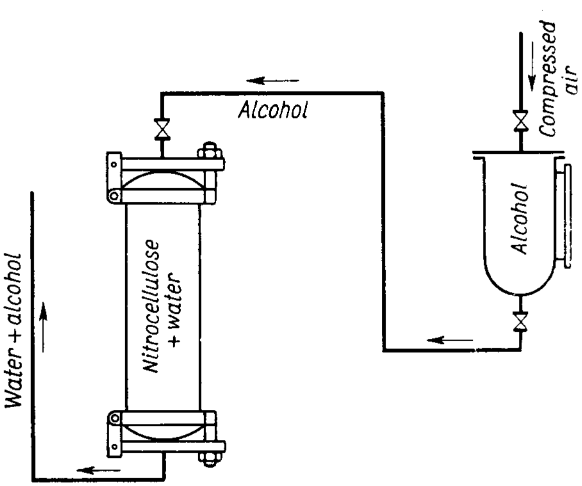

FIG. 200. Schematic view of a pneumatic press (a pressure diffuser) for dehydration of nitrocellulose with alcohol.

a pressure of 5–8 atm. The cylinder is then closed and the alcohol is forced into it from above by compressed air (5–8) atm. The water, followed by dilute alcohol and finally by concentrated alcohol flows out from below.

After dehydration in a diffuser, the nitrocellulose contains about 50% of alcohol. This is obviously too much and on removal from the cylinder the nitrocellulose is again subjected to pressure in a hydraulic press (100–200 kg/cm^2) to reduce the content of alcohol to 30–35%. The method described above requires an expensive installation, more numerous staff and takes longer than dehydration in centrifuges or in hydraulic presses. It does not seem to be in use any more.

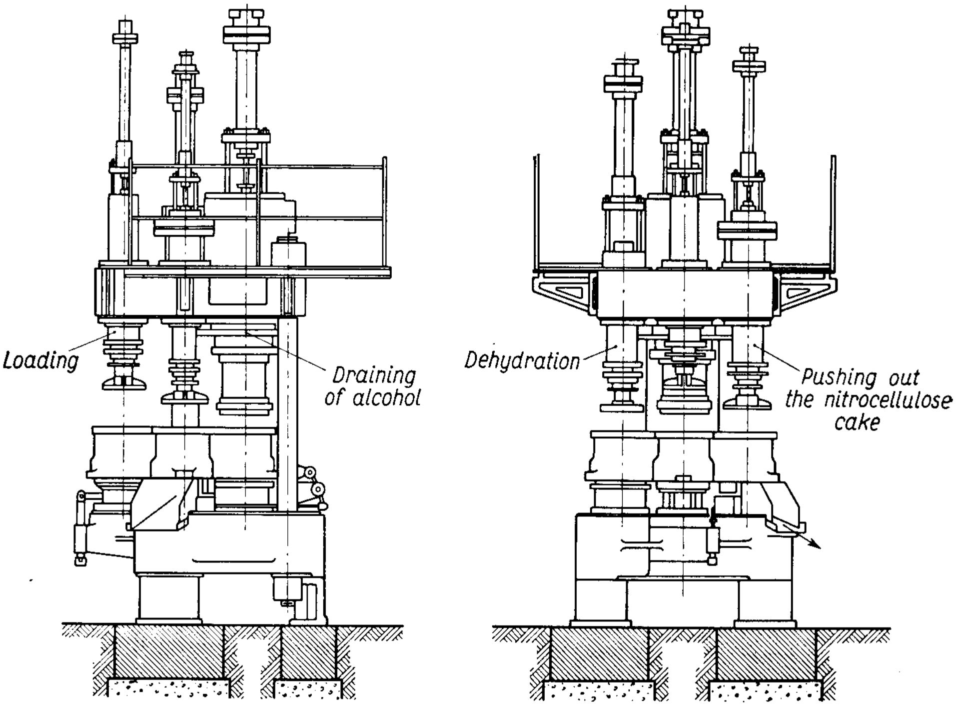

FIG. 201. Champigneul hydraulic press for dehydration of nitrocellulose.

Dehydration in hydraulic presses is the most general method now in use. The Champigneul press (Fig. 201) consists of four cylinders rotating around a vertical shaft and of four pistons taking positions accomodating to the movements of the pots. The pistons can move in a vertical direction and always perform the same successive operations, whereas the set of cylinders rotates, each one taking four positions in turn, corresponding to four seperate operations. The functioning of the press is illustrated by the diagram in Fig. 202. The arrangement of the cylinders as seen from above is shown in section (*I*). Section (*II*) represents all four cylinders as developed on one plane along *AOB'OA'OB*. As can be seen, the diameters of each particular piston are different. This is important since the pressure on the whole piston is proportional to r^2 (r=radius of the piston). The bottoms of the cylinders constitute a lower immobile section (supports) non-rotatable around shaft O, with tubular conduits for the outflow of alcohol.

The operation proceeds as follows: a brass mesh and a linen disk are put on "the bottom" of a cylinder at position *1*, and then 20 kg (dry substance) of wet nitrocellulose is poured in from above. Commonly used types of nitrocellulose (guncotton with collodion cotton) are packed alternately in layers, which in fact constitutes a preliminary mixing. The upper and lower layers are made of the type of nitrocellulose used in the larger quantity. The nitrocellulose is held in place by the lower piston. The upper piston rises and falls, thus ramming the load as it is poured, causing the brass mesh and linen disk to adhere to the lower surface of the load. The pressure of the piston may range from 25–50 kg/cm².

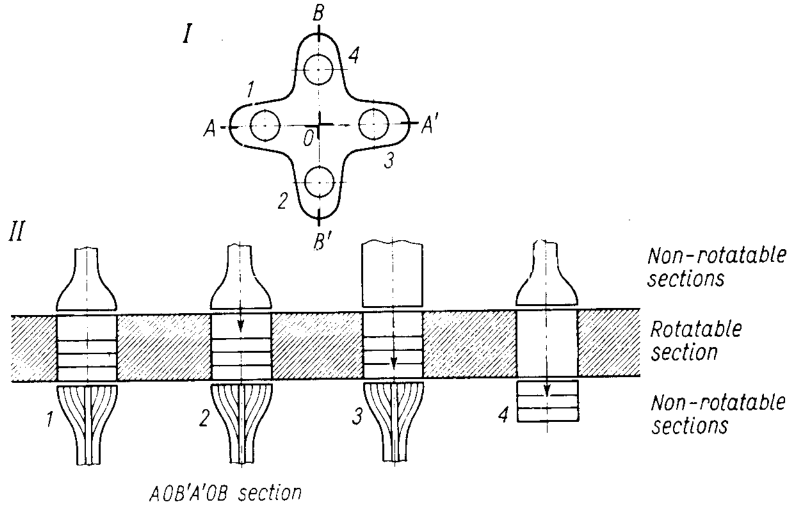

FIG. 202. Diagrammatic view of the operation of the four cylinders of a dehydrating press.

After the cylinder has been loaded at position (*1*), the set of cylinders is turned through 90° so that cylinder (*1*) moves to position (*2*). Here the bottom of the cylinder is formed by a lower piston in which there are furrows and conduits to drain away alcohol and water. About 20 l. of 95–96% refined alcohol is now poured onto the layer of compressed nitrocellulose and forced through this layer by the upper piston at pressures of 50–100 kg/cm². The water, dilute alcohol and finally less dilute alcohol flow out through the conduits in the lower piston.

After the upper piston has touched the layer of nitrocellulose, i.e. after the alcohol has been forced through the dehydrated material, the upper piston rises, while the lower one moves down and the set of cylinders again turns through 90°, so that the cylinder which started from position (*1*) through (*2*) now takes position (*3*). Here the lower piston is again fitted with conduits to drain away the alcohol. The upper piston at position (*3*) has the largest diameter and may develop pressures of 200–300 kg/cm². It reduces the alcohol content to 30–35%. After the upper piston has been raised and the lower one lowered, the set of cylinders once again moves through 90°. The cylinder passes from position (*3*) to position (*4*), where the upper piston pushes the cake of dehydrated nitrocellulose down. The brass mesh and linen disk are removed and the cake is broken up with a wooden mallet and quickly rubbed through a coarse (1–2 cm mesh) brass sieve. The screened nitrocellulose is weighed to determine its alcohol content. The mesh and linen disk are re-placed on the bottom of the cylinder at position (*1*), before starting the cycle again with another load of nitrocellulose.

Dehydration using this type of press precludes the recovery of dilute alcohol. Only 92–96% alcohol is used for dehydration. The waste alcohol below a certain concentration (usually 50%) is discarded. Any of a higher concentration is sent to rectification.

Ponchon [9] studied the course of dehydration of nitrocellulose in a Champigneul press, and drew the graphs indicating how water and alcohol are displaced in each position of the cylinder. The graphs in Fig. 203 denote the process of dehydration when the cylinder is at position (*2*). Curve *I* shows the change in volume, curve *II* the change in concentration of waste alcohol, curve *III* the change in water content of the nitrocellulose and curve *IV* the pressure indicated by the manometer. Changes in all these values are expressed as a function of time. A graph illustrating the process of dehydration when the cylinder is at position (*3*) (separation of alcohol) is shown in Fig. 204. The curves *I–IV* denote the same relationships as in Fig. 203 and in addition curve *V* shows the decrease in alcohol content of the nitrocellulose.

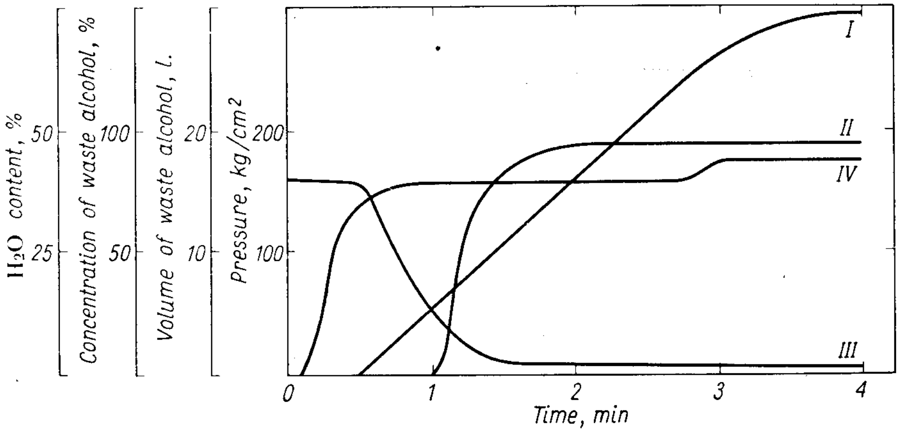

FIG. 203. Characteristics of the dehydration process of nitrocellulose in a Champigneul press (position (*2*) of the cylinder).

Ponchon also produced a graph (Fig. 205) showing the difference between the dehydration of CP_1 nitrocellulose (containing 1.5% of soluble in alcohol) and CP_2 nitrocellulose (containing 5.2% of soluble in alcohol). The graph indicates for both forms of nitrocellulose the volume of waste alcohol (broken lines) and the pressure within the press (continuous lines) against time. The graph shows that the pressure necessary to displace the water is lower with guncotton (CP_1 nitrocellulose) than with collodion cotton (CP_2 nitrocellulose). In CP_1 the alcohol flows out more rapidly. These findings show that CP_1 is dehydrated more readily than CP_2.

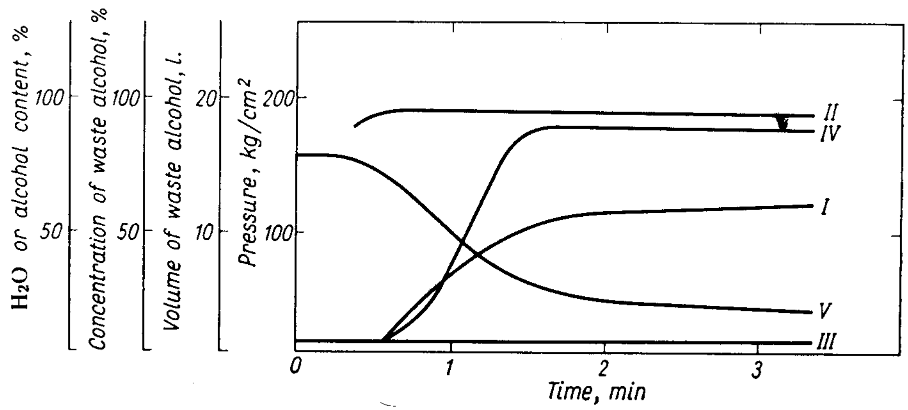

FIG. 204. Characteristics of the dehydration process of nitrocellulose in a Champigneul press (position (*3*) of the cylinder).

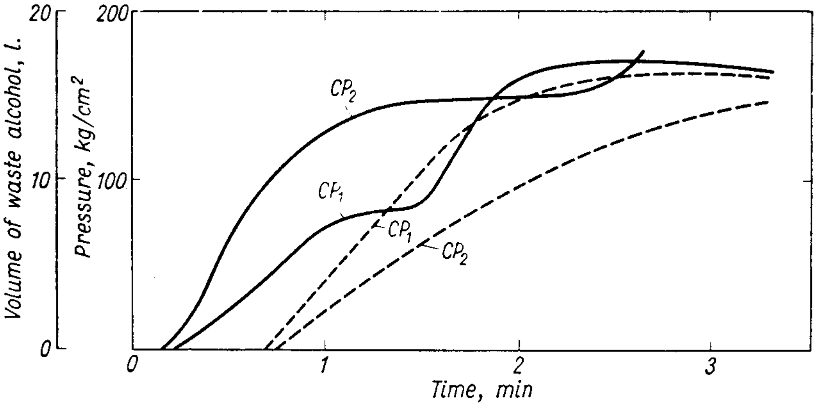

FIG. 205. Comparison of the course of dehydration of CP_1 and CP_2 nitrocelluloses.

Ponchon's experiment led him to conclude that the most advantageous arrangement lies in placing the CP_2 layer on the bottom of the cylinder and the CP_1 layer in the upper part.

As shown in Ponchon's graphs the use of a hydraulic press leads to very distinct changes in the concentration of alcohol on dehydration and permits the collection of alcohol of a definite concentration at a given time. Alcohol of approximately 50% concentration is usually collected and rectified.

Svetlov [10] quotes the following figures characteristic of the output of the Champigneul press. In one working cycle of the press 20 kg of nitrocellulose containing about 6 kg of absolute alcohol (23% of the total weight) and about 0.4 kg of water (1.5% of the total weight) are obtained. In the first stage of the operation (positions *1* and *2*) 12–14 kg of dilute 40–50% alcohol flows out, and in the second stage (position *3*) about 7 kg of 93% alcohol. One working cycle lasts up to 2 min. In one hour approximately 30 charges of nitrocellulose of 20 kg each are dehydrated, e.g. 600 kg/hr.

According to Ponchon 110 kg of 93% alcohol are used for the dehydration of 100 kg of nitrocellulose (dry weight). In French factories (1917) an average of 33 kg of 42–52% waste alcohol was recovered and returned for rectification.

The consumption of energy per 1000 kg of nitrocellulose (dry) is 13.5 kWh.

The Becker and van Hüllen (Krefeld) press is of another design. In this press the wet non-centrifuged nitrocellulose is first dehydrated by removal of up to 20–30% of its water content, and then subjected to further dehydration with alcohol. Partial dehydration of the nitrocellulose takes place in the feeding screw used with this press.

Rectification of alcohol from dehydration

Alcohol from dehydration contains a certain quantity of nitrocellulose, i.e. its soluble fractions, mostly degraded, and a certain amount in suspension. Experiments have shown that about 2.2 g of dissolved nitrocellulose and 1.3 g of nitrocellulose in suspension—a total 3.5 g—occur in 1 l. of 70% alcohol from centrifuges. Sometimes however, the content of nitrocellulose in the alcohol may reach 10–12 g/l.

The nitrocellulose present in suspension readily passes through filters, and should therefore be separated by decantating the alcohol out of the tank in which the waste alcohol is stored. In this manner the nitrocellulose content in the waste alcohol is reduced to 2–3 g/l. In some factories nitrocellulose is removed more completely by diluting the alcohol to about 40% with water (from washing the powder, and therefore containing a small amount of alcohol). By this means a certain quantity of the nitrocellulose is precipitated as sludge. After settling, the alcohol is decanted. This method, however, is troublesome and not commonly used, because the residual nitrocellulose in solution and traces of its suspension in alcohol are liable to decomposition in the course of prolonged heating during distillation. The decomposition of residual nitrocellulose in a distillation still (vat) has several times caused explosions. Moreover due to the decomposition of nitrocellulose there are traces of nitrites, nitrates and even nitric oxides in the distillate. To avoid this, it is advisable to add calcium oxide to the distillation vat, using 1 kg per 100 l. of alcohol. This causes hydrolysis of the nitrocellulose and neutralizes the products of hydrolysis. In addition the vat should be freed from solid residue as often as possible. Losses on rectification amount to approximately 1.5% alcohol.

THE PREPARATION OF NITROCELLULOSE MIXTURES

Nitrocellulose for the manufacture of powder must meet requirements of chemical stability, nitrogen content and solubility in a mixture of alcohol and ether according to the regulations discussed in the chapter on nitrocellulose.

For the manufacture of most kinds of semi-colloidal nitrocellulose powders with a volatile solvent, and recently also for the manufacture of solventless nitroglycerine powders, a mixture of two forms of guncotton is used: high nitrated guncotton, insoluble in a mixture of alcohol and ether, and low nitrated collodion cotton soluble in a mixture of alcohol and ether. In some countries (U.S.A. and U.S.S.R.) pyrocollodion cotton is used and for powders requiring a high nitrogen content, a mixture of pyrocollodion and guncotton.

Since nitrocellulose is stored and weighed in a wet condition (25–30% water), the moisture content should be determined accurately before batching. The powder plant usually receives nitrocellulose in semi-sealed containers. Since these are not uniformly tight the moisture content is liable to some variation. This makes batching more difficult, less accurate and even completely faulty. It is therefore advisable to equalize the moistness of the nitrocellulose by unloading it into concrete pits, holding 5000 to 20,000 kg of nitrocellulose (dry weight) hermetically closed with a sheet iron cover fitted with a rubber seal and storing it there for a few days. The nitrocellulose is then analysed for its water content, nitrogen content and its solubility (dry weight) in a mixture of alcohol and ether. Samples are taken from several places to make the analysis more reliable.

After analysis each form of nitrocellulose (guncotton, collodion cotton, pyrocollodion cotton) is batched separately into a linen bag which for convenience and safety is stored in an air-tight iron vessel (to protect the nitrocellulose from drying up and becoming dusty). Nitrocellulose is batched by charges, the size of which depends on the dimensions and the type of apparatus used. In France, for instance, a total charge of nitrocellulose (CP_1 and CP_2) is 20 kg when dehydrated in a hydraulic press or 30 kg when dehydrated in a centrifuge.

The more modern approach to the problem of mixing nitrocellulose consists of mixing defined types of nitrocellulose in the nitrocellulose factory itself. In this case the two forms of nitrocellulose are mixed under water in mixers as described in Vol. II, p. 374. The water is then centrifuged and the mixture dehydrated with alcohol. This method, however, creates certain inconvenience to the powder factory which loses the possibility of changing (within certain limits) the composition of the mixtures, i.e. nitrogen content and total solubility of nitrocellulose. The powder factory is therefore compelled to limit the number of factors which can be varied to obtain the powder of required ballistic properties.

When treating the nitrocellulose mixture with solvent, only collodion cotton is dissolved and converted into a colloidal state. Guncotton is incorporated into the colloidal mass in the form of fibres. Thus by the solubility of a mixture of nitrocelluloses in a mixture of alcohol and ether, we mean the total solubility of the mixture.

The batching of nitrocellulose consists of weighing the guncotton and collodion cotton in a ratio which gives a mixture of suitable nitrogen content with the required total solubility.

The following rule is helpful in calculating the composition of a mixture. Suppose that a mixture of 30% total solubility is needed consisting of guncotton (CP_1) of 10% solubility and collodion cotton (CP_2) of 95% solubility. To prepare it 65 parts by weight of CP_1 and 20 parts by weight of CP_2 have to be mixed.

$$\begin{array}{llcl} CP_1 & 10 & & 65 \text{ parts by weight of } CP_1\text{, i.e. } 76.5\% \\ & & \searrow\ \nearrow & \\ & & 30 & \\ & & \nearrow\ \searrow & \\ CP_2 & 95 & & 20 \text{ parts by weight of } CP_2\text{, i.e. } 23.5\% \\ & & & \text{Total } 85 \text{ parts} - 100\% \end{array}$$

After the ingredients have been mixed the total nitrogen content in the mixture so obtained must be checked.

The nitrogen content and solubility of the nitrocellulose mixture must be maintained within the following limits according to its intended use (Table 177).

TABLE 177

	Total solubility	Nitrogen content
Rifle powder	18–25%	13.1–13.3%
Powder for smaller calibre cannon (below 90 mm)	25–35%	12.8–13.1%
Powder for heavier calibre cannon	35–45%	12.5–12.9%

The lower the nitrogen content and the higher the solubility of the nitrocellulose in a given solvent, the more slowly the powder made of it will burn. Thus in matching the composition of a mixture of guncotton and collodion cotton to obtain the required total solubility the burning rate of the powder can be regulated within certain limits. E.g. in France, for modern rifle powders, which are faster burning than cannon powders, the mixture of CP_1 and CP_2 is so balanced that the total solubility is 15–20% while for the earlier type of powder Bn_3F (Le Bel rifle) it is 25–30%. For small calibre field guns (75 mm) powder, a total solubility of 30–35% is chosen. For 105 mm field guns powder and for small calibre naval guns it is 40% and for heavy calibre guns 40–50%.

If the powder is made of pyrocellulose, only part of it dissolves in the solvent (usually 60–70%) while a certain amount of the substance remains in fibre form.

PARTIAL DISSOLUTION OF NITROCELLULOSE

For the manufacture of nitrocellulose powder a volatile solvent is used, i.e. a mixture of alcohol with ether in a weight ratio of about 2 : 1.

The alcohol (usually refined to 95–96%) must not be acid. To make a 100 cm^3 sample of alcohol neutral towards phenolphthalein no more than 1.6 cm^3 of 0.1 *N* NaOH is required. A larger quantity of acid is detrimental since it may adversely influence its stability and gives a dark powder. The alcohol should not contain nitrites. A nitrocellulose powder plant should be equipped with a plant for the distillation of alcohol.

Ether, in its common commercial form, is sufficiently pure to be used in admixture with alcohol. Its acid content should not exceed 40 mg (calculated as H_2SO_4) per litre, nor should it contain nitrites. A nitrocellulose powder plant must include a plant for the manufacture of ether.

In France, two types of an alcohol–ether mixtures are used for the manufacture of nitrocellulose powder specified in terms of Baumé degrees:

(1) 56° ether consisting of 64 parts by weight of ether and 36 parts by weight of alcohol.

(2) 54° ether consisting of 56 parts by weight of ether and 44 parts by weight of alcohol.

Nitrocellulose dissolves more readily in 56° ether which is therefore used more often than 54° ether. If, however, the nitrocellulose is very soluble and gives a powder with too slow a rate of burning, the use of 54° ether is recommended, i.e. a solvent which leaves more insoluble material, thus giving a more fibrous powder.

The volatile solvent (alcohol–ether mixture) is used in such an amount that the dough is fairly loose but sticks when pressed between the fingers. The actual amount depends to a great extent on the properties of the nitrocellulose, since some forms require more solvent than others. The amount of solvent is usually determined by experiment. It ranges from 70–150 parts per 100 parts by weight of a mixture of nitrocellulose (dry substance).

With wood nitrocellulose smaller amounts of solvent are used (70–90%). This is accounted for by the lower degree of polymerization of wood cellulose in comparison with that of cotton. With its lower degree of polymerization wood nitrocellulose swells and dissolves more readily, producing solutions of a relatively low viscosity.

With pyrocellulose which contains 60–70% of material soluble in an alcohol–ether mixture, the use of 70–80 parts by weight of solvent per 100 parts of nitrocellulose is sufficient.

A volatile solvent is not used for the manufacture of completely colloidal powders containing nitroglycerine, with the exception of British cordite. For this, acetone is used, which is a solvent well fitted for both high nitrated cellulose (guncotton of 13% N) and nitroglycerine. Small amounts of acetone are also sometimes employed as an auxiliary solvent for the manufacture of ballistite. During World War I, when there was a shortage of acetone an alcohol–ether mixture was adopted as a substitute for the manufacture of cordite. It then became necessary to use a lower nitrated cellulose soluble in this solvent (RDB cordite). This is discussed more fully in the chapter on nitroglycerine powders.

Nitrocellulose is gelatinized (dissolved) and the powder dough is prepared in kneaders so that the dough-like mass is thoroughly mixed. Werner–Pfleiderer type kneaders (Figs. 206, 207, 208 and 209) are most commonly used. They consist of a trough made of bronze (surrounded by a cooling jacket) in which two powerful bronze stirrers in the form of worm-shaped blades rotate in opposite directions, one twice as fast as the other. Effective kneading combined with simultaneous mixing is attained by the movement of the stirrers downwards in the centre and upwards by the walls. The angular speed of the slower stirrer is 20–30 r.p.m. and of the faster one 40–60 r.p.m. The trough is fitted with an outer cooling jacket.

The kneaders in use are of varying capacity, and usually hold a charge of 60 kg of dehydrated nitrocellulose (dry weight) containing alcohol. After the kneader has been loaded its lid is closed (until then the lid is slung on chains from a block attached to the ceiling) and screwed down to the trough as tightly as possible. The stirrers are then set in motion; the ether is fed through a conduit in the lid as is the additional quantity of alcohol. Simultaneously the stabilizer is introduced in such a manner that diphenylamine weighed out in a silk bag is placed into a small container attached to the lid. The latter is connected with the conduit feeding the ether so that the ether flowing down from the batcher to the kneader, on passing through the container with diphenylamine, dissolves it and thus introduces it into the powder dough. To facilitate checking whether or not diphenylamine is present in all the containers, it is advisable to fit an inspection window.

Kneading requires 2.5–3 hr, although in exceptional cases if rapid manufacture is necessary, this period may be shortened to 1–1.5 hr.

Since the mass is heated up during kneading, due to friction, cold water is fed to the cooling jacket during the whole time of kneading so that the temperature does not exceed 30°C, otherwise the ether evaporates. Dissolution may be incomplete and excess pressure may be produced within the kneader which may blow off the lid when it is unscrewed.

When the kneading is finished, the lid is unscrewed and lifted with the block, the stirrers are set to rotate in the opposite direction (upwards in the centre and downwards by the walls) and the trough is tilted up by a special mechanism driven manually or mechanically (Fig. 210) so that the dough falls from the trough into two containers previously placed below. To prevent spilling the dough the containers are covered with a protective hopper made of sheet brass or leather. As a container is filled, the dough is rammed with bronze rammers mounted on wooden handles. Ramming gives a more uniform dough and removes the air. This at a later stage, facilitates pressing.

The containers loaded with the dough are hermetically closed. When unloading, a sample is taken from each kneader to be sent to the testing laboratory to check the presence of diphenylamine. A drop of concentrated sulphuric acid on a sample of the dough gives a blue coloration if diphenylamine is present. If the test is negative the dough is returned for kneading once again with the addition of the required amount of diphenylamine.

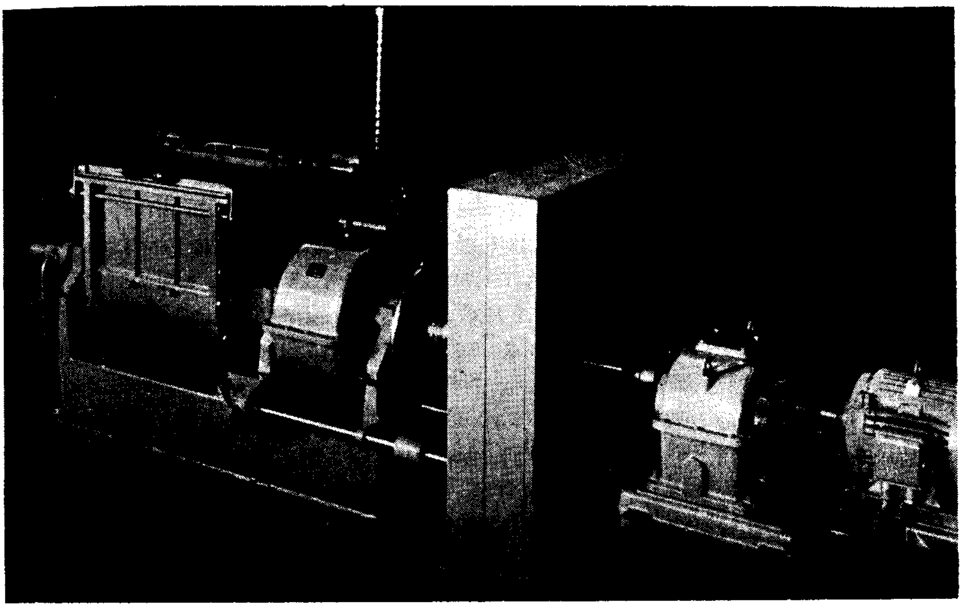

FIG. 206. Werner–Pfleiderer kneader with electric motor shown behind a wall (Courtesy Werner & Pfleiderer, Maschinenfabriken und Ofenbau, Stuttgart).

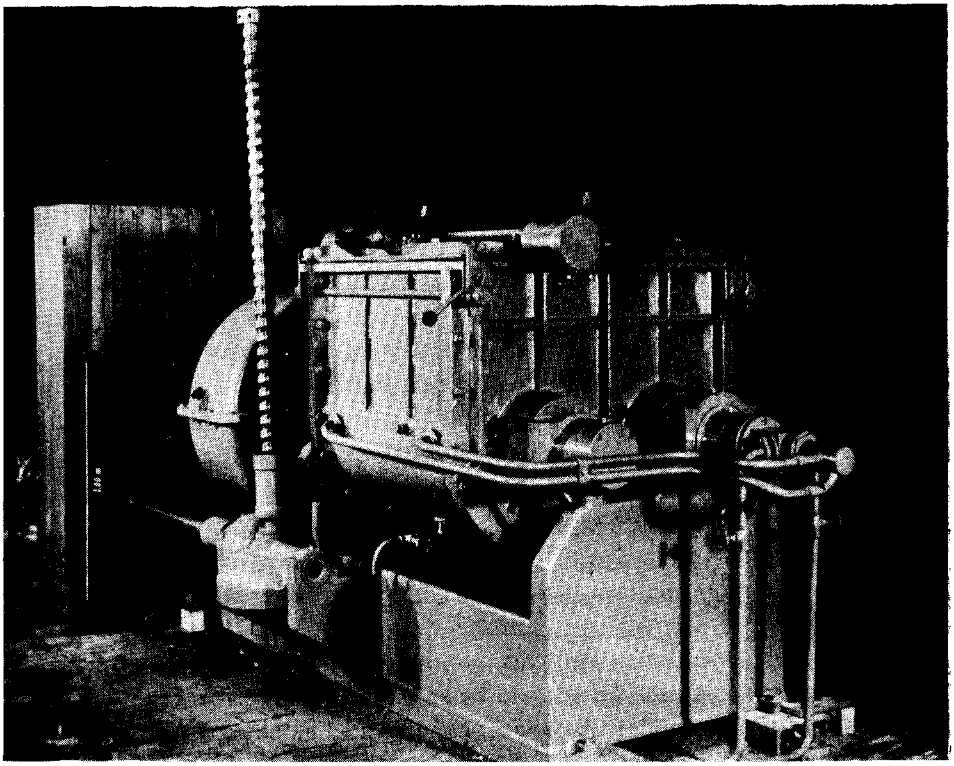

FIG. 207. Werner–Pfleiderer kneader at work (Courtesy Werner & Pfleiderer, Maschinenfabriken und Ofenbau, Stuttgart).

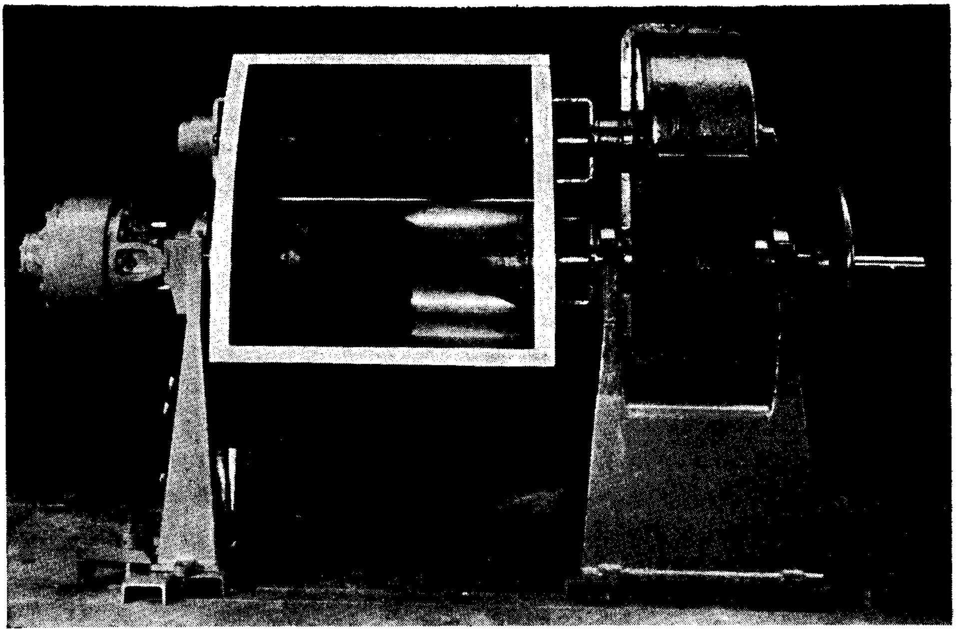

FIG. 208. Werner–Pfleiderer kneader in unloading position (open) (Courtesy Werner & Pfleiderer, Maschinenfabriken und Ofenbau, Stuttgart).

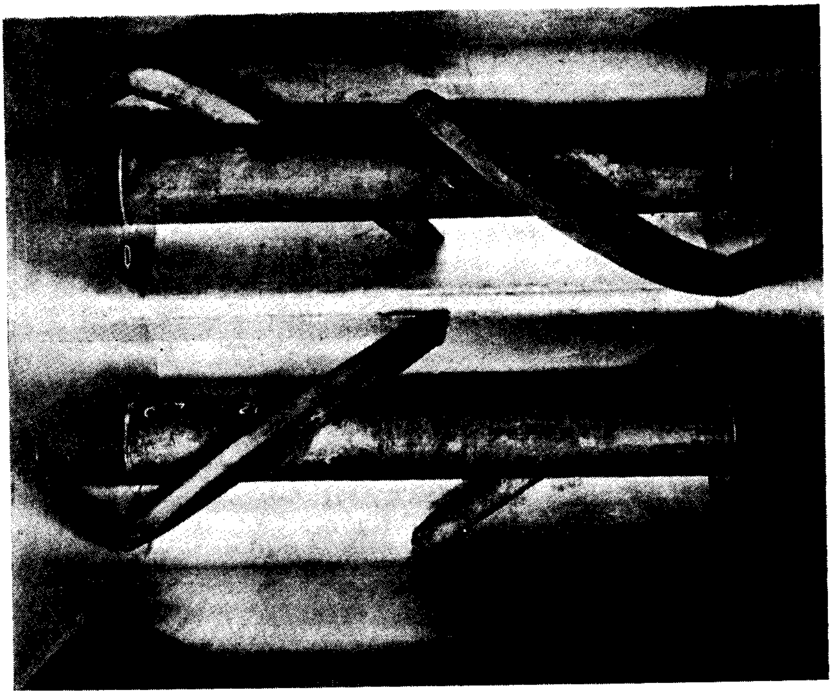

FIG. 209. View of paddles (Courtesy Werner & Pfleiderer, Maschinenfabriken und Ofenbau, Stuttgart).

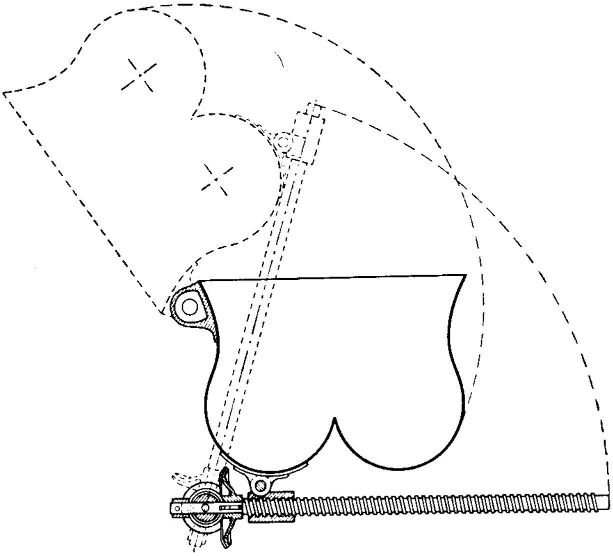

FIG. 210. Mechanism for tilting the kneader.

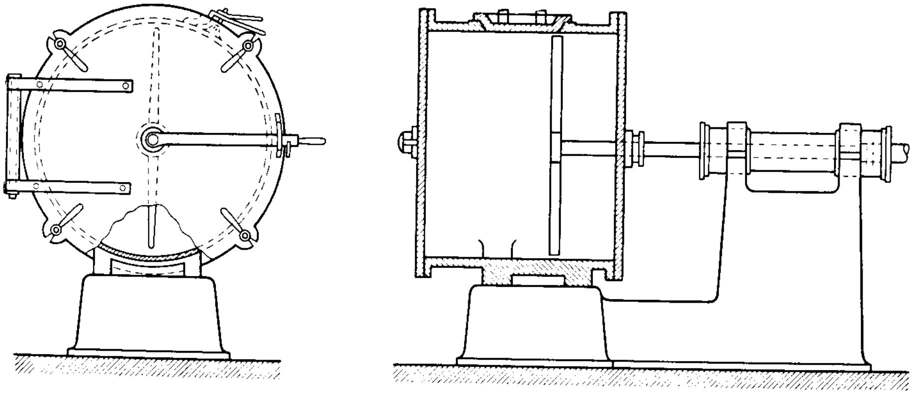

FIG. 211. A diagram of a Chaudel–Page kneader.

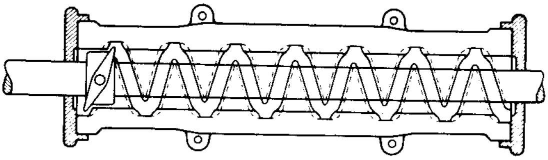

FIG. 212. A diagram of the mechanism for moving the stirrer of a Chaudel–Page kneader in translatory and angular motion, according to Yegorov [11].

In France Chaudel–Page kneaders (Fig. 211) are in general use. These take the form of an iron cylinder in which an iron bar rotates about a horizontal shaft [11]. The bar performs an angular-translatory motion, driven by the mechanism sketched in Fig. 212. A spur-gear rotates in a box with interior left-hand and right-hand threads. The spur-gear is fastened to the horizontal shaft. It turns forwards in the grooves of one of the threads with a translatory motion of the shaft in one direction (e.g. to the right). When the spur-gear reaches the end of the box further movement in this direction becomes impossible. As it turns it falls into the threads imparting a translatory motion to the shaft in the opposite direction. Thus it travels to and fro, and kneads and mixes the contents of the cylindrical kneader throughout its full length.

60 kg of dehydrated nitrocellulose containing alcohol is loaded into the kneader, through a manhole in the upper section of the cylinder. It is unloaded through the lateral cover. Kneading takes as long as that in a Werner–Pfleiderer kneader.

The advantage of kneaders of the Chaudel–Page type is that they take up considerably less space than Werner–Pfleiderer kneaders. Premises which provide accommodation for six kneaders of the Chaudel–Page type can hold at most three Werner–Pfleiderer type kneaders.

Safety in operating kneaders is, in general, fairly high. This stage of production is considered to be one of the safest in the manufacture of nitrocellulose powders, now that it is known how to avoid the danger created by electrification of the solvent, especially of ether. It was observed that numerous explosions and inflammations of ether were caused by discharges of static electricity, e.g. there were accidents caused by the ignition of ether when the valve feeding it to the kneader was opened. Such accidents ceased when all containers and pipes containing solvents were carefully earthed. The kneaders must also be earthed. The equipment driving them—engines, transmission gears etc.—should be situated in a separate room.

The moment of unloading is particularly dangerous since large quantities of ether vapours mix with the air to form an explosive mixture. At this moment any impact of metal against metal which may produce sparks is dangerous (e.g. allowing the heavy lid to strike against the rim of the kneader in the Werner–Pfleiderer system).

Dough containing a considerable amount of solvent is non-flammable and almost non-explosive. Only the solvent burns easily and only if there is an access of air. Indeed, the solvent strongly "phlegmatizes" the nitrocellulose, considerably reducing its explosiveness.

In some countries (e.g. the U.S.A.) the nitrocellulose–alcohol–ether dough is subjected to an additional treatment intended to improving its homogeneity.

This consists of "blocking" which involves pressing the mass for several minutes at a pressure of *ca.* 200 kg/cm^2 (3000 lb/in^2). The block thus formed is transferred to another press of a type much similar to the extrusion press (Fig. 213). Here the dough is forced through a series of screens and perforated plates. This is referred to as "macaroni" pressing owing to the shape of the extruded threads.

The shredded, "macaronied" dough is introduced into the extrusion press, as described in the next paragraph.

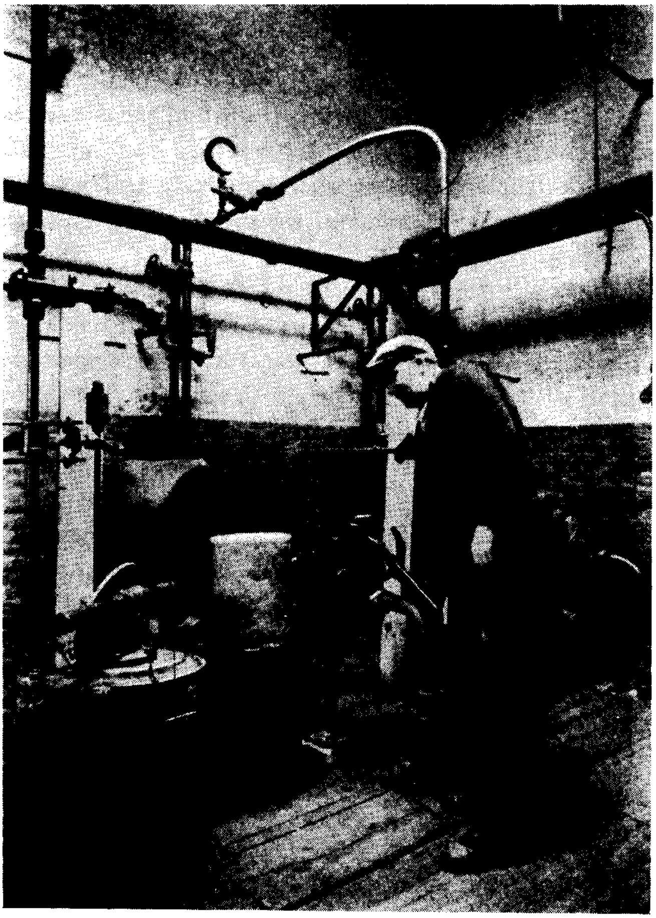

FIG. 213. Blocking press at E. I. du Pont de Nemours and Co. factory, according to Davis [12].

SHAPING THE DOUGH

The dough is usually pressed into the desired shape by extruding it from a hydraulic press. Formerly, the dough was rolled into sheets by passing it between rolls, predried and cut into flakes or strips. This method is retained for the manufacture of some types of nitrocellulose powder, i.e. very fine ones with a very high rate of burning ("coefficient of vivacity"*), used as sporting, pistol, and blank powders.

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* According to French nomenclature "coefficient of vivacity" (coefficient de vivacité) is the rate of increase of pressure during the burning of the main part of the grain of smokeless powders in a closed vessel (p. 530).

Rolling is the most desirable method for obtaining flakes of very low web thickness since it is difficult to obtain strips of a thickness below 0.40 mm by pressing and there is much waste, due to the clogging of the die slots and the folding and tearing of the extruded strips (rolls are shown on Fig. 260).

For rolling the dough should contain a relatively small amount of solvent (should be "dry") otherwise it adheres to the surface of the rolls and is then difficult to remove. On an average, dough to be rolled should contain less solvent (about 50%) than that subjected to pressing. Rolls especially adapted for the manufacture of nitroglycerine powder are most widely used, but not heated.

The use of hydraulic presses makes it possible not only to shape the powders into flakes or strips but also into cords or tubes or even into more complicated profiles. The operation of the press consists of the filling the cylinder so that the highest possible density is obtained with all air spaces eliminated. The piston of the press forces the mass first through a sieve that removes mechanical impurities and then through the die giving it a required shape. It is particularly important to remove all impurities from the dough, otherwise they may interfere with pressing and may distort the shape of the product—troubles that obviously reduce the efficiency of operation and increase operating expenses. If the dough is "macaroni" pressed (see p. 589) it is already filtered and homogenized and extrusion to the final shape is much facilitated.

The extruded strips, cords or tubes are forced from the die directly on to a linen conveyer or other receptacle from which they are passed to the drying room.

The die of press is the most essential structural component of the system since it imparts a definite shape to the dough. If the powder is to be shaped into flakes or strips, a die with a mouth in the shape of a slot or several slots is used. E.g. German rifle powder was extruded in the form of strips 2 mm wide and 0.45–0.55 mm thick. The thickness of strips was modified by the change of die depending on the required time of burning of the powder. On changing the lot of nitrocellulose used for the manufacture of the powder, the experimental batch may indicate that it is more, or less, "vivacious" than the standard powder. To obtain a faster burning powder than that of the experimental batch made of strips, e.g. 0.50 mm thick, a die giving thinner strips, e.g. 0.45–0.47 mm thick is used. If, on the other hand, the experimental batch has too high a "coefficient of vivacity", the die should be replaced by one which gives thicker strips, e.g. 0.53–0.55 mm.

The influence of the web thickness on the ballistic properties of cannon powder is illustrated by the following example of strip powder used for 105–120 mm field guns. The total solubility of this powder is 35%.

Web thickness	Muzzle velocity obtained v_0	Pressure p
2.7 mm	733.5 m/sec	2563 kg/cm^2
2.8 mm	724.2 m/sec	2323 kg/cm^2
2.9 mm	719.0 m/sec	2282 kg/cm^2

With thinner powders the influence of changes in web thickness is greater. E.g. for the powder used for 75 mm field guns:

Web thickness	v_0	p
1.2 mm	547.5 m/sec	3015 kg/cm^2
1.3 mm	538 m/sec	2587 kg/cm^2

The final web thickness of flake and tubular powders, after the removal of solvent, amounts to 53–65% of the web thickness of the strip at the moment of extrusion. The extent of shrinkage depends on such factors as total solubility, the viscosity of nitrocellulose, the quantity of solvent and the composition of the dough at the moment of extrusion. A greater solubility and a higher content of solvent lead to greater shrinkage of the strip.

The die in which tubular powder is extruded is shown in Fig. 214 (according to Yegorov [11]). It consists of two sections (*1*) and (2) inserted one in the other. The lower channel of section (*1*) of the die gives the outer diameter to the tube while section (*2*) of the die contains a centrally-fixed steel wire, the thickness of which determines the inner diameter of the single-perforated tube. Multiperforated dies are of similar design (Figs. 215 and 216, according to Yegorov).

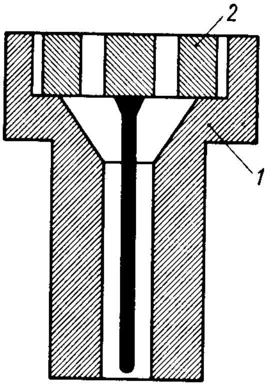


FIG. 214. Design for a die for shaping tubular powder.

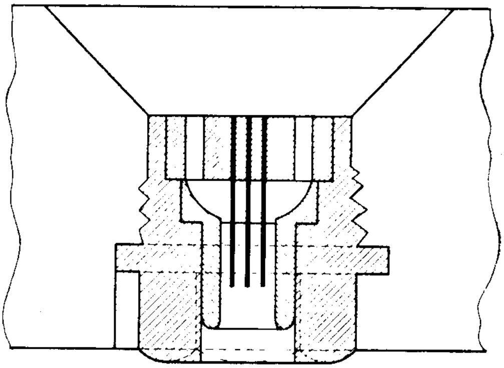


FIG. 215. Design for a die for shaping multitubular powder.

The presses are usually operated with two cylinders working alternately. When the dough is extruded from one of them the other is loaded with material from the kneaders and vice versa (Fig. 217). The dough is loaded in batches, using a brass shovel, together with a ramming piston working under a pressure of about 50 kg/cm^2. A cylinder may hold 15–25 kg of dough (calculated as dry nitrocellulose) depending on the dimensions of the press. When the cylinder is loaded, a dried cake of dough and a leather disk are put over the charge as a seal to prevent the "leakage" of the mass through the gap near the pressing piston. As a cylinder is loaded it is turned through 180° to take up the position at which the piston, working under a pressure of 75–125 kg/cm^2, extrudes the mass through the die.

There are presses in which a cylinder fitted with a die and a system of filters is filled with the dough and turned through by 180°. In other presses, e.g. those of the Champigneul type, the bottom of the cylinder, when filled with the rammer, is formed by a separate piston. When, however, the cylinder takes up the position for pressing the bottom section is formed of a set of filters together with the die. In turning the cylinder from the loading to the pressing position, only the cylinder is moved, while the bottom stays in position. A general view of a press of the Champigneul type used in France and Werner–Pfleiderer used in Germany is shown in Figs. 218 and 219, respectively. Figure 220 shows a hydraulic press used in Sweden (Bofors Nobelkrut).

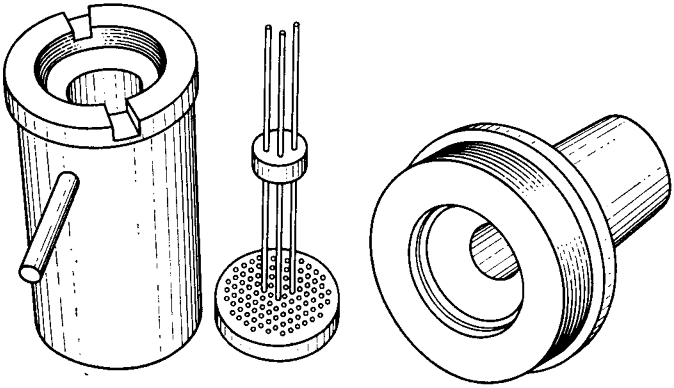


FIG. 216. A view of a multiperforated die.

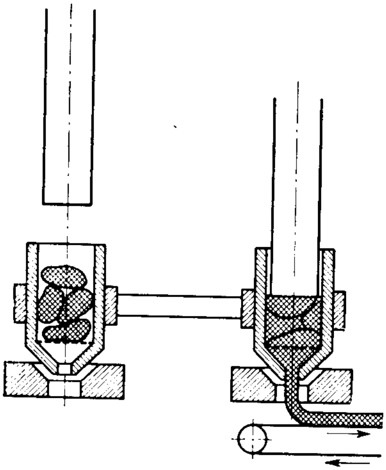


FIG. 217. Schematic view of the functioning of a press for extruding strips and tubes of powder.

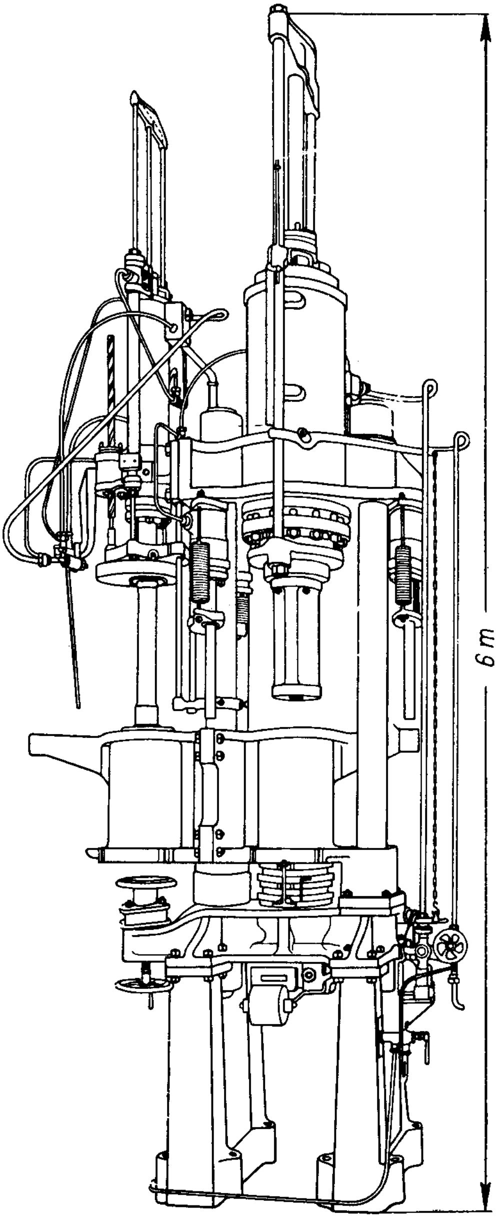


FIG. 218. General view of a Champigneul press used in France for extruding strips and tubes of powder, according to [13].

A horizontal extrusion press used in the U.S.A. is shown on Fig. 221.

The yield of a press depends not only on its design, applied pressure and the dimensions of the extruded strip or tube, but also on the plasticity of the dough. The effect of the dimensions of a strip or tube on the yield of the press is illustrated by the following examples. In a press of the Champigneul type, when pressing a strip 0.70 mm thick for rifle powder (total solubility 30%, amount of solvent 120%), the yield is 90 kg/hr. When pressing a strip 2.8 mm thick (total solubility 40%, amount of solvent 125%) the yield is 175 kg/hr (calculated as dry nitrocellulose). The same powder mass, when pressed into strips 5.0 mm thick, gives a yield of 200 kg/hr.

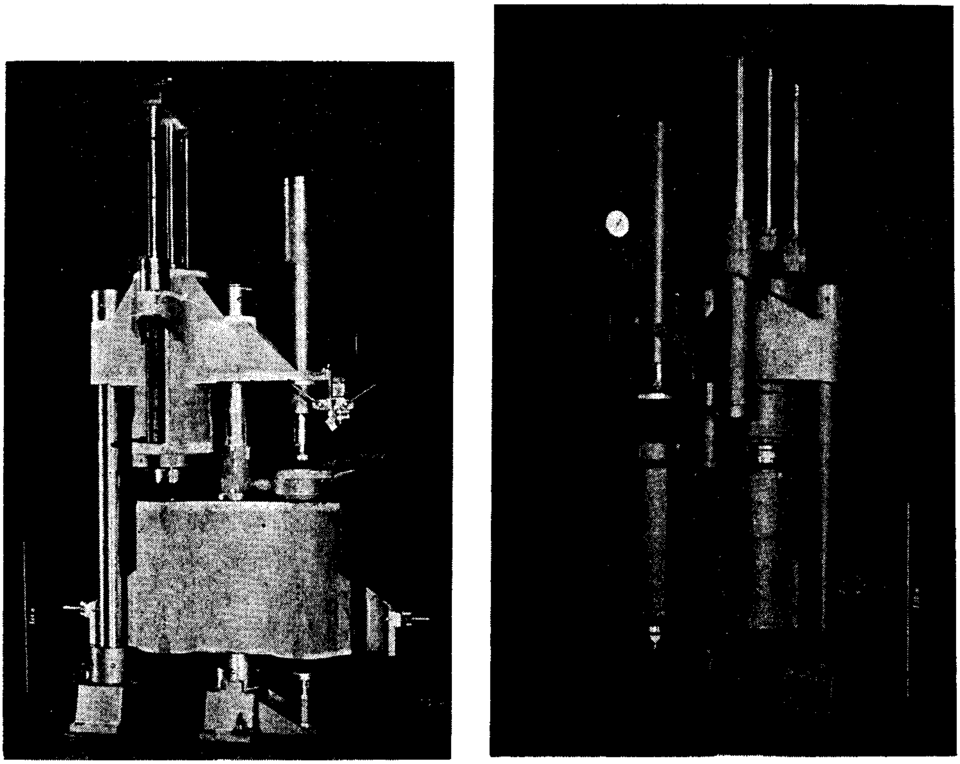

a) b)

FIG. 219. General view of Werner–Pfleiderer powder press (Courtesy Werner & Pfleiderer, Maschinenfabriken und Ofenbau, Stuttgart).

Pressing is not a particularly dangerous operation. Its safety is secured to a great extent by care in ramming the dough in the cylinder, so as not to leave free spaces filled with air. If this is not done an explosive mixture of solvent vapour in air is formed in these spaces and violent (adiabatic) compression of such a gaseous mixtures under the pressure of the piston may occur together, elevating the temperature above that of initiation. This could lead to an explosion. As previously stated, nitrocellulose containing solvent explodes with difficulty, thus there is no danger that the explosion of a vapour–air mixture may bring about an explosion of the whole nitrocellulose mass. Nevertheless it does mean that there may be an explosion of a mixture of air with ether and alcohol present in the pressing room. This would have disastrous consequences.

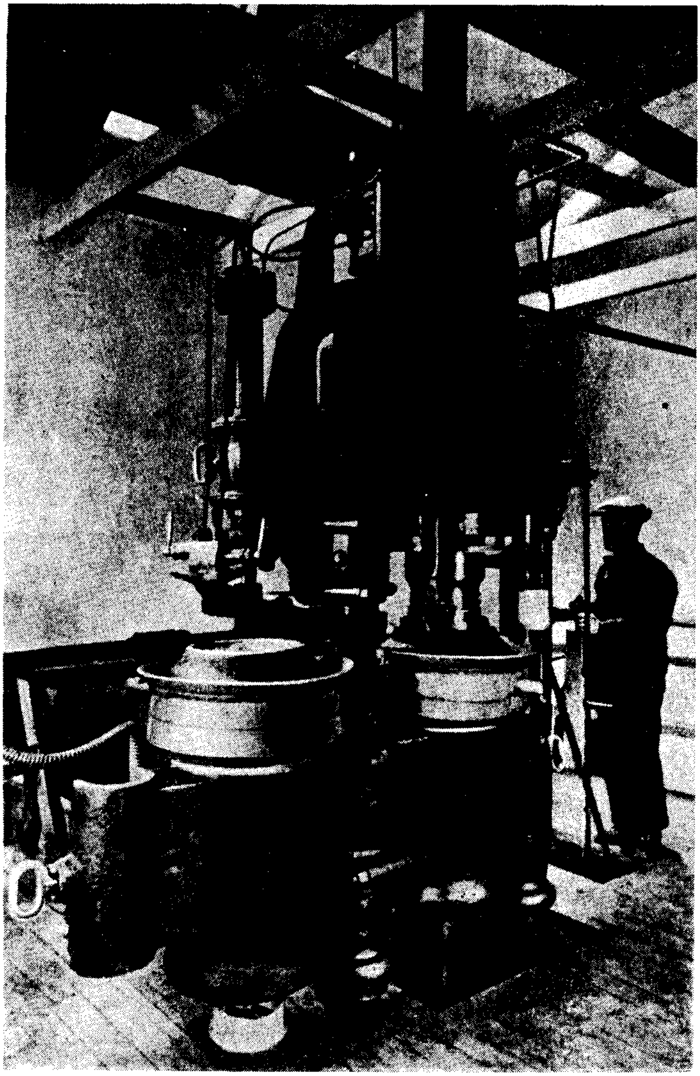


FIG. 220. Extrusion press used in Sweden (Bofors Nobelkrut).

Predrying

After the dough has been shaped, it is subjected to predrying which reduces the solvent content to 20–30%. The mass so dried becomes mechanically resistant and may therefore be cut without being deformed. Due to the presence of residual solvent the mass also retains a certain plasticity and elasticity, preventing crumbling and dusting during cutting.

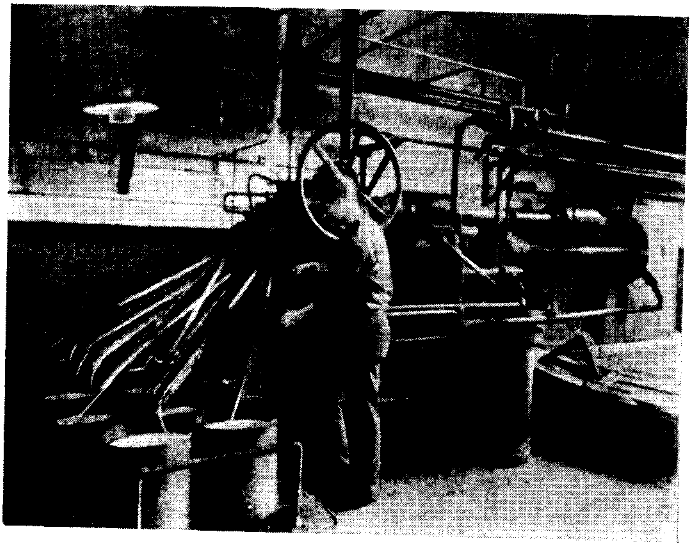


FIG. 221. Extrusion of powder in the form of perforated cylinders at E. I. du Pont de Nemours and Co. Factory, according to Davis [12].

Predrying should be conducted at temperatures as low as possible, i.e. within the range 15–25°C. Higher drying temperatures may cause the powder to swell or crack, due to intensive evaporation of solvent. It is therefore advisable, especially at the beginning, to maintain a low, but not too low temperature—in the latter case water vapour may condense on the powder, leading to the partial precipitation of nitrocellulose from the colloidal sol. This causes bright stains to appear on the surface of the powder. Since the heat of evaporation of the solvent is high, the temperature of the air coming into the drying room should be higher than the drying temperature. The composition of the residual solvent gradually changes. Ether, being more volatile, evaporates more quickly, so that the residual solvent is enriched in alcohol. A small quantity of ether remains in the alcohol, however, and is not removed by simple drying.

Since the rate of volatilization decreases as the ether is removed, the temperature should be raised gradually during drying.

An important factor influencing the dimensions of the predried powder is the viscosity of the nitrocellulose solution. The lower the viscosity of the nitrocellulose, the greater is the shrinkage of the nitrocellulose gel on drying. This produces flakes or tubes of considerably smaller size than those from nitrocellulose of higher viscosity.

Solvent recovery is extremely important from the economic point of view. The solvents are recovered by various methods, dealt with in a separate section (p. 599). From the time the strips or tubes are extruded until they are loaded into the predriers a certain period of time elapses depending upon the type of plant, the method of operation etc.

The amount of solvent escaping into the air depends on this period of time and on the season, the temperature of the air etc. Solvent losses range from 10–25%, calculated as the solvent introduced into the powder mass in the kneaders.

Originally, predrying was conducted in ordinary cabinet driers fitted with racks. Strips or tubes intended for drying were thrown over the racks. This type of drier is however unsuitable for the recovery of solvents since the relatively large surface of the door allows considerable solvent loss on loading and unloading. The cabinet drier used in the U.S.A. is shown in Fig. 222. Here the powder was placed in the drier already cut up since the method of manufacture required that thicker powder tubes must be cut up directly after pressing (before predrying). In some driers of more modern design used in France the surface of the loading and unloading holes is very small in comparison with the drier's capacity (Fig. 223). There are slightly

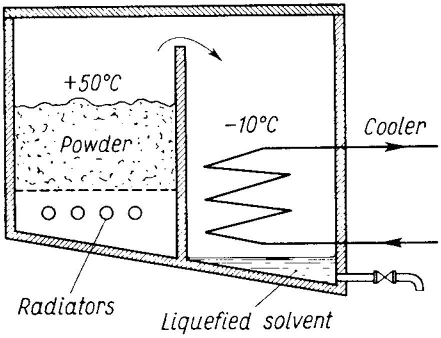


FIG. 222. A cabinet drier for predrying powder and solvent recovery.

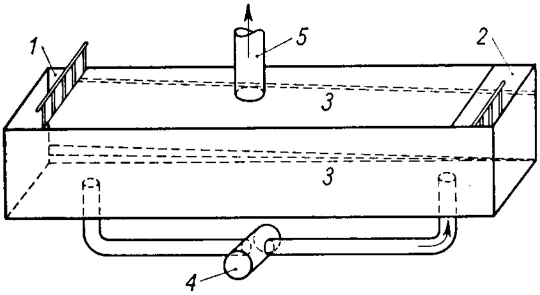


FIG. 223. A cabinet drier for predrying powder: *1*—hole for loading, *2*—hole for unloading the powder strips and tubes, *3*—rails inclined towards the hole unloading, *4*—air supply, *5*—air exit.

inclined rails inside the cabinet, on which the racks in the form of rods fitted with rolls, are moved. The powder strips, tubes or cords are suspended on the racks. Fresh air or air with a reduced content of solvent (depending on the recovery method) enters from the bottom, becomes saturated with the solvent, and escapes through the top. It is most important that the powder is dried as uniformly as possible. Driers of this design should not be too long as this prevents uniformity of drying. The best length is approximately 5 m.

Solvent recovery

Solvent escapes from nitrocellulose powder at various stages of its manufacture. The largest amount volatilizes during the predrying of the freshly shaped strips or tubes in cabinet driers specially constructed for this purpose. Installations for the recovery of this solvent have therefore long been in use in factories.

At other stages of the manufacture of the powder the solvent escapes into the atmosphere.

The losses of solvent in various stages of manufacture, for each 100 kg of nitrocellulose used (based on French findings from World War I) are tabulated below. Losses of alcohol and ether are calculated as alcohol (1 kg of ether equivalent to 1.4 kg of alcohol).

TABLE 178

LOSSES OF ALCOHOL AND ETHER IN THE MANUFACTURE OF NITROCELLULOSE POWDER

No.	Stage of manufacture	Losses of alcohol kg
1	Dehydration	1
2	Kneading	5
3	Loading of presses	5
4	Pressing (for strips 1.8 mm thick on the average)	22
5	Loading and unloading of predriers	9
6	Cutting	7
7	Screening	10.8
8	Soaking	7
9	Refining of alcohol from dehydration	1
10	Refining of alcohol and ether recovered on predrying	7
11	Storing of alcohol and ether	1.2
	Total	76.0 kg

This summary gives the amounts of solvent that escape to the atmosphere of the factory premises at various stages of manufacture. This solvent is partly recovered by means of an additional installation which will be discussed later.

There are two essential methods for the recovery of solvent:

(1) Methods that rely on condensation of the solvent vapours by cooling (or compression).

(2) Methods relying on adsorption or absorption of the solvent.

Condensation methods are successful only when there is a high concentration of solvent vapours in the air. In practice, however, the concentration of the solvent in the air is usually not high enough, so that the efficiency of the installation is relatively low. When the vapours of solvent are considerably diluted in the air, the condensation method cannot be applied and the solvent should therefore be recovered by absorption.

Installations for the recovery of solvent usually consist of main and ancillary sections. The main installation comprises equipment for the recovery of the solvent which escapes from the powder on predrying. The ancillary installation recovers solvent from various production departments. Solvent recovery ducting is installed in rooms containing high solvent concentration. This improves the working conditions by removing ether–alcohol vapours from the atmosphere.

The main installation may be used for the recovery of solvent either by condensation or by absorption. The ancillary installation usually deals with considerably dilute solvent vapours so that the best results are attained by absorption.

Condensation or absorption methods may also be applied to the recovery of the solvent removed from the powder on drying under reduced pressure (p. 614).

The recovery of solvent from the water after soaking the powder and from the vapours evolved on soaking is a separate problem and will be dealt in a section on p. 620.

With more recent solvent recovery methods the consumption of alcohol and

TABLE 179

RECOVERY AND CONSUMPTION OF SOLVENT PER 100 kg OF POWDER READY FOR USE

No.		Solvent (kg)	
		Used	Recovered
	Ether	92–116	–
1	Recovered in installations for predrying	–	44–63
2	Recovered after the soaking of powder	–	–
3	Recovered with cresol or activated coal	–	1–9
4	Consumption	39–56	
	Alcohol	97–148	–
1	Dehydration	–	26–75
2	Recovered in installations for predrying	–	29–35
3	Recovered after the soaking of powder	–	15
4	Recovered with cresol or activated coal	–	1–3
5	Consumption	18–40	

ether in powder manufacture is considerably reduced. In Table 179 figures based on statistical data from various French factories during World War I are summarized.

The consumption of alcohol (1 kg of ether equivalent to 1.4 kg of alcohol) for the production of 100 kg of powder is 72–117 kg.

In choosing a method for the recovery of solvent operational safety is a primary factor to be taken into account. While the machinery is in operation the greatest danger is associated with the mixture of air and alcohol–ether vapour which flows through the pipelines and appears in various parts of the plant.

As moderate concentrations of solvent in the air, i.e. 4–9% are the most dangerous, danger is minimized either by very high concentrations (over 9%) or by very low ones (under 4%). Very high concentrations are only likely to occur in the main installation. There is always a danger, however, that with the predrying of the powder and the condensation of the solvent, the concentration of solvent vapours may fall to a limit at which the gaseous mixture becomes dangerous. The mixture of solvent vapours may also become diluted to the danger limit due to a plant leakage. For these reasons installations which require high concentrations should be considered relatively dangerous. Those which can work on low concentrations of solvent vapours, i.e. considerably below the lower limit of dangerous concentrations (i.e. installations for the recovery of solvent by absorption) permit a greater margin of safety.

Installations for the additional recovery of solvent are an additional hazard in a powder factory, because separate buildings, often some distant apart, are connected by pipelines through which a mixture of air and alcohol–ether vapour flows. This contradicts the basic rule that all buildings in a powder factory should be separate and at a safe distance from each other. There are devices for breaking a flame moving along a pipeline, but their effectiveness is limited, e.g. when weak explosions occur in the gaseous mixture (the design of these fire breakers is discussed on p. 607).

Instances are known of the destruction of nearly whole factories simply due to the fact that the separate buildings were connected with a net of solvent recovery pipelines, e.g. the large explosion at Hasloch, Germany, in 1926.

A method which might ensure safety in the recovery system is based on a partial or total replacement of the air within the pipelines by a gas containing no oxygen that does not form explosive mixtures with alcohol–ether, e.g. by nitrogen or carbon dioxide from exhaust gases. This method, however, proved too expensive, and was not carried beyond small scale tests.

Recovery of solvent by the condensation of vapours. This is one of the oldest methods which once was widely used in many countries (France, U.S.A.) and well checked in practice.

The recovery devices used in France (Fig. 224) function in the following way. Fan (*2*) forces the air, heated in heater (*1*), into the predrying chamber (*3*). The air in the chamber is saturated with the solvent up to a content of approximately 700 g/m^3 (in percentage by volume this amounts to about 30% for alcohol and to about 20% for ether). From there it passes through heat exchanger (*4*) into cooling chamber (*5*), where a temperature of −5°C is maintained. Here part of the solvent is condensed and flows down along the sloping bottom of the chamber. The air leaving the chamber contains about 300 g/m³ of solvent. It then passes through the heat exchanger in which it is preheated to a temperature of 15–30°C (depending on the method used for predrying the powder) and returned to the predrying chamber. Thus the air circulation cycle is a closed one.

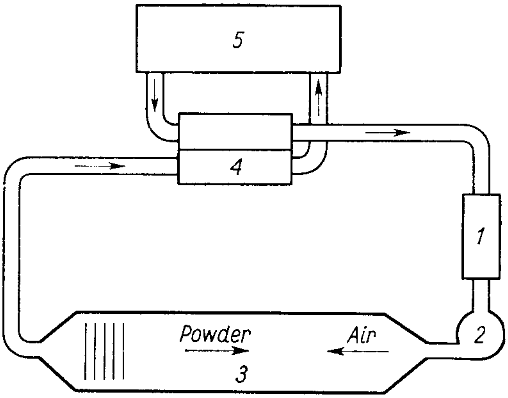


FIG. 224. Schematic view of an installation for predrying powder and solvent recovery, according to [13].

Recovery stops when the content of solvent in the air in the predrying chamber drops to 10%.

In the installation described above 80–85 kg of liquid solvent is recovered per 100 kg of powder (calculated as dry nitrocellulose). Accepting that before predrying the powder contains 110–115% of solvent and after it, 15–25%, the amount of recovered liquid represents 80–90% of the solvent lost by the powder on predrying. This accounts for 60–70% of the solvent used for the manufacture of the powder. Since the recovered liquid contains about 5% of water, its amount is somewhat lower.

The average composition of the recovered liquid is:

Ether	62%
Alcohol	33%
Water	5%

The composition of the liquid varies depending on the temperature inside the predrier (at the beginning it is 10°, by the end 30°C). At a high temperature (e.g. 50°C) the content of water in the liquid is less than 3%.

The composition of the recovered liquid also varies in time. At the beginning the liquid is rich in ether (60–70%) and relatively poor in alcohol (about 30%). By the end alcohol predominates (about 70%), and the content of ether falls to about 25%. The content of water remains almost constant.

The operational safety of this recovery installation is far from perfect. Explosions in driers caused by the impact of steel or even brass tools against iron, by the friction of powder strips against the iron edge of driers or by the electrification of powder strips, are well known.

Recovery of solvent by isothermal compression. This method was proposed by Claude [14]. It was applied to the recovery of alcohol containing camphor which escapes during the manufacture of celluloid. With alcohol and ether this process entails compressing the vapours to 7 atm, thus causing the condensation of the alcohol and after that rapidly expanding them. Ether is condensed by intensive cooling. The necessary plant was very expensive and there was risk of explosion when the mixture of the air with alcohol and ether was compressed too rapidly. It never attained wide application.

Absorption of solvent with sulphuric acid. This is another of the oldest methods for the recovery of solvent. It was first used for the recovery of alcohol and ether in the manufacture of artificial silk by the old Chardonnet process and was then widely applied in the manufacture of powder in Germany and Austria before and during World War I. The air containing alcohol and ether entered the tanks filled with sulphuric acid. The tanks were cooled from outside by spraying with water.

At the Troisdorf powder factory near Cologne, lead towers sprayed inside with sulphuric acid were used for the absorption of the solvent. Air containing alcohol and ether entered from below in counter-current to the sulphuric acid.

The solvents were distilled from the sulphuric acid by heating to 120°C. Alcohol is then partly converted into ether. The yield was low: only 10–12% of solvent used for the manufacture of the powder was recovered. The disadvantages of this method were numerous and the method is no more in use.

Absorption of solvent with cresol. During World War I Brégeat [15] in France suggested the recovery of alcohol and ether with cresol. After successful tests in 1917, installations for solvent recovery by this method were erected in all the powder factories in France. The installations for ducting the air containing solvent were so arranged that they were in operation during unloading of the kneaders, loading of the presses, extrusion of the powder strips in the presses, and the loading and unloading of predriers.

The method is based on the fact that with alcohol and ether cresol forms a molecular compound which may then be decomposed by heating to a temperature of 130–135°C. The absorption is conducted in towers sprayed with cresol. The air and solvent vapour enters the towers from below. The towers are filled with ceramic rings. A diagrammatic view of the installation is shown in Fig. 225. Air plus solvent is introduced from below into tower (*1*), sprayed with cresol containing alcohol and ether. Partly freed from solvent, the air enters tower (*2*), sprayed with fresh cresol pumped from container (*4*). Tower (*3*) serves for recovering the drops of cresol entrained by the air. Cresol containing alcohol and ether flowing down from tower (*2*) is pumped by pump (*5*) into tower (*1*), from which, through pump (*6*) and container (*7*), it is passed to the heat exchanger (*8*) and the retort (*9*), in which alcohol and ether are distilled off. When free from solvent it flows down through the heat exchanger (*8*) and is returned to container (*4*).

Solvent absorption using cresol gives a good recovery yield, but large quantities of cresol are required. This is a drawback, and so is the costly installation required.

The recovery of alcohol and ether by the Brégeat method was used in Great Britain at Gretna during World War I, and was later adopted in Belgium at Caulilles and in Germany at Hasloch.

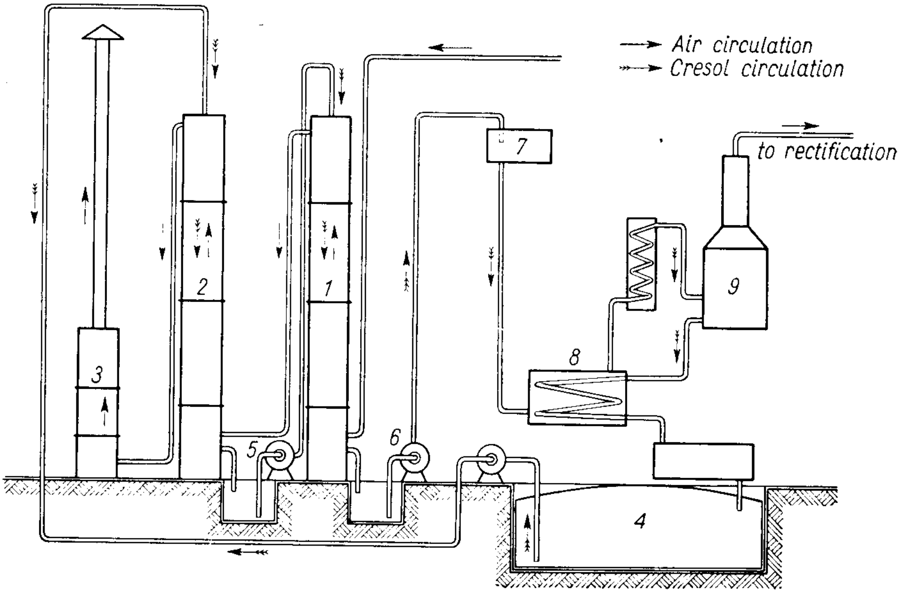


FIG. 225. Schematic view of an installation for the absorption of solvent with cresol (Brégeat method).

Absorption of solvent using water and aqueous solutions. This method, though of no value for alcohol and ether, was used for the recovery of acetone in cordite manufacture in Great Britain. Acetone was also recovered by using a solution of sodium hydrogen sulphite.

Adsorption of solvent on silica gel. Attempts to use this adsorbent failed since activated silica adsorbs moisture from air more strongly than alcohol and ether vapour.

Adsorption of solvent with activated charcoal. This is the most modern method of solvent recovery. It was introduced after World War I and immediately attracted attention by the exceptionally high recovery obtained, amounting to approximately 98% of the solvent entering the plant. The first plants using activated charcoal were used extensively in the oil industry for separating methane from heavier fractions in natural gas.

Initially, adsorption with charcoal was not efficient when used as a main installation in nitrocellulose powder factories. With the high concentration of alcohol and ether in the air the charcoal became very hot during adsorption, and this often led to an outbreak of fire in the adsorber. However, the safety of the operation was considerably higher when this method was applied to ancillary recovery. When working with dilute mixtures of alcohol and ether in air, there was less risk of fire and the yield of solvent recovered was increased. A concentration of solvent of less than 15 g/m^3 of the air (below 1%) is now common.

This method is applicable both for ancillary and main recovery. For the latter, however, a closed cycle is avoided by introducing large amounts of fresh air into the driers, as a diluent.

The simplest device for the adsorption of solvent on charcoal is shown in Fig. 226. The air containing alcohol and ether is introduced from below through valve (*1*) into a cylindrical container (adsorber) filled with activated charcoal. Alcohol and ether are adsorbed on the charcoal and the solvent-free air escapes through valve (*2*). The heat of adsorption raises the temperature of the charcoal by 30–40°C above ambient temperature. When the activated charcoal approaches saturation, the air–solvent mixture is directed to another adsorber. (It takes 5–7 hr to saturate an adsorber, depending on the concentration of solvent in the air.) Valves (*1*) and (*2*) are then closed, valve (*4*) is opened, and steam is introduced through valve (*3*) to remove the adsorbed solvent. Solvent and steam escape from the container through aperture (*4*). After the solvent has been removed, the inflow of steam is stopped, valve (*4*) is closed and hot air (110°C) is introduced through valve (*5*). This desiccates the layer of charcoal and air charged with water vapour escapes through valve (*2*). The evaporation of water from the charcoal during drying leads to a drop in temperature of the charcoal to 100°C or lower. The end of drying is indicated by

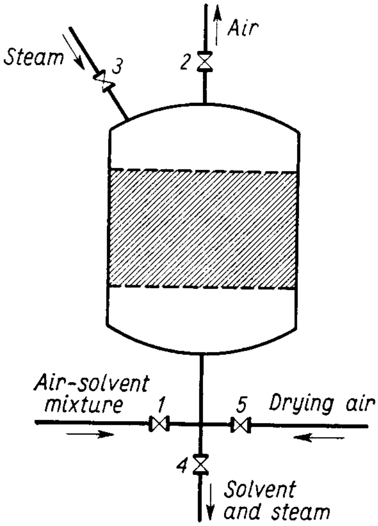


FIG. 226. Schematic view of an activated charcoal adsorber.

a sudden rise of temperature to 110°C. This is a moment of great danger when the charcoal may ignite. To prevent this, carbon dioxide or nitrogen may be introduced into the container towards the end of drying, which may take 6–8 hr (the time is variable and depends on the operating conditions). When drying is completed the inflow of hot air is replaced by one of cold air. Cooling is completed when the temperature falls to 15–20°C, which takes 1–2 hr depending on the season. After the adsorbent has been dried and cooled, the container is ready for the next adsorption cycle.

One adsorber holds a charge of charcoal ranging from 500 to 2000 kg, depending on the dimensions of the charcoal grains. A complete adsorption cycle comprising adsorption, distillation, drying and cooling lasts 14–18 hr.

3000 kg of steam, 0.08 m^3 of water and 0.2 kWh of current are required per 100 kg of solvent recovered. The consumption of activated charcoal (to replace losses due to collapse of the grains or loss of activity) is calculated at 0.05 kg per 100 kg of the solvent recovered.

The large steam consumption acted as an incentive to the development of another and more economic process. In the "Acticarbone" method developed in France between 1925–1926, the heater-cooler was located inside the adsorber, so that heating and cooling the charge was much more economical. In this installation 300 kg of steam was consumed for each 100 kg of the solvent recovered.

However, this system was abandoned because location of the steam heater inside the adsorber was not sufficiently safe. The modified system now most widely used is described below.

Efficiency and safety were improved by changes in design. A schematic view of a more modern "Acticarbone" installation is shown in Fig. 227. The time for each operation in this installation is considerably less than in earlier designs, i.e.:

Adsorption	2 hr
Steam distillation of solvent	$\frac{3}{4}$ hr
Drying the charcoal with hot air	$\frac{3}{4}$ hr
Cooling	$\frac{1}{2}$ hr

In addition to the charge of activated charcoal *A*, a "thermal" layer *T* of broken rock is laid in the adsorber to absorb heat should the charcoal layer ignite. The air plus solvent passes through fan *V*, valve (*1*), layers *T*, *A* and valve (*2*). When the charcoal is saturated with solvent both valves are closed, the steam is introduced through valve (*3*), valve (*4*) is opened and the alcohol and ether are distilled off and passed to the condenser (*5*). The condensed solvent and water is collected in the lower section (*6*), and from there conveyed by pump (*7*) for rectification. After the solvent has been distilled the inflow of steam is stopped and hot air is passed through the adsorber, with valves (*1*) and (*2*) open. When the charcoal is dry the air heater is shut off (it is not shown in the figure) and the charge is cooled by means of cold water, after which the adsorber is ready for another adsorption cycle.

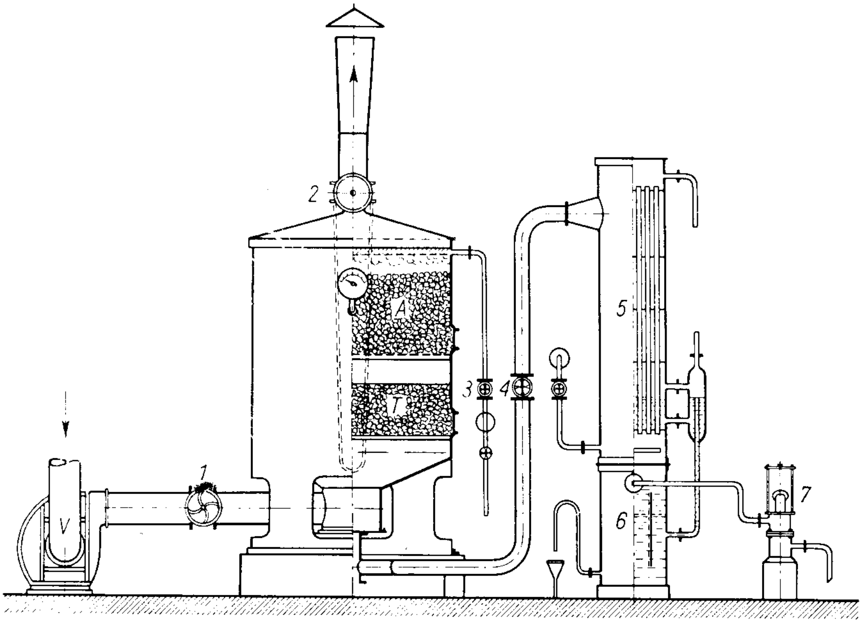


FIG. 227. Schematic view of an installation for the adsorption of solvent vapours (alcohol and ether) with activated charcoal by the "Acticarbone" method.

Fire breakers are used to protect the installation against flame that may arise in the pipelines carrying an inflammable mixture of air and ether–alcohol vapour and to cut off the drier from the pipelines that serve it. Breakers of the Sudlitz [16] type (Fig. 228) have proved the most efficient. In Sudlitz's opinion, the efficiency of the breaker is high if there is a partition in box (*1*), permitting easy passage of the gas and filled with heat-conducting metal. Copper mesh is used to form the partition and spirals, rings or copper shot are used as the filling. The box and pipeline outlets are closed with lids of thin sheet (*2*) so that they break if an explosion occurs in the pipeline. Any excess pressure leading to detonation of the gaseous mixture is thus avoided.

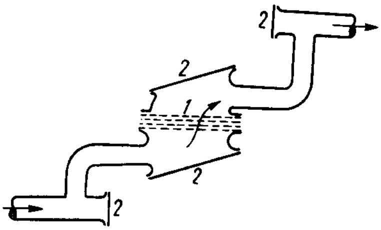


FIG. 228. Schematic view of a Sudlitz fire breaker.

Cutting

In some countries (e.g. in the U.S.S.R. and in the U.S.A.) thick strips (for cannon powders) may be cut immediately after the extrusion of the tubes. This is possible only when pyrocollodion cotton is used for the manufacture of the powder since it is easily soluble and requires only a small amount of solvent (about 80% by weight of nitrocellulose). After cutting the powder is subjected to predrying. When dried to a solvent content of 15–30%, the powder strips or tubes are usually sufficiently plastic and elastic to be cut without breaking or crumbling, caking or deforming.

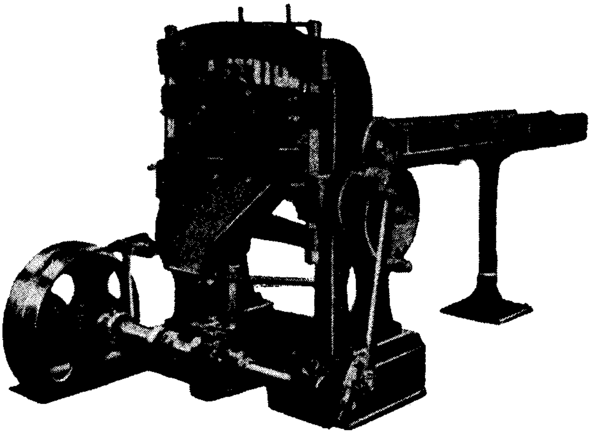


FIG. 229. A guillotine for cutting powder strips into flakes [7].

The cutters are designed according to the required shape of the powder. For cutting the powder strips into square flakes "guillotines" are often used (Fig. 229), in which a bundle of strips is moved forward intermittently, driven by a mechanism synchronized with the knife of the guillotine. The length of the stroke of the driving mechanism can be varied within certain limits. The knives must be very sharp, and are therefore changed frequently (every 0.5 hr). This greatly influences the uniformity of the dimensions of the flakes which, in turn, affects the uniformity of the ballistic properties of the powder.

Similar guillotines are used for cutting powder tubes. For short tubes a guillotine of the design described above is used. Slightly different ones are used for cutting of long tubes which are usually moved under the knife by hand.

Cutters for cutting wide powder strips into square or rectangular flakes are of quite different design, the principle of which is shown in Fig. 230. They consist of two systems of knives. The first is composed of two rollers with rectangular knives of a width corresponding to the required width of the powder flakes. The strip is thus cut lengthwise into ribbons (Fig. 231).

The second system cuts the strips crosswise, i.e., at right angles to the first one, and consists of a fixed knife-edge against which two knife blades rotate.

In this system, which is used extensively in France, a frequent change of knife blades and repeated sharpening are indispensable in order to ensure uniform properties in the powder.

In some factories cutting is combined with rolling (smoothing) the powder strips, if the powder is to be shaped in strips or flakes. Special cutters are used for this purpose (Fig. 232). They are fitted with smoothing rollers (*1*) and cutting rollers (*2*). The rollers are clamped with screws (*3*). Smoothing considerably reduces the quantity of waste resulting from deformation of the powder strips on predrying.

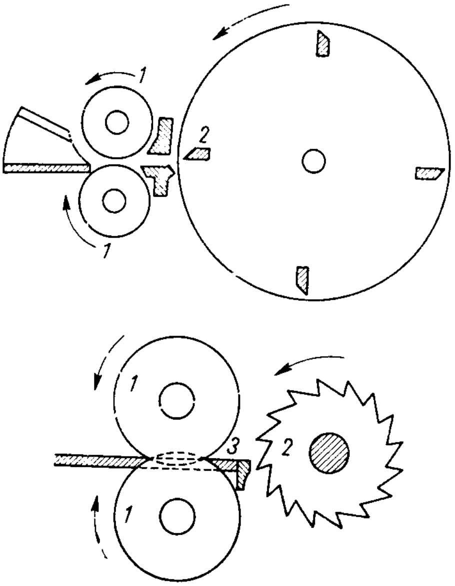


FIG. 230. A French design for cutters for wide powder strip, according to Vennin *et al.* [13]; *1*—rollers cutting lengthwise; *2*—rotational knife cutting crosswise; *3*—fixed knife.

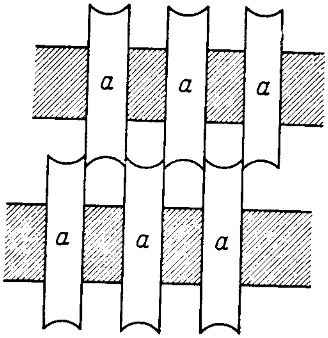


FIG. 231. A design for rollers cutting lengthwise, according to Vennin *et al.* [13]; *a*—cutting knives.

Cutting is a fairly safe operation if the cutters are carefully earthed to prevent them from building up static electricity, which has been a frequent cause of accidents. Care also should be taken to prevent overheating of the cutter component, including the knives. If overheating occurs the cutter must be stopped for some time until the knives are cool.

Grading

After being cut the powder should be graded to remove irregularly-shaped flakes, strips or tubes. The quantity of waste depends on the shape of the powder, its dimensions and on the condition of the cutters. With flake rifle powders, for instance, the smaller the dimensions of the powder flakes, the larger is the quantity of waste. The thicker the strips or tubes, as extruded from the press, the smaller the quantity of waste discarded during grading.

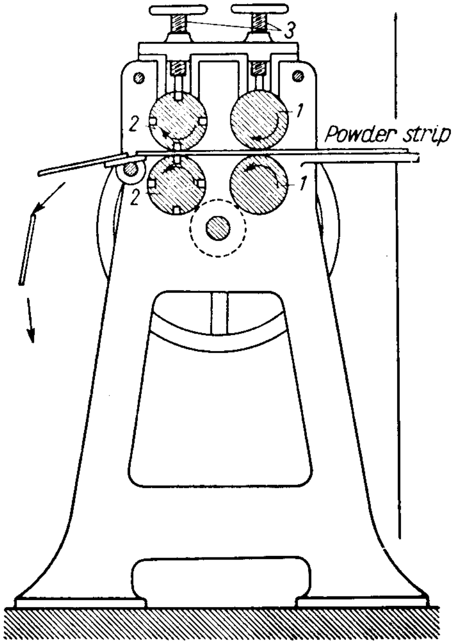


FIG. 232. A cutter for powder strips with smoothing and cutting rollers, according to Yegorov [11].

The method of grading depends on whether a fine-grained powder is to be dealt with or whether it is in the form of strips or long tubes. The former is graded mechanically, the latter manually.

Mechanical grading of fine-grained powder is carried out using vibrating or rotary screens of various designs (Figs. 233 and 234). Dust and oversized or irregular grains are collected in separate receivers together with undersized grains. The screen dimensions (usually made of brass gauze) are chosen in accordance with the type of powder being graded and the required dimensions of the grains. Waste and dust are recycled for processing (this will be discussed in the section devoted to the processing of waste—p. 631).

Manual grading consists of inspecting the strips or tubes and discarding those which are ill-shaped or discoloured (dark-blue stains). Grading is usually carried out on tables from which dust and waste are discarded into special boxes. It is advisable to use tables made of clouded glass lighted from below by electric light. This facilitates the recognition of defects in the powder (stains, wrong colour, etc.). Powder with dark stains is rejected into a separate box so as not to mix it with powder discarded because of faulty shape. The latter is recycled. Dark coloured powder is considered unstable and is either destroyed or made into training or sporting powders which can be used without delay.

The output of manual grading depends on the dimensions of the strips and tubes, i.e. it is higher for larger dimensions of powder. When grading one of the finest types of strip powders (powder for 75 mm field gun), of dimensions 0.7×20×144 mm, output is approximately 10 kg/hr per one worker.

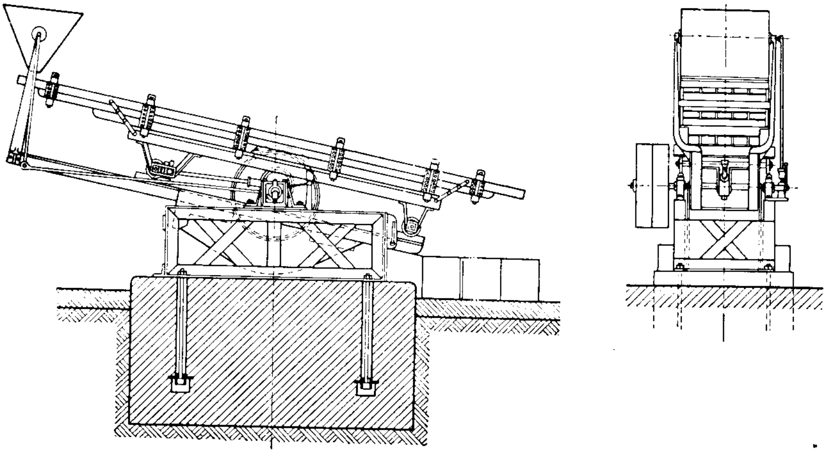


FIG. 233. Schematic view of an installation for the mechanical grading of fine-grain powder (vibrating screen), according to Yegorov [11].

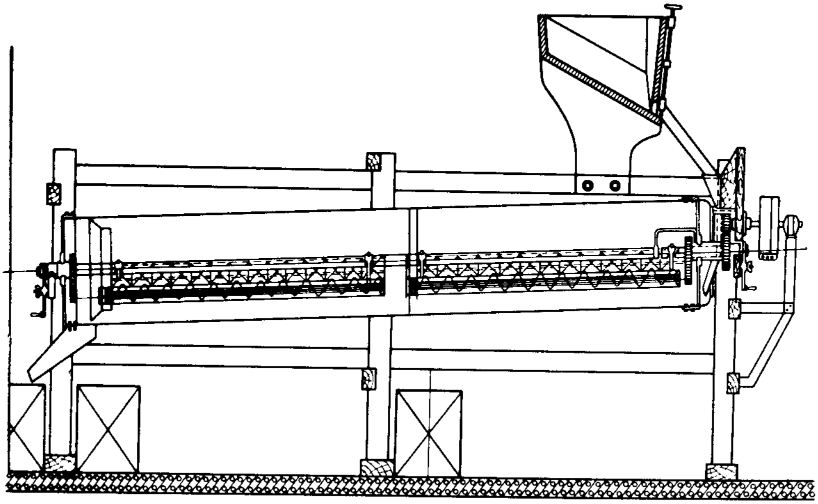


FIG. 234. Schematic view of a Marot installation for grading fine-grain powder (rotary screen), according to Yegorov [11].

Powder which is cut but neither air- nor water-dried is known as "green" powder.

Final removal of solvent

A predried powder burns very slowly since the residual solvent acts as an inhibitor. It is not until the content of residual solvent is reduced below a certain limit that the powder attains a usable rate of burning. It also acquires ballistic stability, so that its ballistic properties are unchanged during storage, since it contains no volatile constituents capable of volatilizing spontaneously and thus of modifying the ballistic properties.

The final removal of solvent from nitrocellulose powder may be carried out by two methods:

(1) By drying at reduced pressure at a temperature of 80°C or at atmospheric pressure at a temperature of 50–60°C.

(2) By soaking the powder in cold or hot water followed by drying.

Drying at reduced pressure. It was widely practised in Germany and often made it possible to avoid the soaking of powder. Driers used for this purpose (Fig. 235) consist of a cylinder made of boiler iron and shelves heated with hot water to a temperature of 60–80°C. The cylinder is tightly closed on both sides with lids clamped down by means of screws.

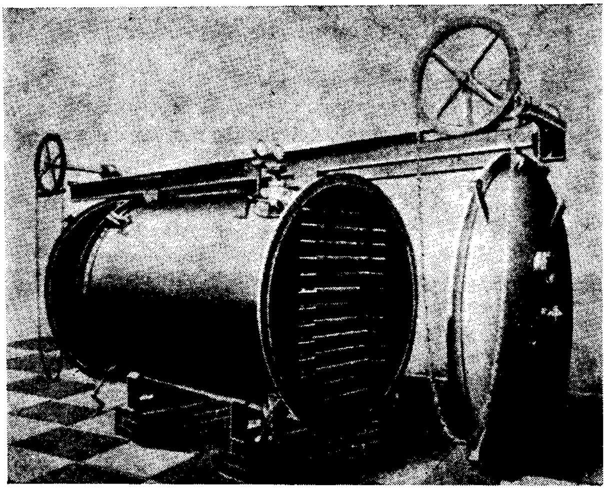


FIG. 235. A drier for drying nitrocellulose powder [7].

The powder is spread on cotton muslin stretched over wooden frames and placed on the shelves. The drier is then closed and the vacuum pump set in motion. The pump usually operates at a pressure of 100–150 mm Hg. When the pressure becomes steady, the screws clamping the lids are released, but the lids continue to adhere hermetically to the drier, owing to the reduced pressure created inside. As a safety precaution the driers work in this manner until drying has been completed. Thus should ignition occur the lids are freely detached. This prevents the powder from burning in a confined space, and exploding, and so destroying the drier. The capacity of the

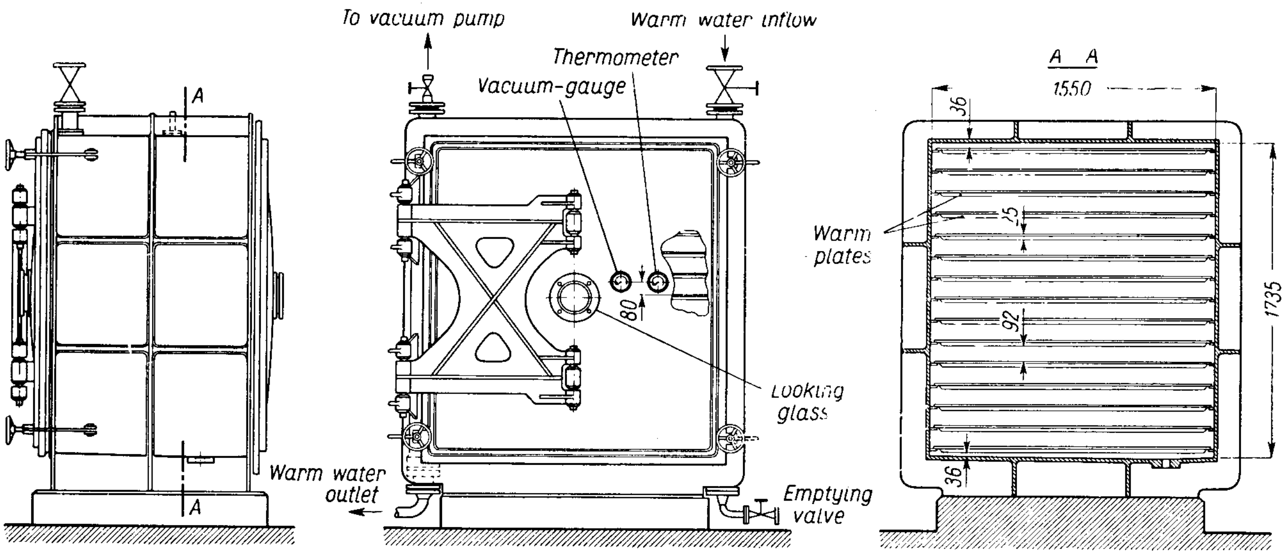


FIG. 236. View of a drying room with an installation for the recovery of solvent at reduced pressure.

drier is 1000–1200 kg of powder (calculated as the weight of dry nitrocellulose). Driers of this type are commonly used for the manufacture of fine-grained powder (e.g. rifle flake powder). Such a powder takes about 24 hr to dry at a temperature of 80°C. Powder dried at a reduced pressure has the advantage of being less porous than that from which the solvent is removed chiefly by soaking. After drying at reduced pressure, the powder may be subjected to soaking to remove residual solvent and then dried again. This treatment does not lead to the formation of additional pores in the grain. A more modern design of vacuum-drier is shown on Fig. 236.

An installation for the recovery of solvent (chiefly alcohol) by condensation is connected with a drier operating at a reduced pressure. The installation works at atmospheric pressure. It consists of two condensers cooled with cold water in which ether and alcohol (containing some water and ether) are condensed. From 10 to 25 kg of 95% alcohol is recovered per 100 kg of powder according to the season (more in winter).

Drying at atmospheric pressure. Various types of driers are used to dry powder at atmospheric pressure. In France drying houses with natural air circulation were often used (Fig. 237). They are reinforced concrete buildings with three stout walls and one—the blow-out wall—made of wood. The building is divided into several compartments each of which holds 600–1000 kg of powder for drying. The partition walls should be thick enough to withstand a high pressure in the event of ignition of the powder, so that only the light blow-out wall is wrecked. A door in the light wall is fitted with a reinforced concrete canopy to protect the drying house from rain and to direct the flame in the required direction should ignition of the powder occur. The canopy walls are of double thickness. There are openings with brass grids in the lower section of the light wall, above the canopy and in the door of the drying house. Air enters through the lower openings and escapes through the upper ones. The air is circulated as indicated by arrows through radiators heated with hot water [17]. They are located under iron shelves on which the trays of powder are set. The trays are made of wire netting stretched over wooden frames. When fine-grained powder is dried they are also covered with muslin. A separate chamber contains an automatic system for keeping the temperature of the water which feeds the radiators constant. This should be higher by 5°C than that inside the drying house and is usually 60°C (inside it is 55°C).

Drying at a temperature of 55°C requires at least 24 hr, but the actual duration depends primarily on the web thickness of the powder. As a guide the following interrelations may be assumed between the time of the drying of strip powder at 55°C and its web thickness:

Web thickness mm	Approximate time of drying hr
0.8–1.5	24
2.3–2.5	36
3.2–7.5	48

When drying has been completed the inflow of hot water to the radiators is stopped and the door is opened for 3 hr to cool the powder before unloading.

The drying house described above is very economical since it does not consume any mechanical energy. Its disadvantage lies in its rather poor air circulation which prolongs the drying process and therefore exposes the powder to the action of a high temperature for a relatively long period of time.

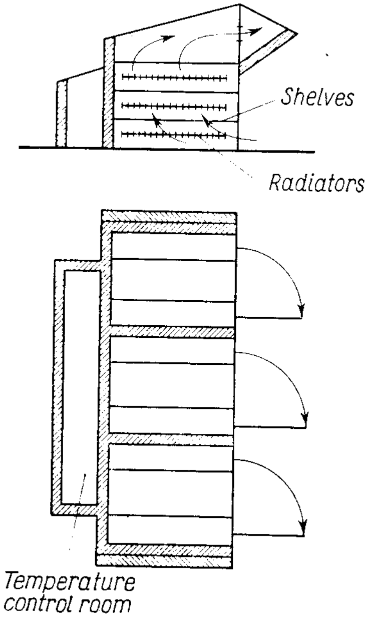


FIG. 237. Schematic view of a standard drying house for nitrocellulose powder used in France.

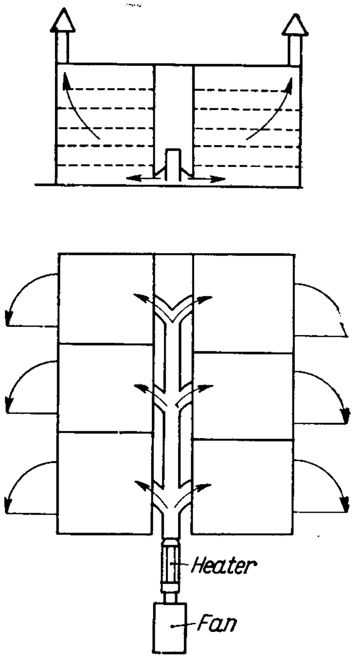


FIG. 238. Schematic view of a drying house with mechanical ventilation.

There exist a wide variety of drying houses with mechanical ventilation. Cabinet driers (Fig. 238) are one of the simplest types. In these the powder is spread on shelves through which there is a free passage of air. The air forced by means of a fan passes through a heater and is then supplied from below by pipelines to each partition of the drying house. The door opens from outside. The outer corridors (not shown in the figure) should be wide enough to allow for the passage of the trucks bringing the powder to be dried or removing it after drying.

There is another method (de Quinan method, Fig. 239) in which the powder is placed in shallow cylindrical (or otherwise shaped) tubs of brass sheet, lined internally with cloth. The bottom of the tubs are perforated. A fan forces heated air through the bottom; the air passes and escapes through an outlet in the roof of the building. When dry, the powder is cooled by cold compressed air. Drying in drying houses with mechanical ventilation takes approximately half the time needed when a natural air stream is used. Drying with mechanical ventilation has the disadvantage that a strong stream of air favours the oxidation of the diphenylamine present in the powder, and thus may easily lead to dark coloration (dark-blue or dark-green).

The drying of powder was formerly one of the most hazardous operations, but since the causes of danger have been eliminated by new methods it is now no more dangerous than any other of the processes for manufacturing nitrocellulose powder. The following rules must always be observed:

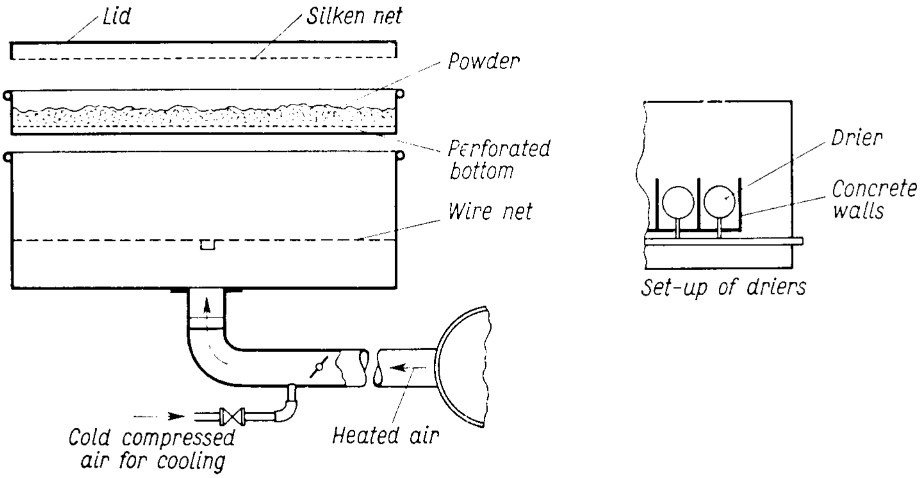


FIG. 239. Schematic view of a de Quinan drier.

(1) All shelves and other metallic parts of drying houses should be earthed.

(2) Doors in drying houses should be shut with clamps made of wood or of non-sparking metal.

(3) The premises must be kept clean with particular attention to the removal of spilt powder. Powder lying scattered on shelves or the floor for long periods undergoes spontaneous decomposition with the passage of years and has often been the cause of the ignition of powder in drying houses. Keeping the radiators clean is particularly important.

(4) The powder must not be removed from the drier until it has been cooled to a temperature of about 30°C.

Drying with infra-red radiation. The studies of Brun and Ratouis [18] show that drying with infra-red rays may reduce the time necessary for the removal of solvent by 20 or even 100 times, although for two reasons it is more expensive:

(1) The heat supplied by infra-red radiation is more expensive (at least three times) than steam heating.

(2) Only thin layers of powder may be dried since in thick layers the surface may acquire a dry skin, leaving a damp layer underneath. This may upset the uniformity of burning.

For the latter reason infra-red radiation is not used for drying nitrocellulose powder.

The design of an infra-red drier will be discussed later in the text (p. 636 and Figs. 254 and 255).

Soaking the powder. It appears that the final removal of solvent by soaking ("bathing") was first applied by Sukhinskii [19] in Russia, in 1892. By this method the solvent is removed from the powder much more rapidly than by any other. Soaking was widely practised in the manufacture of nitrocellulose powders during World War I, since it considerably accelerated production. The soaking temperature was then 80 or even 90°C which was inadvisable for three reasons:

(1) Due to the high temperature of the water some of the diphenylamine dissolves, thus reducing the content of stabilizer in the powder; in addition, the high temperature leads to more vigorous oxidation reactions of the diphenylamine.

(2) Due to the high temperature of the water the nitrocellulose partly coagulates from the colloidal state particularly on the surface.

(3) Powders become porous which is not always desirable.

A soaked powder may be easily distinguished from a non-soaked one. The latter retains a certain transparency while the former is dull, opaque (due to partial coagulation) and usually dark, of a grey-greenish colour, on account of the reactions undergone by the diphenylamine at a high temperature in the presence of water.

Saoking is most efficient if the powder has been only predried, but not dried at an elevated temperature. On drying at an elevated temperature (50–80°C) a dry skin forms on the surface of the powder, and this prevents the solvent inside from diffusing into the water. For these reasons it is most desirable to soak the predried powder at a low temperature (15–30°C) which is then gradually elevated to 50–60°C.

Vigorous prolonged soaking at a high temperature, like drying for a long period, may reduce the stability of the powder. It is believed that the decrease of stability is particularly pronounced when a non-dried powder, which contains a large amount of solvent, is subject to soaking. This may be attributed partly to the fact that on soaking a non-dried powder loses more diphenylamine than a dried powder containing little solvent.

Long detailed investigations have shown that if the powder is predried immediately after extrusion in a damp atmosphere facilitating moisture penetration its stability is impaired. If however drying takes place in a confined space by the action of a stream of dry air, without access of moisture, the stability is not reduced. In the latter case it makes no difference whether or not the powder is soaked after drying. With modern predrying equipment there is no fear of decreasing stability on soaking unless this is done too vigorously (soaking at a temperature of 90°C and over should be considered harmful, at a temperature of 80°C soaking should not exceed 72 hr).

Sometimes, when a highly porous powder is wanted (e.g. a sporting or training powder of high vivacity) the powder strips or cords are soaked in hot water immediately after extrusion from the press. A violent evaporation of solvent then ensues, the strips or cords swell, and holes are formed inside (Bazylewicz-Kniażykowski and

Partyka's method [20]). Powder may also be made porous by the previous introduction into the powder mass of salts soluble in water which are extracted by soaking. Potassium nitrate is generally used for this purpose so that a certain amount of it remains in the powder and enhances its vivacity.

The soaking of nitrocellulose powder in which alcohol and ether were used as a solvent should be carried out so that the solvent (chiefly alcohol) which passes into aqueous solution may be recovered. Nitroglycerine powder manufactured with a volatile solvent such as acetone should never be soaked since water would remove some of the nitroglycerine from the powder.

Soaking may often be replaced by drying at a reduced pressure, as previously discussed (Passburg [21]). This, however, requires expensive installations and is therefore relatively rarely used or only on a small scale.

Soaking is carried out either in cold, non-heated water at room temperature (15–30°C) or at an elevated temperature (50–80°C).

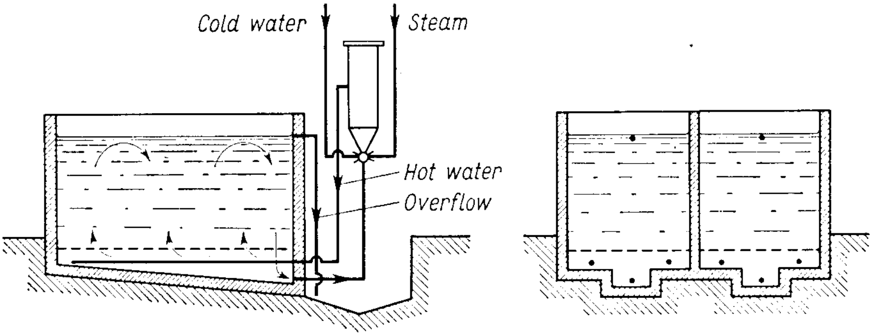


FIG. 240. A concrete basin for soaking tubular powders.

In the first case large concrete basins are used. It is advisable to line them with glazed wall tiles. Fine-grained powder is packed in cloth sacks, although this has the disadvantage that it hinders the circulation of water between the powder grains. Strip and tubular powders may be soaked either in baskets made of brass mesh, perforated brass sheets or in wooden boxes with openings through which the water circulates immersed in a vat. To increase the water circulation and thus accelerate the soaking process, pumps may be installed to circulate the water. The pump delivery must be adapted to the capacity of the vats (e.g. in vats with a capacity of about 3.5 m^3, water is circulated at about 300 l./hr). To facilitate the loading and unloading of the powder an electric lift with a non-spark mechanism may be installed.

Soaking in hot water is carried out in a very similar manner, although it is more convenient to use vats of a smaller capacity. The device for heating the water should also serve for the circulation of the water in the tub.

A powder soaking vat of the type used in France is shown in Fig. 240. It is made of concrete and divided by a partition into two parts, each 2.3 m long, 1.0 m wide and 1.4 m deep. The outer walls are 10 cm thick and it takes a charge of 300–700 kg. At some distance from the bottom a tough perforated sheet of brass is laid. Under the sheet there are pipes that supply hot water and drain the water to be heated from the lower section. Each vat has a heating system of its own with a steam injector and is fitted with an overflow for draining the excess water into a special container. It is advisable to use large containers for heating the water to a temperature of 50°C and to draw it from these containers for soaking the powder. The consumption of steam in the vats described above is:

for heating the water from 50 to 80°C—*ca.* 580 kg/hr
for maintaining a temperature of 80°C—650–850 kg/hr

The soaking time depends on the temperature and the type of the powder, i.e. the lower the temperature of the water and the larger the web thickness of powder, the longer the soaking time. In some factories, as a guide it is assumed that decrease of the soaking temperature for coarse-grained powders (a thickness of *ca.* 7 mm) by 10°C requires a threefold longer soaking time, e.g.: at a temperature of 80°C soaking lasts for 32 hr, at a temperature of 70°C it lasts for 96 hr, and at a temperature of 60°C it lasts 288 hr.

Other data show that finer powders (of a thickness of 0.5–2 mm) require an increase in processing time by 50% if the soaking temperature is decreased by 10%.

The soaking time also depends on whether the powder has been previously dried (to 1.5–2% of volatile matter) or only predried (to 10–15% of volatile matter). In the latter case soaking is much more effective although there is a danger that stability may be reduced.

Soaking greatly increases the vivacity of powder to an extent which depends on the method applied. The following example may illustrate the efficacy of soaking preceded or not by drying. One sample of powder was first subjected to drying for 24 hr at a temperature of 55°C, then to soaking for 12 hr at a temperature of 80°C and finally to drying for 24 hr at a temperature of 55°C. Another portion of the same powder was first soaked for 8 hr at a temperature of 50°C, then for 10 hr at a temperature of 80°C and finally dried for 24 hr at a temperature of 55°C.

It was found that the powder soaked without previous drying was faster burning and in the 75 mm gun gave a muzzle velocity higher by 9 m/sec and a pressure higher by 37 kg/cm^2 than the powder that was dried before soaking.

Table 180 gives data showing the effect of additional soaking (after polishing—see p. 627) on the increase of vivacity of rifle flake powder.

Vigorous soaking may distort the powder strips or tubes, especially thick ones. This is a further reason for recommending that soaking should be conducted at a gradually rising temperature, e.g.: 12 hr at a temperature of 30°C, 24 hr at a temperature of 45°C and 48 hr at a temperature of 60°C. To prevent distortion on soaking, especially at higher temperatures, the strips or tubes can be clipped into bunches with brass collars fitted with brass springs.

After soaking the powder is dried to remove moisture together with some of the residual solvent. Drying at a temperature of 55° requires 4–160 hr depending upon the web thickness of the powder (the duration of drying is given for a drying house with natural air circulation).

TABLE 180

Additional soaking		Increase by a value of	
		Δv	Δp
Time hr	Temperature °C	m/sec	kg/cm^2
24	80	36–44	300–450
24	85	45–60	350–550
24	90	60–70	500–600

After drying, cannon powders, i.e. strips or tubes, are subjected to a second grading as they may have been distorted or discoloured on soaking.

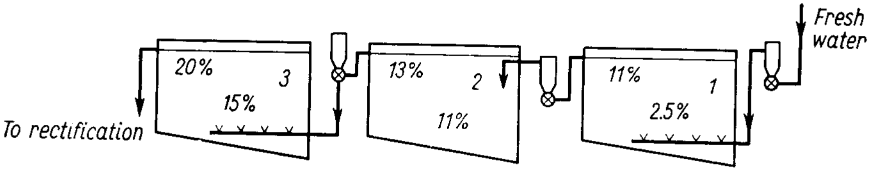


FIG. 241. A battery of powder soaking vats (the content of alcohol in various parts of the vat is indicated).

The recovery of solvent from the water after soaking

The soaking of nitrocellulose powder involves recovery of the solvent (chiefly alcohol) which passes into the water. It is worth while recovering this solvent if the content of alcohol in the soaking water is not less than 5%. By applying the battery counter-current soaking system the alcohol content in the water may be increased to 15–20% and the recovery of solvent thus made more profitable.

Soaking together with solvent recovery was adopted in France during World War I. A battery consisting of three vats was used (Fig. 241). Fresh water heated by steam injection was introduced into vat (*1*). From there it passed through an overflow and injector to the upper section of vat (*2*) and then, to the lower section of vat (*3*). The un-soaked powder was loaded in reverse order: first into vat (*3*), from there after soaking into vat (*2*), and, finally, into vat (*1*). By soaking at a temperature of 50°C, the following concentrations of alcohol were obtained in the vats:

Vat *1*	2.5% in lower section
	11% in upper section

Vat *2*	11% in lower section
	13% in upper section
Vat *3*	15% in lower section
	20% in upper section

The water from the vat containing an average of 18.5% alcohol was recycled for rectification.

It was thought that this method might lead to much greater losses of diphenylamine than with single stage soaking in water (when the concentration of alcohol is less than 6% by the end of bathing). This however was not so. The losses of diphenylamine on soaking by the battery method are less than 0.01%.

Besides recovering alcohol from the water after soaking it is also necessary to recover the ether and alcohol escaping from the vat as vapour, together with steam, when soaking with hot water. E.g. a powder containing 25% volatile matter (thus only predried and not dried) gives the following composition for the liquid formed by the condensation of vapours evolved from the soaking vat (according to Bonneaud [22], Table 181).

TABLE 181

Components of gaseous phase	Soaking at 50°C		Soaking at 80°C	
	Start	End	Start	End
Ether (%)	92	85	82	52
Alcohol (%)	5	10	13	32
Water (%)	3	5	5	16

In these experiments the quantity of liquids condensed from the vapours evolved during soaking at a temperature of 80°C amounted to 2–3%, calculated on the quantity of powder used.

To recover the solvent vapours evolved during soaking in the hot, the vat is fitted with an air-tight lid and a pipe through which vapours for condensation are conducted. 30 kg of liquid containing 96% of ether were obtained per 700 kg of powder in the vat.

At another plant 4 kg of liquid containing 71% ether and 16% alcohol per 100 kg of the powder soaked at temperatures of 60 and 80°C were obtained by condensation of the solvent vapours.

The content of residual solvent and moisture in the powder

Powder produced with a volatile solvent should be freed from it as thoroughly as possible since too large a content of residual solvent is detrimental to the ballistic stability of the powder. In nitrocellulose powders the content of residual solvent should be lower than 1%; in coarser powders (thicker flakes, strips or tubes) its content may be relatively higher, while it is relatively lower in finer ones. Powders gelatinized on the surface with camphor also contain a certain amount of camphor unbound with nitrocellulose which may volatilize on heating or storing.

Apart from residual solvent, nitrocellulose powder contains a certain quantity of water, either in the form of residual moisture, incompletely removed by drying, or in the form of moisture introduced to the powder.

Nitrocellulose powder is slightly hygroscopic since it partly consists of non-colloidal fibrous nitrocellulose which is hygroscopic. The colloidal part of the powder is less hygroscopic but retains a certain amount of residual solvent, chiefly alcohol, which as a hydrophilic substance increases the hygroscopicity of the whole mass. The hygroscopicity of nitrocellulose powder mainly depends on the total nitrogen content in the nitrocellulose, the latter being less hygroscopic the higher its nitrogen content (Vol. II, p. 283). Powder made of nitrocellulose with a total nitrogen content of 13% absorbs 1.0–1.5% of moisture. With a nitrogen content of 12.5–13.0% the moisture content of the powder may increase to 1.5–2.0%. These figures are characteristic for the climate of Central Europe. They are lower in a dry climate and higher in a humid one. According to Hansen [23] for a flake or tubular powder of web thickness over 0.8 mm the hygroscopicity may be expressed by the formula:

$$y = \frac{a}{x}$$

where a is a constant, x is the web thickness of the powder flake or tube, and y the moisture content as determined by drying at a temperature of 80°C for 3 hr.

Nitrocellulose powders gelatinized on the surface with centralite, camphor or nitro compounds are less hygroscopic since the layer of gel on the surface constitutes a non-hygroscopic coating which prevents the powder inside from attracting moisture. Nitrocellulose powders containing aromatic nitro compounds, e.g. dinitrotoluene (DNT) or dinitroxylene (DNX) are less hygroscopic.

Davis [12] reports the following figures characteristic of the hygroscopicity of pyrocollodion cotton containing various substances:

Pyrocollodion cotton with	Hygroscopicity
5% hydrocellulose	2.79%
10% crystalline DNX	2.09%
10% DNX oil	1.99%
10% crystalline DNT	1.92%
20% crystalline DNT	1.23%
25% crystalline DNT	1.06%

Nitroglycerine and nitrodiglycol powders are the least hygroscopic (practically non-hygroscopic) since nitroglycerine–nitrocellulose or nitrodiglycol–nitrocellulose gels are virtually non-hygroscopic. For this reason even those nitroglycerine and nitrodiglycol powders which contain highly nitrated nitrocellulose, partly in a fibrous state, are non-hygroscopic.

Analytical methods for the determination of moisture content and residual solvent content are of the utmost importance in view of the effect exerted by these properties on the ballistic properties of the powder. Various methods are used in different countries. During World War I the moisture content in nitrocellulose powder was determined as follows:

in Russia	6 hr of drying at 100°C
in France	4 hr of drying at 60°C
in the U.S.A.	6 hr of drying at 60°C, under reduced pressure.

Vieille investigated the loss in the weight of nitrocellulose powder on heating at temperatures from 40 to 130°C. He obtained a typical curve (Fig. 242) which consists of two parts: *I* is very steep and *II* is gently inclined. Part *I* of the curve corresponds mainly to the evolution of moisture and part *II* to that of the residual solvent.

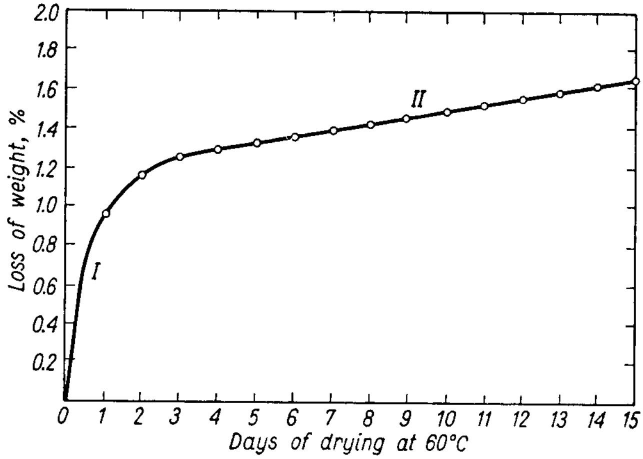


FIG. 242. Loss of weight of nitrocellulose powder at a temperature of 60°C: *I*—evolution of moisture ("elimination"), *II*—evolution of solvent ("coefficient of emission") [24].

By comparing the losses of residual solvent at temperatures of 110, 75 and 40°C Vieille found that identical losses are obtained on heating the powder for an identical number of

hours at 110°C
days at 75°C
months at 40°C

In France Vieille's experiments provided a basis for the determination of the loss of weight during the first 4 hr of drying at a temperature of 110°C, i.e. the so-called "elimination" (period *I*) and of the loss of weight during the next 16 hr, i.e. the so-called "coefficient of emission" (period *II*).

The coefficient of emission is a function of the content of residual solvent in a powder. It usually amounts to 0.3–1.00%, while the content of residual solvent ranges from 1.5 to 3.5%. The determination of the coefficient of emission is a convenient and rapid method for acquiring an idea of the content of residual solvent.

The total content of residual solvent is determined by partially dissolving a weighed sample of the powder in a solvent (a mixture of alcohol and ether) and adding water so as to precipitate the nitrocellulose from the solution in flocculant form. The weight of this nitrocellulose is determined by evaporation to dryness, repeated dissolution and precipitation with water, and by final drying. The difference between the weight of the powder sample and that of the nitrocellulose is the weight of the residual solvent.

Davis [25] distinguishes:

(1) Total volatile content (TV)

(2) External moisture (EM) (determined by drying at 100°C, for 1 hr)

(3) Residual solvent (RS) (calculated from the difference of $RS = TV - EM$)

Increase in the moisture content leads to a decrease in the vivacity of the powder. According to Vieille the coefficient of the vivacity of powder (p. 530) decreases by 13% when the moisture content increases by 1%.

In small arms and small calibre cannon increase of the moisture content by 0.1% reduces the muzzle velocity by 4–5 m/sec and the pressure by 50–70 kg/cm^2.

In the climate of Central Europe the moisture content, as determined by drying at a temperature of 60°C for 4 hr, should be constant within the limits of 1–2%. If the moisture content is determined under more drastic conditions the figure is correspondingly higher.

Surface gelatinization

Attempts have been made to improve the ballistic properties of fine-grained (flake or tubular) powders for rifles by coating the grains with a layer which would burn more slowly than the inner part of a grain. Such grains would give a better ballistic effect (would be more "progressive") since after a certain time of burning the surface of the flakes would decrease and the higher rate of burning would thus facilitate maintaining a steady pressure.

At first, attempts were made to coat the powder grains with gum arabic or gelatine. An aqueous solution of these substances left a layer of phlegmatizing substance on drying. In practice, powders of this kind gave a somewhat better ballistic effect (were more "progressive") although the most favourable results were obtained by the gelatinization of the surface of the grains with centralite, camphor or DNT. Since nitrocellulose powder contains a considerable quantity of fibrous, non-gelatinized guncotton, coating the grains with a non-volatile solvent gives a totally gelatinized slow burning surface layer. The concentration of the solvent gradually decreases towards the inside of the grains, so that the rate of burning of the powder increases with the combustion of the outer layers.

Surface gelatinization is almost always accompanied by polishing the grains with a small amount of graphite. The duration and temperature of gelatinization depends to a great extent on the type of gelatinizing agent. With a strongly gelatinizing agent the process is shortened and the temperature may be lower. E.g. when using camphor (the strongest employed gelatinizing agent) the temperature may be kept at 30–35°C, while with centralite it should be 50–55°C and with DNT (the weakest gelatinizing agent used) 80–90°C.

The polishing of rifle powder

Flake or tubular rifle powder should be subjected to surface gelatinization and coating with graphite. This is usually called "polishing" and constitutes the most delicate operation in the manufacture of rifle powder (for calibres from 7.6–20 mm).

Polishing is usually carried out in copper or brass drums. These may be cylindrical, with a horizontal axle, and fitted with an opening for loading and unloading and with another for supplying the solutions and predrying the powder (Fig. 243). Drums for the manufacture of dragées used in the confectionery and pharmaceutical industries ("sweet barrels") may also be adopted (Fig. 244). Some designs of dragée apparatus provide for heating jackets which surround the polishing vessel, thus making it possible to obtain a higher temperature (50–80°C) inside. The inside of the drums is ribbed which enhances the polishing effect by making the powder rise higher as the drum rotates. The capacity of the drum ranges from 100–300 kg of powder. The rotational speed is approximately 30 r.p.m.

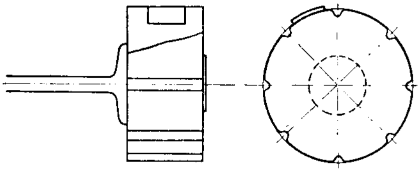


FIG. 243. Schematic view of a design for a drum for polishing fine-grained nitrocellulose powder.

Polishing is usually carried out as follows: the soaked and dried powder is placed into the drum together with the graphite (0.01% by weight of powder). The presence of the graphite from the beginning of the operation increases the conductivity of the powder and prevents it accumulating static electricity, thus reducing the possibility of accidents during polishing.

After a preliminary "dry" polishing for several minutes, an alcoholic solution of a gelatinizing substance—centralite (p. 645) (3% in relation to the weight of powder) or camphor (1.5–2%)—is introduced through an opening in the side wall of the drum. These substances are usually injected in the form of a 10–20% solution sprayed with compressed air. The solution should have a temperature of about 50°C when centralite is used, or 30–35°C when camphor is used. With centralite the temperature of the powder in the drum should not exceed 40–50°C and with camphor 25–30°C. These temperatures may be attained by maintaining a sufficiently high temperature in the premises where the polishing takes place. The latter temperature should be lower by some degrees than that which is required within the drum since the temperature of the drum contents is somewhat higher than ambient temperature.

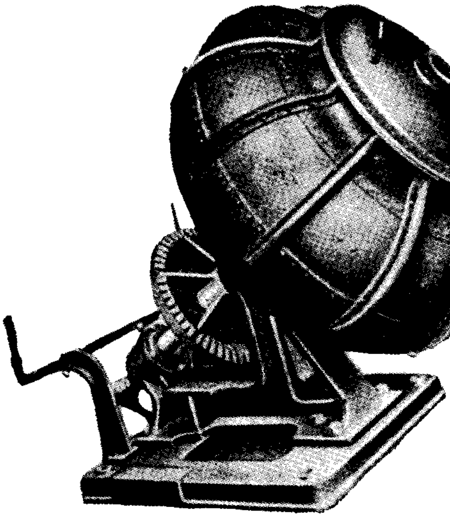


FIG. 244. A dragée apparatus ("sweetie barrel") for polishing fine-grained nitrocellulose powder [7].

The solution is introduced into the drum, which is then closed with a lid and set in motion for one or more hours. A side lid is then opened permitting alcohol to evaporate thereby gradually predrying the powder. During the latter operation a small amount of graphite is added so that its total content amounts to 0.25–0.3%. The evaporation of alcohol from the drum may be combined with the recovery of this solvent. For this purpose the lid is not removed but connected with a duct producing a reduced pressure within the drum. The solvent thus drawn off is then recovered either by condensation or adsorption.

The whole polishing operation lasts for 4–20 hr depending on the method employed. The efficiency of polishing may be checked by measuring the apparent density, which amounts to about 0.700 before polishing and to 0.800–0.900 afterwards. In some factories a charge of wooden balls equal to $\frac{1}{3}$ of the charge of the powder is added when polishing flake powder. The balls hasten the surface smoothing of the powder flakes and their acquisition of the required apparent density. They also prevent caking of the powder grains by the gelatinized solution.

There are various modifications of the polishing process, e.g. the introduction of centralite or camphor without a solvent or in the form of a hot (e.g. 80°C) aqueous emulsion. This is the last stage of polishing, based on the volatilization of the water. The use of a tilting drum with a heating jacket hastens evaporation of the water or solvent.

After polishing, the powder is soaked for a short period (4–8 hr) at temperatures from 50–80°C, and then dried. This is an operation of great importance designed to remove from the powder any excess of gelatinizing agent unbonded with nitrocellulose. The content of the gelatinizing agent in the powder is thus stabilized. If the powder is not soaked after polishing, but only dried, it may change its ballistic properties on storage. In particular there may be a decrease of muzzle velocity and an increase of pressure, i.e. the powder becomes less progressive, because the excess of the gelatinizer unbonded with nitrocellulose present in the non-soaked powder penetrates into the deeper layers of the powder on storage.

In some countries (U.S.A.) DNT is used for the surface coating of tubular rifle powder, instead of centralite or camphor. The polishing is carried out in the presence of water at a temperature of 80°C, i.e. above the melting point of DNT. As the polishing proceeds, the water is removed by evaporation under reduced pressure, the DNT remaining on the surface of the powder tubes.

Polishing was a hazardous operation until the drums and all the pipelines supplying alcoholic solutions were carefully earthed. Before such precautionary measures were taken there were frequent serious accidents of ignition during polishing.

The polished powder, bathed and dried, should undergo final screening to separate dust and powder grains.

Finishing the powder

In the finishing of powder there are two operations: blending and damping.

Blending. This operation aims at obtaining a large, uniform lot of the product, amounting to 5000–50,000 kg. Powder is produced in small batches (in a kneader 60 kg; from a press still smaller quantities are extruded), so that it is difficult to obtain an identical product each time, due to slight deviations in weighing CP_1 and CP_2, in adding the solvent, diphenylamine etc. At later stages of processing, uniform batches increase in size and reach a quantity corresponding to the capacity of the soaking vat or the drier. Lots amounting to 1000 kg are obtained in this way. In rifle powders a polishing drum charge, which amounts to about 300 kg of powder, is considered to be acceptably uniform.

For powders which require a high precision in manufacture (polished rifle powders) the ballistic properties are determined for the contents of each polishing drum charge and the contents of all the drums are blended on the principle that powders of various ballistic properties give a mixture with properties corresponding to the arithmetic mean.

The ballistic properties of ordinary cannon powders are more easily controlled, therefore those of individual batches intended for blending are not examined. Exceptions are made when manufacture is restarted after a long interruption or is commenced with a new type of nitrocellulose, or when there are doubts as to the quality of production for some reason or other. In these cases every manufactured batch (e.g. the charge of every drier) is subjected to ballistic tests and then blended according to the rule expounded below.

The blending method depends on whether the powder is a grain (flake or short-tube) or a strip powder (or long-tube).

In the first case (cannon or rifle grain powder) blending is easy and simple funnel equipment, similar to that for blackpowder blending (p. 359) may be used. In the U.S.A. a continuously operating plant, consisting of towers, is used for blending. The towers contain a series of funnels placed one above the other (Fig. 245). The powder from several drying houses is conveyed to the upper funnel. It flows successively through all the funnels, is partially blended, and falls onto a conveyer which carries it to the upper section of another system of funnels, where the procedure is repeated. Again the powder flows down, is further blended, falls onto the conveyer and is carried to the upper section of the first system of funnels and so on. After several passages the powder is sufficiently blended. A general view of a mixing house is given in Figs. 246 and 247.

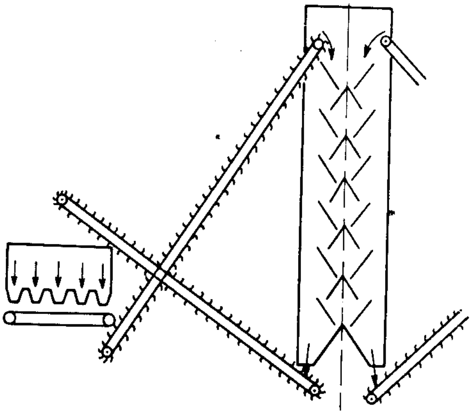


FIG. 245. Schematic view of equipment for blending powder by continuous working.

Strip powder or long tubular powder can be blended by hand, in the following manner. Sacks with powder from different drying houses are placed around a cloth onto which the workers pour out the strips or tubes and blend them by holding the four corners of the cloth. The powder so blended is poured back into the sacks and the whole process is repeated.

Figure 248 shows an arrangement for blending operations that permits them to be carried out meticulously. Diagram *I* represents the order in which the sacks from 6 units (driers) are placed for blending. Diagram *II* shows the final position of the

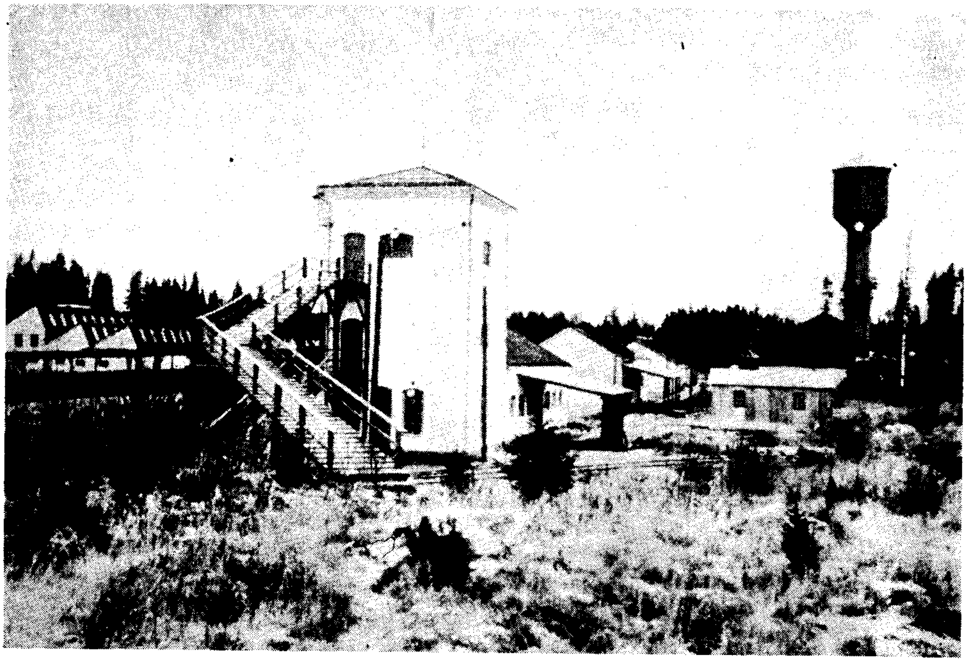


FIG. 246. Mixing house for nitrocellulose powder. Each day's output is hoisted to the upper floor where it passes through a mixing apparatus to form uniform batches of 10–50 tons (Bofors Nobelkrut Factory).

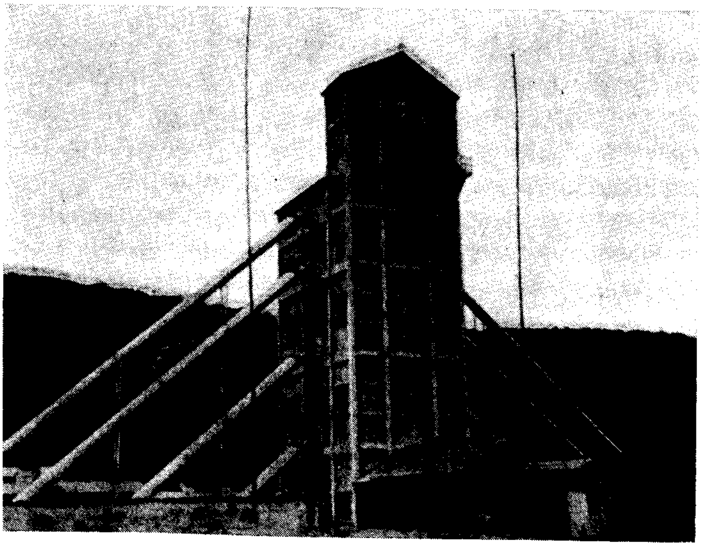


FIG. 247. Smokeless powder blending tower, according to Zaehringer [26].

sacks. A worker walks along each side of the rectangle, as indicated by arrows and empties out the sacks of tubes in turn. After blending on the cloth the contents are dumped into the sacks denoted by letter *A* in the figure. The next stage of blending on the cloth gives a new, more or less uniform batch denoted by letter *B*. After the contents of all the sacks placed around the cloth have been blended, the blending operation with sacks *A*, *B* etc. is repeated several times until a sufficiently uniform product is obtained.

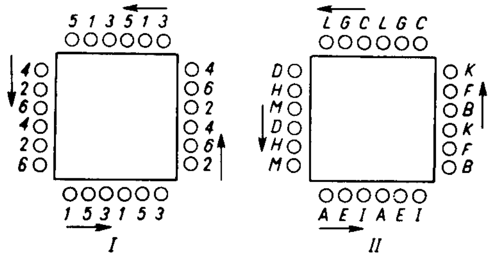


FIG. 248. An arrangement for blending larger grains of powder.

Damping. After soaking and drying the powder usually contains less moisture than that required by standard specifications and should therefore be damped. Methods of damping, like those of blending, depend on whether the powder is in grains, strips or long tubes.

The simplest method of damping granular powder consists of loading it in a rotary drum and injecting the calculated amount of water into it, in accordance with an analytical determination of the powder's moisture content. After rotating the drum with the lid closed for about 30 min the moisture content in the powder becomes uniform.

Strip or tubular powder is usually damped by placing it in a room, either on shelves or on grids standing on the floor, on which vessels of water are placed or water is spilled. A sample of powder is taken every few hours and its moisture content is determined. After one or more days, when the moisture content reaches the standard specification, the powder is taken out of the damping machine and poured into sealed boxes.

The standard specifications permit the moisture content to range within certain limits. This enables the producer to regulate the moisture content to obtain the required ballistic properties. If the powder is too vivacious it should be moistened to the upper limit, while if it is less vivacious, the lower limit is preferable. In determining the moisture content the following practical rule should be observed. In rifle powder an increase of the moisture content by 0.01% lowers the muzzle velocity v_0 by 4–5 m/sec and the pressure by 50–70 kg/cm^2. In cannon powder the variations of ballistic properties are smaller and depend on the type of powder and on the calibre of the gun.

The processing of waste products

There are two principal types of waste products:

A. The waste products of non-soaked powder,

B. The waste products of soaked powder.

The utilization of these waste materials differs in principle. The former are returned to the kneaders to be reworked while, as a rule, the latter are never recycled in the normal manufacture of powder. It is generally recognized that a soaked powder must not be added to the powder dough since it reduces the chemical stability of the powder, except when it is intended for immediate use.

Waste products A derive from various stages in the manufacture of the powder, prior to soaking. They are:

(1) Scrap comprising remnants of dough from the kneaders and conveyers.

(2) Shapeless strips or tubes extruded from the press.

(3) Cakes remaining in the press between the bottom of the press piston and the die.

(4) Flakes, strips or tubes with non-standard dimensions or shapes, graded after cutting, non-dried or sometimes dried (when graded after drying).

More of materials (2) and (4) is produced from powder of smaller dimensions.

These products are processed by dissolving them in a mixture of alcohol and ether, kneading into a dough, filtering in a hydraulic press to remove mechanical impurities and adding to the fresh powder mass in the kneaders.

Since products (1) and (2) contain a considerable amount of solvent (60–100%), they are loaded directly into the kneader together with the solvent, kneaded for 1–2 hr and filtered in a press in which the die is replaced by a steel plate with circular openings, approximately 1 mm dia. Since there is less ether in the residual solvent in the powder than is primarily used for its manufacture, the solvent added to the waste products should be richer in ether (approximately 70% by weight of ether and 30% by weight of alcohol).

Waste products (4) take longer to dissolve since they contain less residual solvent (20–30%). They are poured into hermetically closed tins (in batches of 30–35 kg) and flooded with solvent, so that its total amount ranges from 100–150%. The solvent should be rich in ether (70–75% by weight of ether and 25–30% by weight of alcohol) as for waste products (1) and (2). After the solvent has been poured in, the tins are sealed, and tumbled through 90° every 15 or 30 min for 2–4 hr. The thicker the powder strips or tubes, the longer they take to dissolve. The tins are then turned upside down and a few hours later returned to the normal position.

With fine-grained powders (web thickness of 0.5–1.5 mm) the contents of the tins may be transferred after a few hours to the kneaders to produce a uniform mass. With coarse-grained powders the dissolution of the waste material requires from four to ten days or more; e.g., with a web thickness of 3 mm the time is 4 days, while with a web thickness of 7 mm it increases to twenty days. After being mixed in the kneaders the dough is filtered and added to the normal dough in the kneaders.

In principle waste products (3) are processed in the same way as waste products (4), although they contain a large amount of solvent. The reason for this is that the cakes are thick and therefore dissolve slowly. To hasten the process the cakes may be cut into several pieces before being placed in the tins.

The quantity of waste products added to the fresh dough in the kneaders varies depending on the amount of factory waste arising during manufacture. From 20 to 90 kg of waste products may be added per 100 kg of fresh nitrocellulose. Naturally the waste products added to fresh powder should have a suitable nitrogen content and total solubility.

Waste materials from soaked powder are used chiefly for preliminary ballistic tests. They can also be converted into less valuable types of powder, earmarked for rapid consumption (practice or sporting powders). Such powders are treated with solvent in the same way as waste products (4), although they require a longer time to dissolve. Thus, during the World Wars, when powders were consumed rapidly, soaked waste products were utilized for this purpose.

THE STABILIZATION OF AN UNSTABLE POWDER

If the stability of the powder does not deviate greatly from the required standard, it may be improved by soaking it in an alcoholic solution of diphenylamine.

For this purpose the powder is put into cylinders, filled with a diphenylamine solution, sealed and left to stand for several days. The concentration of diphenylamine must be such that its total amount is no higher than 0.5–1.0% of the weight of the powder.

Some methods recommend the use of an alcoholic solution with a small addition of ether, e.g. one part of ether per five parts of alcohol. The ether causes part of the nitrocellulose to swell and facilitates the penetration of the diphenylamine solution into the strips or tubes. It should not be used in such an amount as to cause the nitrocellulose to dissolve.

BALL-GRAIN POWDER

Between 1936 and 1940 Olsen *et al.* [27] designed a process for the manufacture of nitrocellulose powder in the form of uniformly shaped balls (Fig. 250). The manufacturing process at Western Cartridge Co., Division of Olin Industries, Inc. at East Alton, Illinois, U.S.A. has been described by Olive [28].

A diagrammatic presentation of the process is shown in Fig. 249. The nitrocellulose containing about 13.45% N is stabilized in kiers, cut in beaters and introduced under water into still (*1*) fitted with a stirrer, containing ethyl acetate with a small amount of diphenylamine (Fig. 251). Calcium carbonate is also added. The presence of water is not harmful when dissolving nitrocellulose in ethyl acetate. Diphenylamine remains in the organic solvent phase (ethyl acetate), thus neutralizing the acid products dissolved in the ethyl acetate, while the calcium carbonate remains suspended in the aqueous phase and neutralizes the acid derived from nitrocellulose and passing from the organic to the aqueous phase. The neutralization of the acid products in the nitrocellulose and the final stabilization of the nitrocellulose are thus completed, Olsen claims that for this reason there is no need to use a completely stabilized nitrocellulose since the same process may be performed more quickly and equally successfully with a nitrocellulose which has not been stabilized in boilers and poachers.

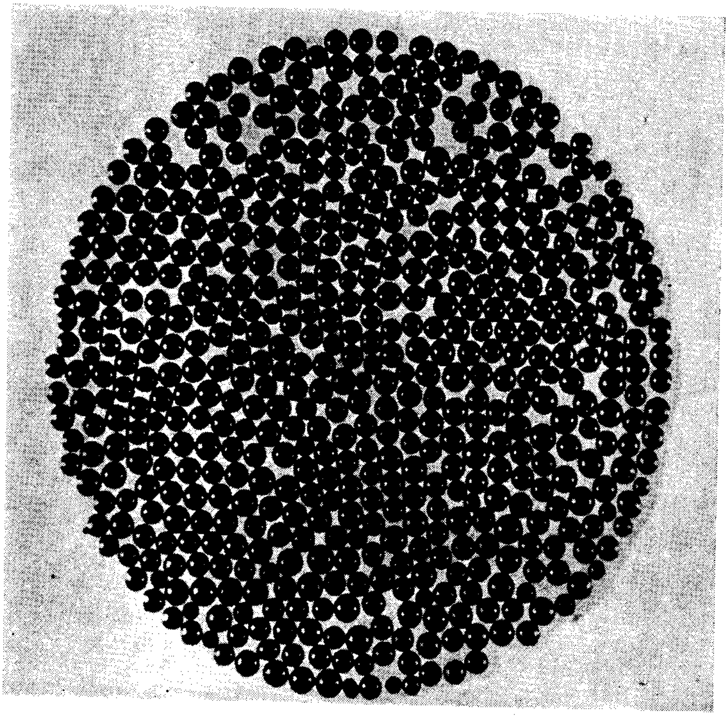


FIG. 250. Ball-grain powder, according to Olin Industries, Inc. [29].

After the contents have been mixed for 0.5 hr a solution of a protective colloid (gum arabic or starch) is added to secure uniformity of the suspension. The material is then stirred vigorously until small balls are formed. From that moment the procedure varies depending on whether porous, fast burning or dense, slow burning balls are required. In the first case ethyl acetate is distilled off rapidly by reducing the pressure in the still. During distillation the balls harden, but should retain their shape. If the solvent is distilled too quickly, the grains become elongated. The distillation rate should be such that the solvent is evaporated from the surface of the grains no faster than it moves from the interior to the surface. The distillation should therefore be slow at first and more rapid towards the end when the hard surface of the balls is already shaped. Since they contain much water, drying, which is the next operation after grading, makes them porous.

If, however, the balls are dehydrated before hardening, i.e. before distillation of the solvent, they have a high density. To dehydrate them some sodium sulphate is introduced into the apparatus. Due to the high osmotic pressure of the aqueous solution surrounding the balls water moves from them to the solution, so that they are dehydrated. The degree of dehydration is controlled by altering the time, the temperature and the concentration of the sodium sulphate.

The distillation of ethyl acetate is carried out either by reducing the pressure in the apparatus or by raising the temperature to 77°C (the boiling point of ethyl acetate under atmospheric pressure).

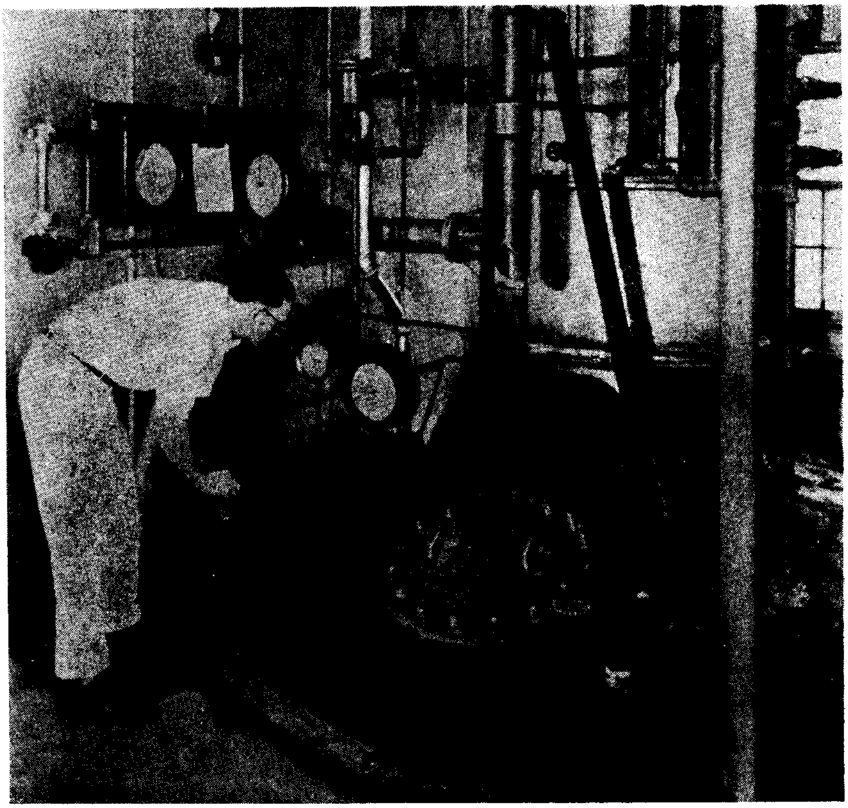


FIG. 251. General view of the large still (Courtesy Olin Industries, Inc.) [29].

The distillate (in receptacle (*2*)) consists of a layer of ethyl acetate plus water and a layer of water in which 8% ethyl acetate is dissolved. The aqueous layer is rectified to recover the solvent. In all, 95% of the ethyl acetate used is recovered from the distillate and recycled for manufacture.

After the balls have cooled in the slurry they may be coated with nitroglycerine. For this purpose they are treated with an aqueous emulsion of nitroglycerine dissolved in toluene, using nitroglycerine up to 15% of the weight of the powder. By heating at a reduced pressure the toluene is distilled off, leaving a solid solution of nitrocellulose in the nitroglycerine deposited as a layer on the surface of the balls. This surface may then be coated with centralite, applied in a similar manner, i.e. in the form of an emulsion dissolved in a solvent immiscible with water, in which the nitrocellulose is insoluble, i.e. in toluene.

If the ball-grain powder is to be a true double base powder with a relatively high content of nitroglycerine, the nitroglycerine is usually introduced at the first stage of manufacture, together with the ethyl acetate solvent. This forms a solution of nitrocellulose and diphenylamine in nitroglycerine and ethyl acetate. Subsequent procedure is similar to that described above, i.e. ethyl acetate is rapidly mixed in, the balls are dehydrated and solvent distilled off. The whole operation, from dissolving to the end of graining, takes approximately 16 hr for a batch of 3000 kg.

The aqueous slurry of grains produced in this way is conveyed to storage tank (*3*) and held there pending a laboratory report on the suitability of the product. If this shows that balls have incorrect dimensions, they are separated from the water and returned to be re-dissolved in ethyl acetate and recycled.

If the laboratory report is satisfactory, the balls in the slurry are graded by pumping the slurry over a succession of water-sprayed, rotating, drum-type screens. Fig. 252 gives an idea of their design. The graded balls are directed to storage tanks (*5*), from which the slurry is pumped over into a still (*6*) in which the balls are coated with a gelatinizing agent—usually dibutyl or diphenyl phthalate, with or without the addition of carbamite (centralite). Formerly centralite alone was used for coating.

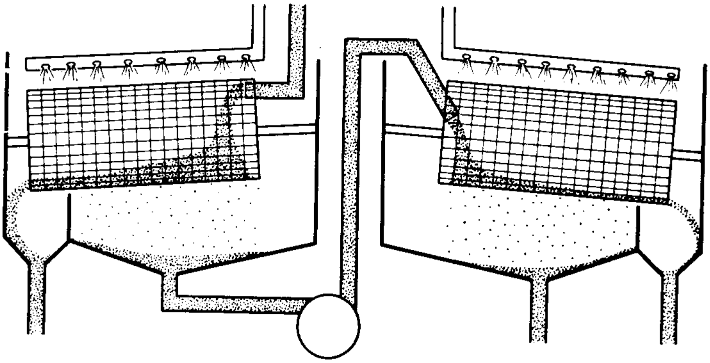


FIG. 252. Diagrammatic presentation of rotating drum screens, according to P. Brown [30].

The gelatinizer is introduced into the still as an emulsion. The proportion of water to powder in the still is 3 l. of water per 1 kg of powder. Steam is introduced into the heating jacket and the charge is slowly agitated until the gelatinizer has penetrated to the desired depth. To coat a batch of 5000 kg takes 4–5 hr, after which the coated grains are separated from the water on a vacuum filter (*7*). A cross-section of a coated grain is given in Fig. 253. After filtering about 8% of water remains in the powder. The damp powder is dried on a conveyer in a tunnel drier equipped with infra-red lamps (*8*). The conveyer is a travelling belt of rubber and canvas 48 in. wide and 80 ft long (Figs. 254 and 255). The tunnel walls consist of light metal panels, insulated and hinged to serve as explosion hatches. One hundred and forty infra-red lamps, each of 250 W, are arranged in twenty-eight rows of five lamps each, more closely spaced at the wet than at the dry end. They are placed about 18 in. above the bed of powder. A relatively weak current of air flows counter to the direction of movement of the powder.

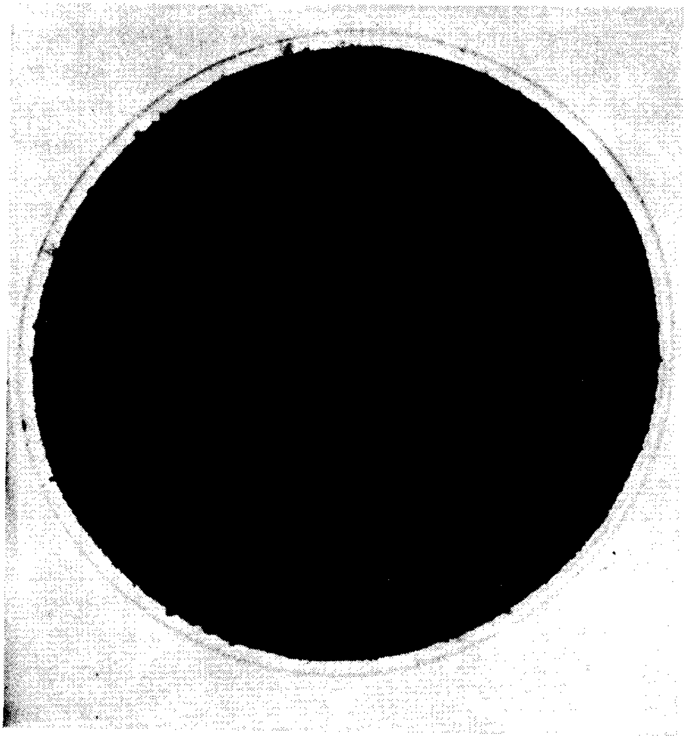


FIG. 253. Cross-section of a ball powder grain magnified 300 times. The light ring on the outside indicates the location of the gelatinizer (phlegmatizer). (Courtesy Olin Industries, Inc. [29].)

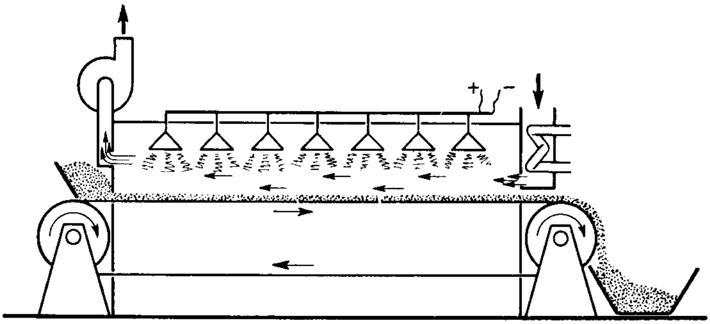


FIG. 254. Diagrammatic presentation of infra-red drier, according to P. Brown [30].

The damp powder is fed directly to the belt from a hopper containing an agitator, and drying is accomplished at a rate of 140 lb (53 kg) per drier per hour, at a temperature of 72°C. The air supplied is heated to about 50°C by steam coils, and the temperature in the tunnel rises due to the heat from the lamps.

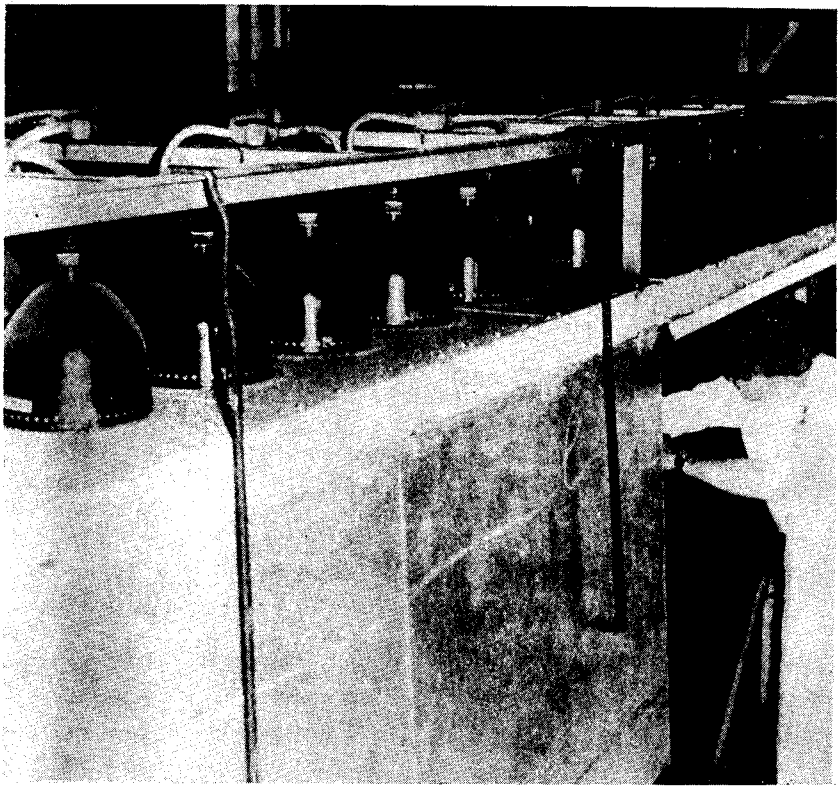


FIG. 255. General view of infra-red drier (Courtesy Olin Industries, Inc. [28]).

The temperature of the powder is controlled by thermocouples on the surface of the moving bed from which three banks of lamps are automatically controlled. In addition six other thermocouples per drier actuate recorders but do not control.

Power consumption of the driers averages 0.196 kWh per pound of dry powder and drying time is approximately 60 min. The operation is safe. The only fire which occurred between 1942 and 1946 was one that was started deliberately to see what the result would be. It was brought under control so quickly that production was resumed in less than two hours, with no damage to the lamps, belt or housing (Olive [28]).

Since the shape of the balls is ballistically unfavourable, they may be flattened between rolls before the final drying so that they acquire a more favourable form.

The balls are conveyed to the rolls in a slurry from apparatus *(6)* and pass through a feed tank, and then between the rolls *(9)*. A general view of the rolls is given in

Fig. 256. Larger balls may be flattened to reduce their dimensions and burning time. E.g. U.S. 0.45 ammunition requires balls of 0.006–0.010 in. dia. They may be produced by rolling balls to a web (minimum) thickness of 0.004 in. Rolled powder grains are shown in Fig. 257.

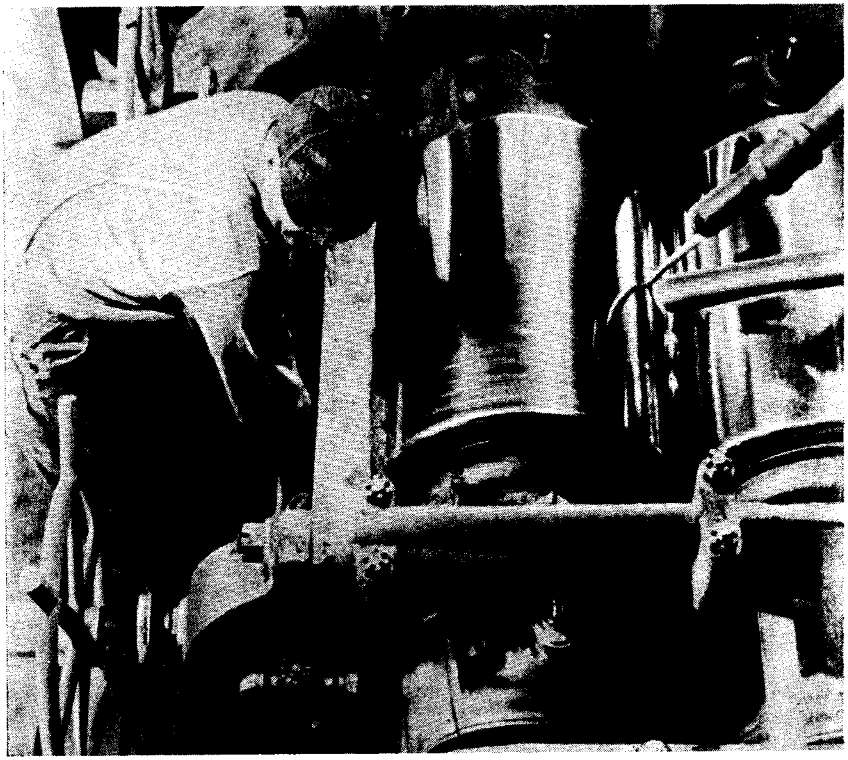


FIG. 256. General view of rolling operations (Courtesy Olin Industries, Inc. [29]).

After flattening, the slurry passes to the centrifuge (*10*) (Fig. 249) for dehydration and then to the drier (*8*), as described above.

The ball-grain powder is then processed in the conventional manner, i.e. being weighed (*11*), polished and coated with graphite (*12*), blended in towers (*13*), similar to those described above (pp. 628–629), and stored (*14*).

The gravimetric density of ball-grain powder varies from 0.400 to 0.975.

Olsen suggested using old nitrocellulose powder, withdrawn from use due to insufficient chemical stability, for the manufacture of ball-grain powder, instead of nitrocellulose. The powder is milled in disintegrators under water containing a suspension of calcium carbonate to neutralize the acid decomposition products. Coarse grains are thus formed which after the excess water has been removed in a centrifuge are introduced into ethyl acetate containing diphenylamine. The substance is then stabilized and traces of acid are removed. Further processing is as described above.

The advantage of this method of powder manufacture is that it is quicker and much safer than the usual methods, since kneading, pressing and cutting are eliminated and all operations are carried out under water.

Olin Industries [29] report that the safety is further enhanced by the fact that at any moment a relatively small amount of material is being processed.

A third important safety feature is the continuous drying by infra-red radiation. No "drying" to remove solvent is required and so no dangerous mixtures of organic vapours in air are formed as in the conventional process. Approximately 100 lb of powder is dried at a time. This amount is within the safety limits for this type of equipment.

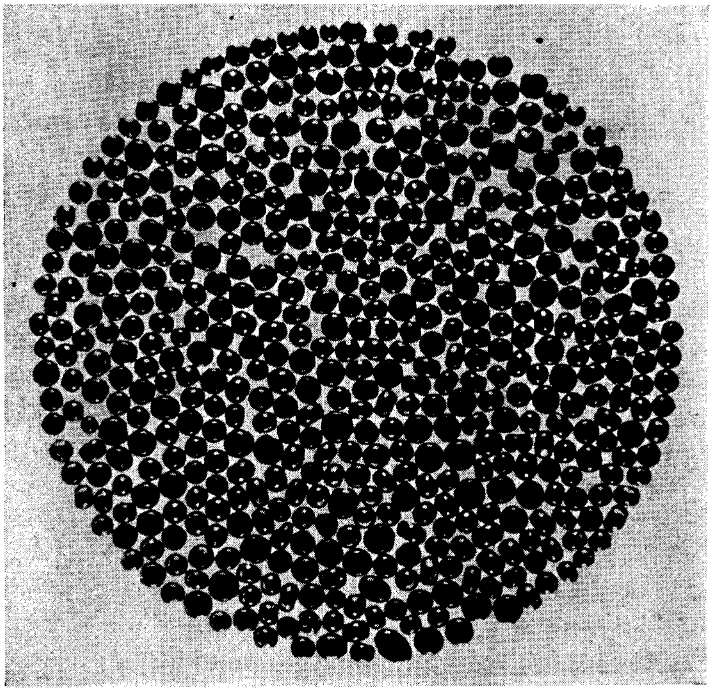


FIG. 257. Powder rolled from 0.020–0.025" dia. to a thickness of 0.018" (Courtesy Olin Industries, Inc. [29]).

Olin Industries report that no fatal accident attributable to ball powder has occurred in twelve years of manufacture, during which time more than 60,000,000 lb of ball powder have been produced. Labour requirements are low: ball powder can be manufactured by using fifty man hours per 1000 lb of finished powder as compared with 125–200 man hours per 1000 lb required by the conventional process for making extruded powder.

NITROCELLULOSE BULK POWDER (SCHULTZE POWDER)

These propellants containing mainly fibrous non-colloidal nitrocellulose are usually referred to as Schultze powder, after the inventor—see p. 528.

In Great Britain they are frequently referred to as E.C. powder (this stands for Explosives Company, one of the early manufacturers in England). In the U.S.A. they are usually referred to as bulk powder, probably because they were loaded in bulk, volume for volume, with blackpowder.

The production of nitrocellulose bulk powder is based on the same principle as that of blackpowder. Nitrocellulose together with water, potassium or barium nitrate and a binding substance (e.g. gum arabic, gelatine, agar-agar, starch) is mixed in edge runners, granulated, screened and dried. On drying the grains harden like those of blackpowder. The mixture may also include vaseline, which facilitates the adhesion of the grains, or camphor, acting as a binder by gelatinizing the nitrocellulose. Powders of this kind are extremely fast burning and are used in sporting or practice ammunition. The composition of some of them is tabulated below (Table 182).

TABLE 182

COMPOSITION OF SOME SCHULTZE SPORTING POWDERS

Ingredients	EC	Amberite	Schultze	Kynoch	Chasse M
CP_1 (guncotton)	40	13	63	—	56
CP_2 (collodion cotton)	40	59	—	53	15
KNO_3	4.5	1.5	2	1.5	5
$Ba(NO_3)_2$	7.5	19	26	22.5	20
Vaseline	—	6	5	—	—
Starch	—	—	4	—	—
Woodmeal	4	1.5	—	3	—
Agar-agar	—	—	—	—	1
DNT	—	—	—	20	—
Camphor	4	—	—	—	3
Heat of explosion (kcal/kg)	762	745	786	807	—

According to the method adopted in France the manufacturing process consists of the following operations:

(1) Mixing the ingredients in an edge runner with the addition of about 10% water which takes approximately 1 hr. Sometimes, in addition to water a certain amount of alcohol–ether mixture is added (e.g. 50–60% of the weight of nitrocellulose). Mixing should then be commenced in a hermetically sealed kneader to avoid losing ether and alcohol. After mixing and the partial dissolution of nitrocellulose the mass is reloaded into edge runners, and after kneading again is further processed.

(2) Rubbing the mass through a 1.5–2 mm mesh sieve to form grains.

(3) Granulating, which is carried out by placing the grains in a rotating wooden drum, in which they are rounded off, forming granules of different sizes.

(4) Drying. The granules obtained in the wooden drums are dried at a temperature of 45°C. Volatilization of the water makes the grains harden.

(5) Grading. The dried grains are graded by passing them through 0.5–1.5 mm mesh sieves.

(6) Polishing. The graded grains are placed in small rotating drums made of brass. An alcoholic solution of camphor, or acetone with alcohol, or an alcohol–ether mixture is injected into the powder charge in the drums. The introduction of solvent causes the formation of a coating on the grains which makes them harder and makes the powder burn more progressively, i.e. the outer layer burns more slowly than the interior of the grain. The gravimetric density of the grains increases slightly on polishing. E.g., with Poudre Chasse M it increases from 0.380 to 0.400–0.430.

(7) Drying and final grading are the same as (4) and (5).

There are designs which make it possible to carry out operations (3), (4) and (5) in one apparatus comprising a drum that acts as a granulator, a drier and a grading machine. This is a long, inclined rotating drum with a system of screens inside. Warm, drying air is passed through the drum. As the drum rotates the grains are polished, dried in the air stream and graded between the screens.

According to U.S. Army Specification No. 50-13-8B E.C. powder should pass two tests [31].

When the powder is to be used in blank ammunition the wad from the round loaded with a specified weight of powder when fired in a 0.30 calibre rifle shall not penetrate a craft screen placed at a specified distance in front of the muzzle of the rifle. Only 1% of variation is permitted.

The same powder can be used as a high explosive to fill hand grenades. On detonation it should give 40 ± 10 fragments large enough to be held on a 2-mm mesh screen.

DOUBLE BASE POWDERS

As with nitrocellulose powders the manufacturing processes of nitroglycerine powders described below should be regarded as examples of typical methods which may vary from one country to another. As before, the author has endeavoured, as far as possible, to draw attention to the differences in methods adopted in various countries.

Smokeless powders containing nitroglycerine are classified into two types: those produced with the use of a volatile solvent and those produced without such a solvent. In both types nitrocellulose is in a completely colloidal form.

Powders with a volatile solvent are becoming obsolete and are now produced in only a few countries (Great Britain) whereas those without a volatile solvent are being used increasingly. Nitroglycerine powders are designated as follows: France—SD; Germany—RPC; Great Britain—Cordite SC (solventless cordite); Poland—BR; the U.S.S.R.—letter H (Russian "N") following the figures showing the dimensions of tubes. In the U.S.A. nitroglycerine powders are called "double base powders" i.e. those composed of two explosive ingredients: nitroglycerine and nitrocellulose.

Double base powders, i.e. nitroglycerine powders without a volatile solvent also include modern flashless powders containing nitroguanidine.

NITROGLYCERINE POWDERS WITH A VOLATILE SOLVENT

Cordite Mk I and Cordite MD

British cordite is a typical powder of this kind. There are two types: the obsolete Mark I and the more modern modified cordite MD. They differ in composition (Table 183).

TABLE 183

COMPOSITION OF CORDITES (%)

Ingredient	Mark I (abbr. Mk I)	MD
Nitrocellulose (12.9–13.1% N)	37	65
Nitroglycerine	58	30
Vaseline	5	5

Cordite MD is an improved powder. It contains less nitroglycerine than Mk I and is, therefore, less erosive. Cordite owes it name to the fact that it is made of cords, the size (diameter) of which is denoted by a figure giving the diameter of the die in hundredths of an inch. Thus, for instance, Cordite 50 denotes a powder in the form of a cord extruded from a die of ½ in. (50/100 in.) dia.

Cordite MD is manufactured by a method very similar to that used for the manufacture of nitrocellulose powder.

Drying the nitrocellulose. Dehydration with alcohol is not possible in this case since in powders of this kind there is no alcohol in the solvent. To improve operational safety in the drying house, and especially to prevent the formation of dust, the damp nitrocellulose is pressed into cylindrical blocks. Natural draught drying houses are used. Drying takes several days at a temperature of 43°C. The operation is dangerous because of the sensitiveness to friction of dry nitrocellulose and its inflammability. Precautionary measures should therefore be taken, especially when unloading the nitrocellulose from the drying house. It should be unloaded only after cooling, with great care to avoid friction. The regular removal of nitrocellulose dust by sweeping the floor and dusting the radiators, shelves etc. is also of great importance.

Premixing nitrocellulose with nitroglycerine and incorporation. For this purpose a special lead table in the form of a trough is used. One of its ends is slightly raised and perforated with holes 1–1.5 mm dia. which form a kind of screen. Blocks of nitrocellulose are placed in the trough and a weighed amount of nitroglycerine is poured into it. A worker wearing rubber gloves first mixes the ingredients, and then rubs the mixture carefully through the lead screen, from which it falls into a bag attached below.

The cordite paste so obtained is next loaded into Werner–Pfleiderer kneaders where it is incorporated with vaseline and acetone. The quantity of acetone in relation to the nitrocellulose is 50–60%. Kneading lasts for 2.5–3.5 hr.

Next the dough is formed into cords by pressing it in hydraulic presses with suitably shaped dies.

The pressing of nitroglycerine powder is quite a hazardous operation. The cordite extruded from the press often ignites although this is not dangerous since the presses are small with a cylinder of low capacity. The presses should be arranged so that the workers operating them have a speedy exit from the building if a fire breaks out.

Drying. The solvent is removed from the cordite by drying at temperatures of 38–43°C for several days to a volatile matter content of 0.4–0.6%. The drying time depends on the thickness of the powder cords. Cordite MD loses its solvent more easily than cordite Mk I and therefore dries more quickly.

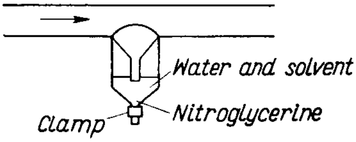


FIG. 258. A device for trapping nitroglycerine in pipelines.

The drying houses employed for cordite consist of rooms with shelves heated from beneath by radiators. Natural draught or forced circulation may be used. Air containing acetone from the drying houses is passed into recovery towers where it is sprayed with water. A dilute aqueous solution of acetone is thus recovered and then rectified. There is better recovery of acetone if the towers are sprayed with sodium hydrogen sulphite which reacts with the acetone (R. Robertson and Rintoul method [32]). The solution is then concentrated and after acidification the acetone is distilled off. The air exhaust ducting (especially with forced air circulation) should be fitted with equipment for trapping the entrained nitroglycerine (Fig. 258) so as to prevent the penetration of nitroglycerine to the machinery (e.g. to the fan).

Blending and packaging. Individual lots of cordite are blended to obtain a uniform product by the usual methods. It is then packed into wooden semi-hermetic boxes since it is non-hygroscopic (p. 532).

Cordite RDB

Since there was a great shortage of acetone for the manufacture of cordite in Great Britain during World War I, a solvent composed of alcohol and ether in a weight ratio of 2 : 3 was used. Since the nitrocellulose usually employed for the manufacture of cordite is insoluble in this mixture, nitrocellulose containing 12.9–13.2% N was replaced by a much lower nitrated one which contained 12.2% N and was soluble in the alcohol–ether mixture. The composition of cordite RDB was:

Nitrocellulose (12.2% N)	52%
Nitroglycerine	42%
Vaseline	6%

About 90% solvent was used, consisting of 58% ether and 42% alcohol.

In principle the manufacture of cordite RDB was similar to that of ordinary cordite with the difference that instead of drying the damp nitrocellulose it was dehydrated with alcohol and the required amount of ether and additional alcohol were introduced in the kneader. The manufacture of cordite RDB was discontinued after the war since its ballistic properties were inferior to those of common cordite.

Powders of the cordite type were never widely used outside Great Britain. For a certain time before World War I cordite was in use in the U.S.A. Navy. Before and during World War I a tubular nitroglycerine powder, similar to cordite in its composition, was manufactured in Austria–Hungary. It contained 30–40% nitroglycerine and 60–70% nitrocellulose (13.2–13.4% N). Acetone was used as a solvent. In Germany a similar powder containing 25–30% nitroglycerine was manufactured up to 1912.

SOLVENTLESS NITROGLYCERINE POWDERS

In completely colloidal nitroglycerine and nitrodiglycol powders these nitric esters are non-volatile, explosively active solvents. Similarly, triethylene glycol dinitrate (nitrotriethylene glycol) is used as an ingredient in some powders without a volatile solvent.

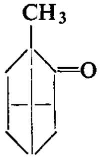
Aromatic nitro compounds may also be used as active solvents. During World War I they were adopted to compensate for the shortage of nitroglycerine. They have also been used more recently to reduce the heat of explosion and flash. In World War II they were used partly for this purpose and partly to make up for the lack of such non-volatile, explosively inert solvents as carbamite (centralite), acardite and urethanes. When they are included in nitroglycerine and nitrodiglycol powders, it is possible to reduce the content of these nitric esters by increasing the content of nitrocellulose. This gives a powder of a lower calorific value and erosiveness. Non-volatile solvents are also used in the surface gelatinization of semi-colloidal nitrocellulose rifle powder (see above, p. 625). They produce an outer layer that is completely colloidal, which burns more slowly and thus improves the progressiveness of the powder.

Camphor was also used for the same purpose. It has the advantage over centralite of being a better solvent for nitrocellulose so that it can be used in smaller quantities and can be gelatinized at lower temperatures.

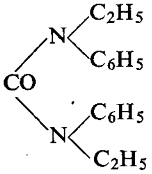
Centralite (called in Great Britain carbamite) is *sym*-diethyldiphenylurea. It was obtained by Zentralstelle für wissenschaftlich-technische Untersuchungen in Neubabelsberg and first used in powder manufacture in 1906. Shortly afterwards a homologue of this substance—*sym*-dimethyldiphenylurea—was prepared and put to use. The diethyl derivative was named Centralite I and the dimethyl derivative Centralite II. Other urea derivatives have also been developed and used, e.g. Acardite—*unsym*-diphenylurea.

During World War II N-arylurethanes were extensively used for the manufacture of nitroglycerine powder, e.g. ethylphenylurethane, diphenylurethane, *o*-tolylurethane, also, to a lesser extent, N-arylsubstituted amides of aliphatic acids, e.g. formyldiphenylamine were used. The latter was used in Japan [33] as gelatinizer and stabilizer.

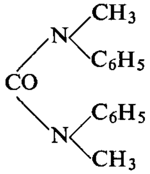
The formulae of the most important non-volatile solvents are given below. All of them are characterized by the presence of carbonyl groups and with the exception of camphor by the presence of the amido group $-\mathrm{CO}-\mathrm{N}\langle$.



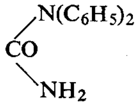
Camphor



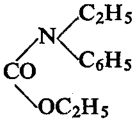
Centralite I (Carbamite)



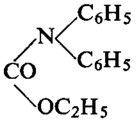
Centralite II



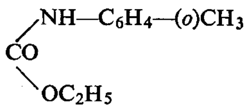
Acardite



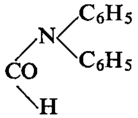
Ethylphenylurethane



Diphenylurethane



o-Totylurethane



N—Formyldiphenylamine

Non-volatile phthalic esters, (e.g. butyl phthalate) are also used for the manufacture of some nitrocellulose and nitroglycerine powders.

Individual non-volatile solvents vary in their capacity for dissolving nitrocellulose. The type of nitrocellulose dissolved is also a factor to be considered. Marqueyrol and Florentin [34] report the following figures which denote the amount of solvent required to obtain a uniform gelatinous film (Table 184).

TABLE 184

Solvent	CP_1	CP_2
Dimethylphenyl-*o*-tolylurea	260	65
Dimethyldiphenylurea	—	80
Diethyl sebacate	320	65
Diethyl phthalate	360	95

Davis [25] found that non-volatile solvents vary in their capacity for gelatinizing nitrocellulose, depending on the liquid in which they are dissolved. The following data show the gelatinizing power of pyrocollodion cotton (Table 185). The figures indicate the parts of non-volatile solvent required for the complete gelatinization of 100 parts of pyrocollodion cotton.

TABLE 185

ABILITY TO COMPLETELY GELATINIZE PYROCOLLODION COTTON OF VARIOUS NON-VOLATILE SOLVENTS, ACCORDING TO DAVIS [25]

Solvent	In alcohol	In benzene
Methylurea	100	100
Ethylurea	100	100
Sym-dimethylurea	60	70
Sym-diethylurea	50	50
Asym-dimethylurea	100	100
Tetramethylurea	80	–
Sym-diphenylurea	100	100
Asym-diphenylurea	100	100
Triphenylurea	–	35
Tetraphenylurea	160	30
Centralite II	70	25
Centralite I	70	30
Asym-dimethyldiphenylurea	60	–
Carbamic acid ethyl ester	140	80
Methylcarbamic acid ethyl ester	90	60
Ethylcarbamic acid ethyl ester	90	60
Phenylcarbamic acid ethyl ester	20	90
Phenylcarbamic acid phenyl ester	200	200
Diphenylcarbamic acid phenyl ester	80	70
Methyl phthalate	95	70
Ethyl phthalate	95	50
Isoamyl phthalate	95	50
DNX oil	120	130
TNT	–	300

Symmetrically substituted, especially tetra-substituted, urea derivatives have particularly good gelatinizing properties.

The manufacture of solventless nitroglycerine (also nitrodiglycol) powders (i.e. powders without a volatile solvent) differs from that of powders with a volatile solvent at the stage when the nitrocellulose is converted into a colloidal state. This highly important stage is not accomplished in a kneader, but between rolls heated to a high temperature (80–90°C). An elevated temperature is needed during pressing to obtain the required plasticity.

Nitroglycerine powders are produced in the form of flake powder, which is easy to manufacture (ballistite). They are also produced as tubular powders.

Huffington's [35] investigations showed that nitroglycerine powder manufactured without a solvent is not completely uniform, the nitroglycerine being present in the form of small drops. This means that nitroglycerine powder burns rather irregularly at relatively low pressures (e.g. 27 atm) common in rockets. The irregularity manifests itself as successive periods of slow- and fast-burning due to the explosions of the nitroglycerine drops.

Huffington carried out his experiment with a powder containing 29% of nitroglycerine and 10% of dinitrotoluene, as mentioned before (pp. 644, 650 and 653).

Ballistites

Ballistites initially consisted of equal amounts by weight of nitroglycerine and soluble nitrocellulose CP_2 with the addition of aniline or diphenylamine as stabilizers. It was found, however, that the presence of aniline and diphenylamine is detrimental to the stability of the powder, and they were therefore omitted. The valuable properties of centralite as a solvent of low basicity were then recognized and it was used both for its ability to dissolve the nitrocellulose and for its stabilizing action.

This led to the development of ballistite 50/50 which is still in use. It consists of:

Collodion cotton	49–49.5%
Nitroglycerine	49–49.5%
Centralite	1–2%

Ballistite 40/60 has a reduced content of nitroglycerine. It consists of 60% collodion cotton and 40% nitroglycerine. To this mass 1–2% centralite is added.

The manufacture of ballistite is divided into the following stages.

The incorporation of nitroglycerine and nitrocellulose. The two ingredients and carbamite are simply mixed in hot water by stirring with compressed air. Water is heated to a temperature of 60°C. Nitrocellulose is suspended and nitroglycerine poured into the slurry of nitrocellulose. The required amount of centralite may be dissolved in nitroglycerine. On mixing, the nitrocellulose absorbs the nitroglycerine. After 15–30 min, when the nitrocellulose is uniformly mixed with the nitroglycerine, the contents of the vat are poured into a cloth filter. The vat was usually emptied either by tilting (convertor principle) or by lowering a flap clamped with a lever to an outlet in the bottom.

The water may be removed from the nitrocellulose–nitroglycerine "paste" by centrifuging. The system described is primitive and virtually obsolete, but it is quite adequate for the manufacture of ballistite and is therefore still in use. A more modern system, giving a uniform paste with more evenly incorporated nitroglycerine is based upon the use of an aqueous emulsion of nitroglycerine (see Fig. 268).

Rolling (for drying). The damp mass is passed between rolls heated to a temperature of 50–60°C. Most of the water is removed and at the same time dissolution of the nitrocellulose in the nitroglycerine is promoted. This causes the mass to form into lumps which are here and there transparent. For this operation horizontal rolls are commonly used. (Fig. 259). Under the roll there is a tin tray to catch the water pressed out of the mass, and the pieces of paste that drop during rolling.

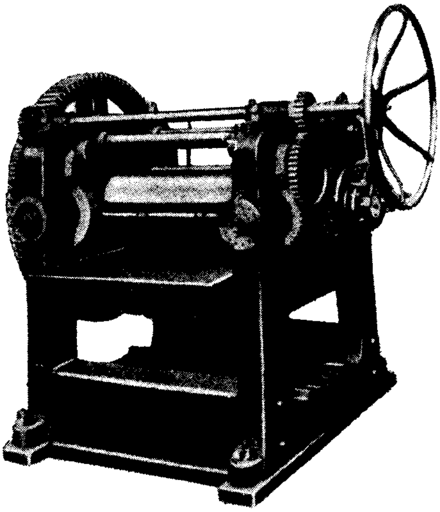


FIG. 259. Horizontal drying rolls [7].

Drying is complete when no more water is squeezed out of the paste. The amount of moisture is reduced to *ca.* 5%.

Very often the "differential rolling mills" are used here: two horizontal cylindrical rolls rotate at different circumferential speeds (the ratio of the speeds being 1.5–2 to 1). This uneven rotation produces a shearing action which facilitates mixing. The further processes of manufacture may vary. Usually the paste is subjected to a final rolling.

Final rolling. This operation aims at obtaining a uniform translucent, completely colloidal mass in the form of a flat sheet. It is conducted at an elevated temperature (70–95°C), and consists of repeatedly passing a sheet folded in various directions between the rolls. Calanders are usually used for the final rolling (Fig. 260). They have a highly polished surface and the spacing between them may be regulated with a high accuracy (to 0.05 mm).

Rolling is considered to be complete when the sheet is quite uniform to the eye, translucent and without streaks or stains. In some factories during the final rolling a weighed amount of centralite is added, spread over the sheets during rolling.

Both cylinders should run at the same speed. This increases the safety of the process by minimizing the friction. In spite of this the operation of final rolling is considered relatively dangerous (see p. 651).

Cutting. Warm sheets (at about 50°C) are cut on a guillotine into squares, by first cutting the sheet into strips and afterwards, crosswise, into squares. The sheets must be warm in order to keep them plastic, so that they are easy to cut. Cold sheets, which are hard and brittle, soon blunt the knives, the cut flakes are not sufficiently regular in shape, and more dust is produced.

Ballistite is usually cut into "squares" with sides ten times larger than their web thickness (e.g. flakes of 1×10×10 mm or 3×30×30 mm are obtained). The dimension ratio may, however, be varied, e.g. for sporting ballistite, requiring a high vivacity, the dimensions are 0.1×1.5×1.5 mm.

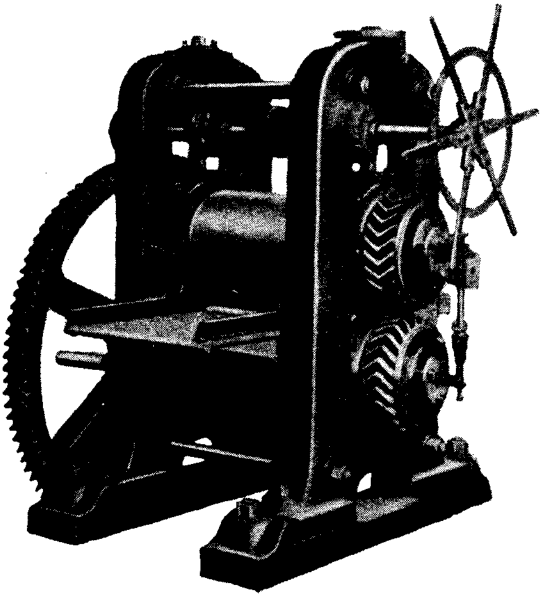


FIG. 260. Finishing rolls (calanders) [7].

Grading. After they are cut, the powder flakes are graded on vibrating screens to separate out flakes of the right size from dust and coarse or irregularly shaped flakes. The waste material is returned to the dried mass prior to final rolling.

Graphite glazing. The ballistite flakes are glazed with graphite in drums. For this purpose 0.1% graphite is added to the powder and the drum is rotated for 15–30 min. The powder is then regraded, mainly to remove any graphite adhering to the surface of the flakes and the dust formed when the sharp edges of the flakes are rounded off, and is then ready for use. Its ballistic properties are tested and the mass is blended in hoppers or drums.

The method for the manufacture of ballistite outlined above gives good results only when totally soluble nitrocellulose is used, the solutions of which are not too viscous. A high viscosity hampers gelatinization while a low viscosity gives solid solutions that are too brittle. This makes the sheets brittle, causes a larger amount of wastage on cutting and impairs the strength of the flakes, which may be damaged during transport. It is of great importance, therefore, that a plant manufacturing ballistite should always use nitrocellulose of the same properties, especially as far as solubility and viscosity are concerned.

Some factories (e.g. in Austria) which before and during World War I encountered many difficulties in manufacturing ballistite by the method described above modified the process: after the mass had been rolled to dry it, it was transferred to kneaders and a small amount (2–8%) of acetone was added. This greatly facilitated the next, final rolling which could be then conducted at a lower temperature (70°C).

The powder so obtained contained some acetone which did not volatilize on final rolling. After cutting, grading, glazing and final grading, therefore, it had to be dried at a temperature of 40–43°C, which took up to two days.

Ballistite is virtually non-hygroscopic and is therefore transported and stored in tightly closed wooden boxes, lined with cloth or waxed paper with a lid fixed with brass screws.

Attenuated ballistites

In some countries, especially during World War I when nitroglycerine was in short supply, it was partly replaced by aromatic nitro compounds, e.g. liquid DNT (a liquid mixture of DNT and TNT isomers). Partial replacement of nitroglycerine by nitro compounds also reduced the erosive effect of the powder by lowering the heat of explosion and the flame temperature during explosive decomposition.

The composition of such flake ballistite WP (Würfelpulver) was:

Collodion cotton	61%
Nitroglycerine	20%
TNT	15.25%
DNT	3.50%
Centralite	0.25%

Another type of attenuated ballistite (WP) containing less nitroglycerine and an increased content of nitrocellulose was also produced in Germany. It consisted of:

Nitrocellulose (12.6–12.7% N and 50–70% solubility)	60%
Nitroglycerine	40%

To this mass 0.5–1.0% centralite was added.

During World War I and later attenuated ballistite (Ballistite ATT) in which the nitroglycerine was partly replaced by DNT was used in France. To prevent excessive attenuation the collodion cotton was partly replaced by high nitrated nitrocellulose (CP_1):

Nitrocellulose (CP_1)	30%
Collodion cotton (CP_2)	30%
Nitroglycerine	25%
DNT	15%

In this case DNT also acted as a stabilizer.

Progressive ballistite

To obtain ballistite with a more progressive rate of burning, attempts were made to produce laminated flakes, with the two outer layers made of attenuated ballistite and an inner one, sandwiched between, made of ordinary ballistite. In the attenuated ballistite DNT was substituted for part of the nitroglycerine. However a powder of this type retained its ballistic characteristics for only a few months, since, due to diffusion, the composition of all three layers gradually became equal.

Safety in the manufacture of ballistites

Final rolling is a dangerous stage of the manufacture, since the powder may ignite, especially when it is rolled to a low web thickness (below 1 mm). Ignition may be caused in various ways. Sometimes a foreign body (e.g. a grain of sand) can increase friction, or a pocket of air confined in a fold of the sheet may be violently compressed when the latter is introduced between rolls.

A hot sheet of powder burns very fast. Special automatic installations are used to extinguish fire as soon as possible with a strong jet of water. The simplest system consists of suspending above the rolls a vessel filled with water which is balanced with a strip of smokeless powder. The strip is burned out at once, by the flame that shoots upwards when a sheet ignites, and the vessel immediately falls over and pours its contents onto the fire.

This equipment, however, may not apply the water quickly enough if the sheet does not burst into flame immediately below the strip of powder.

A more modern installation comprises a system in which a photoelectric cell detects the first flash of flame emitted by the sheet of powder. The electric current generated by the photoelectric cell passes through an amplifier and ignites a charge of 2 g of smokeless powder which a quarter of a second after the accident opens a 9 in. dia. water release valve. This method has proved reliable and very useful in industrial practice [36].

All workers must wear special clothes of heavy wool, leather or asbestos to protect them from brief but very hot flame. Hands must be protected with gloves that leave the fingertips bare so that the workers retain the sense of touch in the fingers, otherwise the hand may be drawn between the rolls.

In the course of their work the staff are exposed to the risk of inhaling nitroglycerine vapours but most people grow accustomed to this without detriment. The centralite vapours present in the air also exert an irritating effect upon the upper respiratory tract and it is advisable, therefore, to provide the staff with light respirators containing cotton wool or an adsorptive layer.

SOLVENTLESS POWDERS WITH A LOW CONTENT OF NITROGLYCERINE

Powder with a low content of nitroglycerine is simply called solventless powder to distinguish it from ballistite.

Solventless powder is usually tubular. It was first produced at the Düneberg factory, in 1912, under the name of RPC/12 (Rohrenpulver mit Centralit 1912). Initially the manufacture of this powder was based upon the use of easily soluble nitrocellulose (11% N), plus guncotton to bring the total nitrogen content up to 11.7%. About 25% nitroglycerine was used plus a large quantity of centralite (4–5%) as a non-volatile solvent.

The manufacturing process was divided into the following stages:

(1) Preparation of the mixture of ingredients;
(2) Rolling, to promote drying and gelatinizing;
(3) Hot pressing (at 90°C) into tubes.

Since the powder contains no volatile solvent it does not require long drying (cf. the manufacture of cordite). Drying lasts only a few hours and its purpose is solely to equalize the moisture content in the powder tubes.

The rapid manufacture of RPC/12 powder was one of reasons for the protracted resistance of the Central Powers during World War I. The lack of acetone suffered by the Central Powers at that time had no effect on the production capacity of this powder in German factories.

Another of its advantages was that various substances, e.g. flash-reducing compounds, could be introduced into the powder mass. During World War I potassium oxalate or potassium tartrate were used to reduce or suppress flash. These salts cannot be introduced into nitrocellulose powder since they would be washed out with the water during soaking.

Potassium hydrogen carbonate and vaseline were also tested as flash reducing agents and stabilizers.

Powder of the RPC/12 type proved not very erosive, no more so than common nitrocellulose powders. The only disadvantage of this powder is that it is hazardous to manufacture. Rolling and hot pressing often leads to ignition. This has caused a large number of explosions. The manufacture of this powder was kept secret and not disclosed until after World War I, when the essential features of its production were revealed. The type of nitrocellulose used for the manufacture of the powder is of great importance. Mixed nitrocellulose is required since more uniform tubes are then obtained, and the presence of non-gelatinized guncotton facilitates ignition and increases vivacity. A powder made from one type of nitrocellulose containing 11.7% N is irregular, less vivacious and ignites with greater difficulty, hence its ballistics are less uniform. The uniform ballistic properties of RPC/12 powder were achieved by accuracy in production and particularly by strict production control in terms of the heat of explosion. This property was therefore kept within narrow limits.

After World War I the manufacture of solventless powder was started in other countries: France under the name of powder SD (sans dissolvent), Great Britain as Cordite SC (solventless cordite) and the U.S.S.R.

According to Wheeler, Whittaker and Pike [37] British solventless powder consisted of:

Nitroglycerine	41%
Nitrocellulose	50%
Diethyldiphenylurea	9%

At that time the composition was improved by the addition of a small amount of graphite which acts as a lubricant and so facilitates extrusion. In many cases centralite was replaced either by Acardite or by phenylethylurethane or diphenylurethane. In Japan formyldiphenylamine was applied.

In the U.S.S.R. a type of solventless powder was introduced in which organic nitro compounds, e.g. DNT, partly replaced the nitroglycerine. DNT acts as a non-volatile solvent and as a stabilizer. Since it also reduces the heat of explosion these powders are either flashless or partly so.

During World War II large quantities of flashless powder containing nitrodiethyleneglycol and nitroguanidine were produced. Nitroguanidine has the advantage of considerably reducing the heat of explosion, although it cannot dissolve nitrocellulose and is, therefore, only mechanically incorporated into the colloidal mass.

Two operations in the manufacture of solventless powder are of particular importance:

(1) Careful mixing of the ingredients.

(2) Uniform, hot pressing of the powder tubes.

Mixing. Mixing is conducted first by making a slurry of the nitrocellulose in water and then stirring in the nitroglycerine in which the centralite is dissolved. When, however, solventless powder is prepared with a small amount of nitroglycerine, the "paste" obtained is not sufficiently uniform in spite of continuous stirring. Uniformity is adequate, if the mixture is to be made into ballistite, i.e. if the content of nitroglycerine is relatively large (40–50%). The manufacture of the powder is then concluded by rolling and cutting the sheets. If however, the nitroglycerine content is relatively low (20–30%) and the sheets are to be extruded into tubes, the primitive method described above gives insufficient uniformity and this is not improved by mixing in kneaders. The most effective method is to allow the paste to stand in a wet condition (after removing the water by filtering or centrifuging) for some time, usually two weeks. In this "ripening" period, the composition of the mass is partially equalized by the diffusion of liquid nitroglycerine, the swelling of the nitrocellulose and its partial dissolution in the nitroglycerine.

It is obvious that this method has some serious disadvantages:

(1) The manufacturing process is considerably prolonged.

(2) Large concrete pits must be installed for storing the ripening paste.

The difficulties in obtaining a uniform paste were completely eliminated when nitroglycerine or dinitrodiethyleneglycol was used in the form of an aqueous emulsion for mixing with nitrocellulose under water (see pp. 647 and 661). Nitrocellulose adsorbs nitroglycerine very uniformly from an aqueous medium, so the paste thus obtained may be utilized for further processing immediately after the removal of water. This is best achieved in centrifuges. They reduce the water content to about 30%, while for further reduction (to 8–10%) screw presses are preferable.

Rolling. The paste intended for the manufacture of solventless powder is first rolled between drying rollers (at 50–60°C) and then between gelatinizing rollers, as in the manufacture of ballistite. This operation must be very carefully controlled.

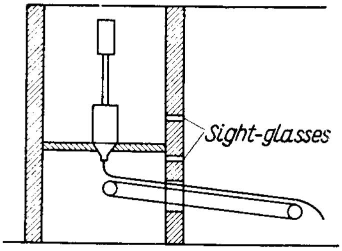


FIG. 261. A press for the extrusion of solventless powder tubes.

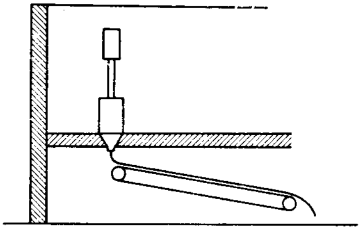


FIG. 262. A press for the extrusion of solventless powder tubes.

The powder paste should always contain the same proportion of water. The rollers used for a given powder paste should always be heated to the same temperature and their peripheral speed should also be constant (the diameter of the rollers should be directly proportional to their angular speed). The distance between the rollers, the amount of material to be rolled and the number of passages between the rollers must not be changed during the operation. Rolling of the paste should be more prolonged than with ballistite, since this improves the uniformity of the tubes extruded by the press, and gives them a smoother surface. An increase in the number of passages, however, may lead to difficulties in pressing, primarily in an increase of the pressure required for pressing since the paste becomes more gelatinized.

Powder containing dinitrodiethyleneglycol is much safer to roll than that containing nitroglycerine powder.

Pressing. This is an operation of the greatest importance since the quality of the powder tubes and their ballistic properties depend to a high degree on its proper execution. It should be carried out under a uniform but moderate pressure to give tubes with an even, smooth surface, and identical dimensions.

The tubes are extruded from the hot material, under high pressure (200–700 kg/cm^2) using hydraulic presses, with the cylinders heated with hot water to a temperature of 90°C. Since the pressing operation is rather dangerous and sometimes leads to explosion, the cylinders are usually fairly small and hold at most 10–25 kg of paste. As a safety precaution the press should be separated by a wall from the conveyor receiving the extruded tubes (Figs. 261 and 262). In addition, the press itself may be fitted with safety devices protecting it from explosion. There are presses, for example, in which the die is joined to the cylinder by crocodile clips. If the pressure inside the cylinder increases to above 1200 kg/cm^2 it exceeds the mechanical strength of the clips so that they are broken, the die is thrown out and the gases inside the cylinder can expand freely.

The causes of explosions during the pressing of hot, solventless powder have not yet been fully explained. They may include: discharge of electricity accumulated by intensive friction, friction itself, and compression of hot air present between the layers of paste. Fleury [38] suggests that almost all the piston work is converted into heat energy which may lead to local overheating, up to the initiation temperature of the mass.

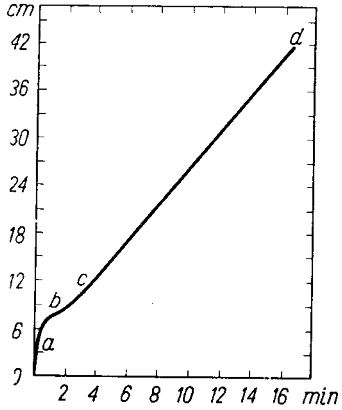


FIG. 263. Piston speed during pressing.

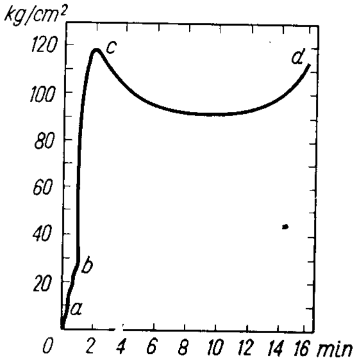


FIG. 264. Hydraulic pressure in terms of time.

In fact, the material is pressed at such a high temperature that explosive ingredients particularly sensitive to friction and impact such as nitroglycerine and nitrocellulose may be exploded by a minute initiating thermal or mechanical impulse.

The mechanism of the pressing process should be known in great detail in order to recognize the dangerous moments. Fleury [38] investigated the pressing of solventless powder, and recorded the following:

(1) A diagram of the piston speed (Fig. 263).

(2) A diagram of the variation of hydraulic pressure with time (Fig. 264).

(3) Diagrams of piston acceleration (curve *V* in Fig. 265) and of piston work (curve *P* in Fig. 265).

Two distinct sections *ab* and *cd* of different piston speed can be seen in Fig. 263. The speed for the first section *ab* is distinctly high. This is followed by a short, transistory section *bc*, that passes into the third section *cd* in which the speed becomes steady. The diagram in Fig. 264 shows that from the point *b* a sudden rise of pressure begins and persists for the first two minutes, while curve *P* in Fig. 265 shows that during the first 30 sec the piston work increases violently with intense heat emission and then falls almost to zero, soon increasing again. These changes correspond to the following stages: first the kneading of the mass continues for half a minute, when the piston is slowed down, since the pressure is still too low to cause the outflow of the mass through the die. Next the pressure increases and the mass commences to flow out.

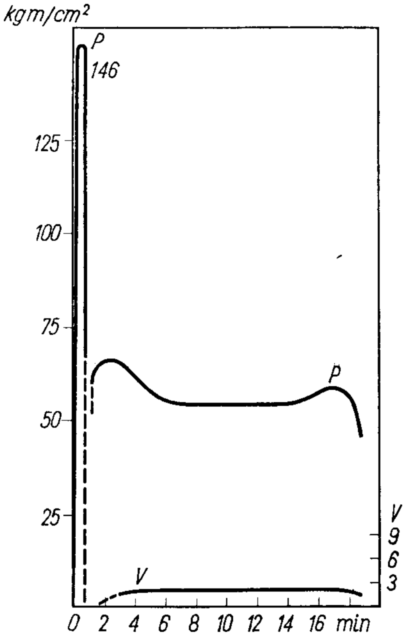


FIG. 265. Piston work in terms of time *P*; *V*—acceleration of piston motion.

Fleury used the above diagrams to explain some explosions which occurred in an experimental factory at Sevran-Livry, in September and October, 1929.

In all these accidents the explosions occurred during the first stage of pressing (points *b* on diagrams in Figs. 263 and 264), when the pressure (*ca.* 40 kg/cm^2) was considerably lower than the maximal one, but when the piston speed was fairly high (section *a–b* in Fig. 263) and the amount of heat from the transformation of its work into heat energy was very large (curve *P* in Fig. 265).

Fleury concluded that it is necessary to determine experimentally the most appropriate piston speed for a given press and a given powder mass. During the whole process the speed of the piston should be so adjusted as not to produce an excessively large quantity of heat that might lead to an explosion. The danger is particularly great during the initial period of pressing since the quantity of heat than produced may be exceptionally large.

The most important factors influencing the pressing process are listed below.

Uniformity of the paste is a prerequisite for good pressing. This depends chiefly on the uniformity with which the ingredients are mixed under water and on the uniform gelatinization of the mass between the rollers. Insufficient accuracy or defective execution of either operation can be highly detrimental to the pressing process, sometimes rendering it impossible.

In addition the results of pressing also depend upon filling the cylinder with the sheets of gelatinized substance as completely as possible and upon the maintenance of a uniform temperature inside the cylinder (for nitroglycerine pastes about 90°C, for nitrodiethyleneglycol pastes about 70°C). The cylinder is properly filled by competent loading. There are two methods which differ in economy of materials. In the first method disks with a diameter equal to that of the inner diameter of the cylinder are cut from a sheet and are then piled onto each other ("sandwich loading"). In the other method the sheet is coiled into a rouleau (roll) with a diameter as above ("carpet loading"). The first of these methods is less economical since cutting the disks from the sheet leaves a considerable amount of waste clippings. Although they are recycled for rolling, this leads to an increase of running costs. Carpet loading gives only an insignificant quantity of clippings, when the edges are cut from a big sheet, and this method is therefore the more widely used.

To maintain a steady and uniform temperature within the cylinder the surface of the disks or rouleaux must not be allowed to cool during cutting or other operations preceding loading. To prevent such cooling, in many factories the powder sheets are cut or rolled on tables heated with hot water and the material is then immediately loaded into the cylinders of the press. If the disks or rouleaux should happen to cool down, the tubes extruded by the die are uneven, often shredded, and should be rejected.

Uniformity of pressure depends upon the uniformity of the charge in the press. The amount of pressure applied depends on a number of factors. For example, a higher temperature of the paste enhances its plasticity thus facilitating extrusion and making it possible to carry out the pressing under a lower pressure.

On the other hand there are a number of factors which lead to an increase in pressure, i.e.: a reduction in the dimensions (diameter) of the openings of the die, an elongation of the outlets of the die or a large number of passages between the rollers as described above.

The pressure is also greatly influenced by the composition of the powder mass, in particular by the nitrogen content of the nitrocellulose. The highest pressure should be applied to nitrocellulose with a 12.0–12.3% nitrogen content. With a lower or higher nitrogen content a lower pressure is required. An increase of the content of gelatinizing agent (e.g. over 9% centralite) may also involve increased pressure during the pressing operation. Similarly the pressure increases when a paste with a larger content of nitrocellulose is used.

However, the pressure may be considerably reduced by the addition to the powder mass of substances such as graphite, or magnesium oxide, or both, that act as a lubricant by reducing the internal friction. The presence of graphite also diminishes the danger of electrification of the powder tubes during extrusion. Pressing is also facilitated if a certain percentage of water is left in the sheets coming from the rolls.

The uniformity (smoothness) of the surface of the tubes extruded by the press is favourably influenced by the following factors:

An increase in the number of passages in rolling;

An increase in the length of the die.

The use of nitrocellulose with a nitrogen content below 12% also increases the smoothness of the surface of the tubes. The addition of higher nitrated cellulose is not detrimental in this respect if the production process is well managed.

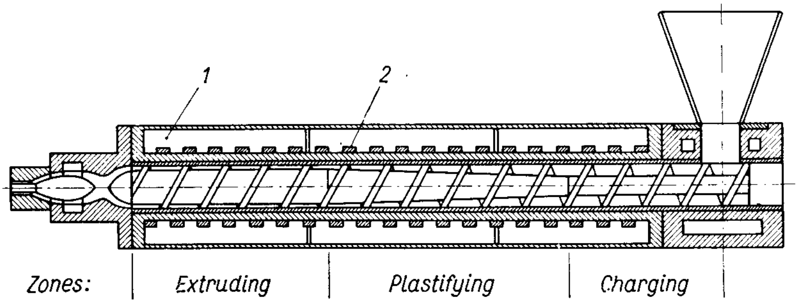


FIG. 266. Diagram of a screw press, according to Schenkel [40]. *1*—heating and cooling jacket, *2*—heating elements.

The surface becomes less smooth due to:

(1) An increase in the extrusion speed of the tubes;

(2) A rise in temperature of the mass in the cylinder.

The surface of the tubes often looses smoothness if the centralite content in the powder is increased above 9%, while it is improved when the content of nitrocellulose is increased above 50%. It was ascertained experimentally that a well gelatinized paste, containing 50% nitrocellulose of 12% N content may give tubes with a rough, uneven surface, while a paste containing nitrocellulose with the same nitrogen content but composed of a mixture of lower nitrated (about 11% N) and higher nitrated (about 13% N) nitrocellulose gives a smoother surface.

The outer diameter of the tubes extruded by the die is somewhat larger and the inner diameter somewhat smaller than the corresponding dimensions of the die. This is due to the fact that the paste is to a certain extent elastic and therefore expands after the pressure is discontinued. The shorter the die, the greater the expansion, but a longer die requires a higher presure. Thus, under a pressure of about 230 kg/cm^2, with a die about 1 mm long, the tubes may expand by about 12%. When using a considerably longer die—about 25 mm—the pressure must be raised to approximately 400 kg/cm^2 for the same paste, to obtain the same speed of extrusion of tubes. Under these conditions, the expansion barely amounts to 5% (the above figures relate to a definite type of powder only—they may differ for other types).

The expansion of the tubes also depends on other factors. It increases with an increase in the speed of extrusion, a rise of temperature of the mass in the cylinder, and an increase in its centralite content. An increase in the number of passages between the rollers may also lead to a greater expansion of the tubes. The expansion also depends on the nitrogen content in the nitrocellulose, being nearly inversely proportional to it. Thus, when using nitrocellulose which contains approximately 11% N, the expansion is much greater than with nitrocellulose which contains 12.3% N.

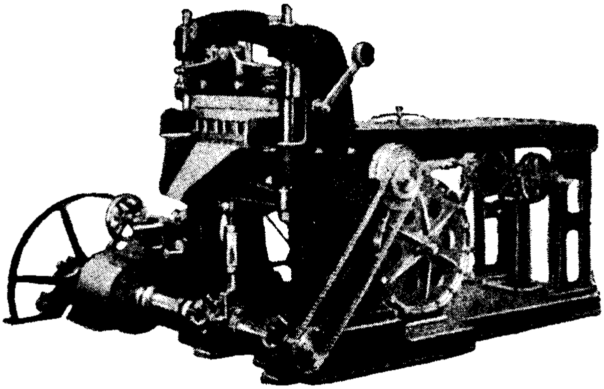


FIG. 267. "Guillotine" cutter for powder tubes [7].

The uniformity of the diameter of the powder tubes is also influenced by different factors. Greater uniformity is obtained with longer dies and an increased number of passages between the rollers. A decrease in the nitrocellulose content to 50% reduces the uniformity of the tube dimensions as does an increase in the centralite content.

Recently a new technique of extrusion of solventless powder dough was introduced, in which extrusion is effected by a worm screw extruder instead of a hydraulic press.

A few patents have been issued covering the use of screw presses [39], but they do not include details of the design of the presses. However these do not differ from the screw presses widely used for extrusion of plastic rods, tubes and other shapes. A detailed description of the screw presses used in plastics technology can be found in monographs [40, 41]. A diagrammatic representation of a screw press is given in Fig. 266.

Cutting. Tubes extruded as described above are cut on a "guillotine" (Fig. 267). The powder should be warm when cut (about 50°C), and the trough of the guillotine is therefore heated externally with warm water. This makes it possible to maintain an adequate temperature and elasticity of the powder and prevents it from cooling down and cracking when being cut.

THE MANUFACTURE OF SOLVENTLESS POWDER IN GERMAN FACTORIES [42]

Notation

German nitroglycerine powders were all marked with letters Ngl. at the beginning of the code name. This was followed by letters denoting the form, e.g. R.P. for tubular powder, Bl.P. for square plates powder etc., as described earlier (nitrocellulose powder, p. 572). After that a figure denoting the calorific value in hundredth of kcal/kg was given, followed by the dimensions in brackets. E.g. Ngl. Bl.P.-12,5-(4·4·1) meant: nitroglycerine powder in square plates with a calorific value 1250 kcal/kg and the dimensions 4 mm×4 mm×1 mm; Ngl. R.P.-8,2-(100.2/1) meant: nitroglycerine tubular powder of 820 kcal/kg, 100 mm long, with external and internal diameters 2 and 1 mm, respectively.

Diglycoldinitrate powders had the same notation as nitroglycerine powders with only one difference, the calorific value was marked with letters for the sake of secrecy.

The letter A denoted calorific value 930 ± 25 kcal/kg
E denoted calorific value 740 ± 10 kcal/kg
K denoted calorific value 690^{+40}_{-10} kcal/kg
G denoted calorific value 690^{+20}_{-10} kcal/kg

E.g. Digl. R.P.-G. followed by dimensions in brackets meant diglycoldinitrate tubular powder of calorific value 690^{+20}_{-10} kcal/kg.

DGDN powder usually contained flash reducing salts. Their quantity was indicated by a figure following the letter denoting the calorific value, e.g. G.0. meant no salts are present, G 1,5 denoted 1.5% salts.

Flashless powder containing nitroguanidine was called "Gudol Pulver" and was marked with an abbreviation Gu. This was followed by the usual notation giving the form of the powder grain. Next was the letter giving the calorific value (usually A in nitroguanidine powders) followed by a figure indicating the amount of flash reducing salts. The absence of such salts was indicated by O; e.g. Gu.Bl.P.AO meant Gudol square plates powder, calorific value 930 ± 25 kcal/kg, without flash reducing salts; Gu.R.P.A. 1,2 meant Gudol tubular powder, of 930 ± 25 kcal/kg with 1.2% flash reducing salt.

Manufacture

The following method has been described as that used in Krümmel and Düneberg during World War II. First the crude powder paste was prepared. The ingredients comprised (weight of dry substance):

Nitrocellulose	70%
Explosive oil (nitroglycerine or nitrodiethyleneglycol or nitrotriethyleneglycol or nitrometriol)	30%

The nitrocellulose used for the manufacture of the mass consisted of a mixture of two qualities: high-nitrated nitrocellulose S (13.15–13.25% N), with a solubility of about 10% and a degree of fineness of about 85 cm * and low-nitrated nitrocellulose EH (11.3–11.45% N), with a solubility of 100% and a degree of fineness of about 90 cm.

For nitrocellulose supplied in hermetically-sealed containers (35–10% of water) the water content was determined by drying for 12 hr at a temperature of 45°C. Both types of nitrocellulose were then mixed to obtain the required nitrogen content. In Krümmel, mixtures were used with the following nitrogen contents:

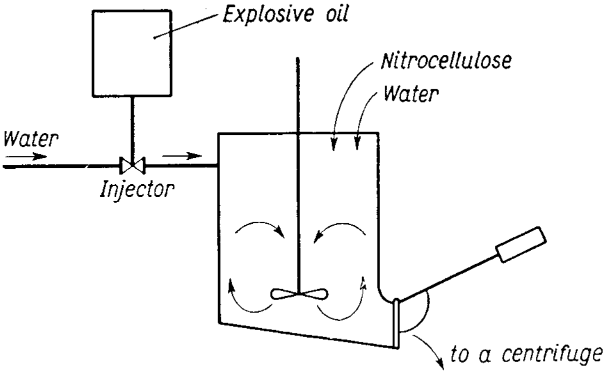


FIG. 268. Schematic view showing an arrangement for mixing powder with an injector for producing the explosive oil-in-water emulsion.

I	11.5% N	IV	12.6% N
II	12.0% N	V	12.75% N
III	12.2% N	VI	13.0% N

Mixtures II, IV and VI were used most frequently.

The nitrocellulose was weighed in rubberized bags and conveyed by electric trucks to the mixer.

The explosive oil (usually dinitrodiglycol) was used in the form of an aqueous emulsion. It was drawn from a wooden container lined with lead and introduced through a feeder into a water injector in which the aqueous emulsion formed. This emulsion was introduced into the mixer, filled with an aqueous suspension of nitrocellulose (Fig. 268).

Incorporating. Approximately 1.6 m³ of water and 280 kg of nitrocellulose (weight of dry substance) were poured into a mixer 3 m³ in capacity and a mechanical stirrer was set into vigorous motion. After 10 min of stirring, when both modifications of nitrocellulose were uniformly incorporated and a slurry was formed in water,

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* The figures characterize the volume of a layer of nitrocellulose settling from a suspension of 10 g in 250 ml of water. The finer the nitrocellulose the smaller the figure.

120 kg of the aqueous emulsion of explosive oil was introduced. The whole was stirred for a further 10 min and then poured into a centrifuge. After centrifuging the paste contained about 35% of water. The centrifuge discharged its contents from below into rubber bags which were placed into larger cloth sacks and transported by electric trucks to the store where the crude paste was kept.

The water flowing from the centrifuge was collected in large tanks in which particles of crude paste carried out with the water settled on the bottom. The clear water was returned to the mixer and the sediment from the bottom of the tanks was removed from time to time, when larger amounts had collected.

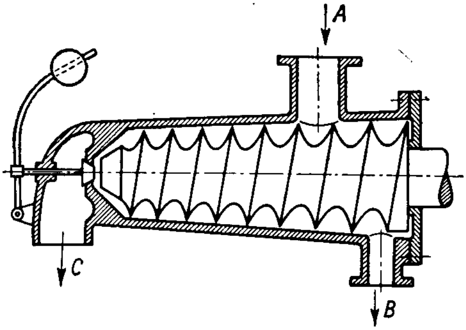


FIG. 269. Worm drying and mixing machine: *A*—inlet for introduction of dough with a 30% water content, *B*—water discharge outlet, *C*—exit for the mass containing 8% water.

Storage. The crude paste was emptied out of the bags in thin layers into large wooden boxes of 10,000 kg capacity. To attain a uniform sample, the mass for processing into powder was taken in vertical layers.

The crude powder paste was conveyed to the adjacent factory in Düneberg, where it was processed into charges ready for use in the following way:

To make the crude paste uniform in composition it was mixed in a large wooden drum and loaded into Werner–Pfleiderer kneaders heated to about 50°C. The remaining ingredients of the powder (Centralite or Acardite, graphite, magnesium oxide etc., depending on the type of powder) were then added. From the kneaders the mixture was placed in air-tight cans. To ensure good results in subsequent operations, the paste was allowed to ripen for about a week. After ripening the mixture may be rolled, but its moisture content should first be reduced from 30 to 8% by passing it through a worm press (Fig. 269) to facilitate subsequent rolling operations.

Rolling. It was carried out using horizontal rollers 40 cm dia. and 100–120 cm in length, rotating with a speed of 11 r.p.m. For paste made with dinitroglycol it was sufficient to maintain a temperature of 70–80°C. A charge of about 15 kg was rolled for 18–30 min. The sheets issued from the rollers completely gelatinized. In cannon powders 3–5% water was left in the sheets since this facilitated the formation of tubes.

To load the press one or two sheets, with the edges evened-off, were coiled around a brass rod approximately 4 cm dia. This gave charges of 15–30 kg which were placed into the cylinders of a hydraulic press. The diameter of the cylinders ranged from 17–24 cm, and the temperature when pressing dinitrodiglycol powder was 70–80°C.

For pressing powder of large dimensions the Mamut press was used. This had a cylinder with 52 cm dia., a charge height of 65 cm and a charge weight of 210 kg. The pressure applied was 60–70 kg/cm^2. If the powder extruded was damp (3–5% of moisture) it had to be dried to 1.0–1.2% moisture content.

SOLVENTLESS POWDER IN JAPAN

The manufacture of solventless double base powder began in Japan in 1924.

It appears that the Japanese Army and Navy used two types of double base powders [33] (Table 186).

TABLE 186

Ingredients	Names	
	G OTSU Mk I	G OTSU Mk II
Nitrocellulose	63.9–64.3 (11.85% N)	58.9–59.3 (12.79% N)
Nitroglycerine	27.0	35.0
Centralite	4.0	2.5
Formyldiphenylamine	4.0	2.5
Inert compounds in proportion:		
Ammonium oxalate 50	1.1–0.7	1.1–0.7
Sodium bicarbonate 50		
Graphite 10		
Properties		
Heat of explosion (kcal/kg)	726–734	960–967
V_0 (l./kg)	979–980	892–893
t (°C)	2410–2427	3006–3025
f (m)	9946–10,016	11,077–11,148

Powder G OTSU Mk I was designed for general ordnance use. It was characterized by low corrosion.

Powder G OTSU Mk II was mainly used in naval revolving turret guns.

FLASHLESS CHARGES AND FLASHLESS POWDERS

The first flashless charges were made during World War I. They were developed from an observation of Dautriche [43] that addition of blackpowder reduces and attenuates flash or even entirely prevents the formation of a secondary flame. The French therefore added blackpowder to nitrocellulose powder and during World War I regularly loaded part of their machine gun ammunition with a mixture consisting of nine parts of smokeless powder and one part of blackpowder. In their cannon they used silk anti-flash bags filled with potassium hydrogen tartrate. Since this substance reduced the muzzle velocity, an extra charge of smokeless powder was used. E.g. in 155 mm naval guns, 305 g of BM_7 powder were added to restore the muzzle velocity to a charge of 10 kg of BM_7 powder with a priming of 115 g of blackpowder, when three bags of 500 g of potassium hydrogen tartrate were used.

Another method used in France was to add anti-flash pellets, consisting of four parts of potassium nitrate and one part of DNT, to propellant charges. The pellets weighed one gramme each and were about 2 mm thick and 15 mm dia. They were sewn in silk bags, in numbers depending on the calibre e.g. 200–300 were used for a 155 mm gun. Such pellets behaved as a propellant charge and did not reduce the muzzle velocity.

The Germans used anti-flash charges containing potassium chloride in their cannon propellants. The charges, in bags of artificial silk or cotton cloth, were loaded between the base of the projectile and the propellant. Obviously, all the additions described above increased the smoke formed when the rounds were fired.

After World War I FNH powder was produced in the U.S.A. It was flashless, and non-hygroscopic and according to one of the relevant patents [44] consisted of:

Nitrocellulose (13.15% N)	76–79%
DNT	21–24%
Diphenylamine	1%

or

Nitrocellulose	84%
DNT	10%
Butyl phthalate	5%
Diphenylamine	1%

Flashlessness was attained by reducing the heat of explosion with an addition of DNT. At the same time, however, smoke was increased.

Other patents of the interwar period include several that specified addition of substances rich in carbon, e.g. of powdered hydrocellulose, to obtain flashless charges. In the U.S.S.R. nitroglycerine powder was used in which a part of the nitroglycerine was replaced by aromatic nitro compounds. During World War II the most widely used flashless powder contained nitroguanidine (in Germany called "Gudol" powder).

The idea of adding nitroguanidine to smokeless powder had been already considered by Vieille [45]. He suggested adding nitroguanidine to reduce the erosiveness of the powder (see p. 548)

The idea was revived by various authors (e.g. Recchi [46]).

It was difficult to manufacture since the nitroguanidine had to be introduced into the powder mass in a state of fine subdivision, otherwise the powder was not uniform. In some factories, therefore, methods were worked out to obtain nitroguanidine in the form of fine dust.

The introduction of a large amount of nitroguanidine would be very difficult, were it not for the replacement of the nitroglycerine by dinitrodiethyleneglycol which

TABLE 187

FLAKE POWDER FOR TRENCH MORTARS, HOWITZERS AND FIELD GUNS [42]

No.	Purpose	Dimensions	Composition (%)											
			Nitrocellulose		Nitroglycerine	Nitrodiglycol	Nitroguanidine	Centralite	Acardite	Graphite	Magnesium oxide	Potassium sulphate	Other ingredients*	Calorific value (kcal/kg)
				Nitrogen %										
1	8 cm trench mortar	Flakes 1×1×0.2	54.5	13.0	44.0	–	–	1.1	–	0.05	–	–	0.35	1250
	7.5 cm infantry gun	Rings 0.4×60/30	54.5	13.0	44.0	–	–	1.1	–	0.05	–	–	0.35	1250
	7.5 cm infantry gun	Rings 73.5×0.8	54.5	13.0	44.0	–	–	1.1	–	0.05	–	–	0.35	1250
2	10.5 cm field howitzer	Flakes 3×3×0.8	60.2	13.0	–	39.0	–	0.3	–	–	–	–	0.5	1050
	10.5 cm field howitzer	Flakes 4×4×1.2	60.2	13.0	–	39.0	–	0.3	–	–	–	–	0.5	1050
3	10.5 cm field howitzer	Flakes 10×10×0.2	60.2	13.0	–	39.0	–	0.5	–	–	0.05	–	0.25	1050
4	Heavy howitzer	Rings 1.9×15/4	59.1	13.0	–	40	–	0.3	–	0.05	0.05	–	0.5	1050
5	No full information	?	63.65	13.0	–	35.8	–	–	0.5	–	0.05	–	–	1050
6	No full information	?	54.4	13.0	–	44.5	–	–	0.5	0.05	0.05	0.5	–	1050
7	No full information	?	38.0	13.0	–	31.2	30.0	–	0.5	0.1	0.2	–	–	1050
8	To reinforce the primer	?	54.2	13.0	44.4	–	–	–	1.3	0.05	0.05	–	–	1250

* No full information.

TABLE 188

TUBULAR POWDER WITHOUT NITROGUANIDINE FOR ANTI-AIRCRAFT AND HEAVY GUNS [42]

No.	Purpose	Composition (%)										
		Nitrocellulose										
			Nitrogen %	Nitrodiglycol	Centralite	Butyl phthalate	Graphite	Magnesium oxide	Potassium sulphate	Vaseline	Dimensions	Calorific value (kcal/kg)
1	3.7 cm anti-aircraft gun	68.2	12.0	29.2	2.2 or 1.7 +0.5 of acardite	—	0.1	0.1–0.25	0.05–0.2	—	195 × 2/0.85	820–870
2	8.8 cm anti-aircraft and 10 cm K18 heavy gun	67.65	12.0	29.0	3.0	—	0.1	0.25	—	—	490 × 4.9/2.1	825
3	8.8 cm anti-aircraft gun	64.1	12.0	27.5	5.3	0.90	0.1	0.25	—	1.85	?	730
4	7.5 cm (40) tank-mounted gun	61.5–64.1	12.0	26.4–27.0	7.5–8.0 or 9.25 and 0.8 of diphenylurethane	0.65–0.8	0.1	0.25	2.0	1.6–1.8	420 × 3.8/1.5	690–700

TABLE 189

CANNON TUBULAR POWDER WITH NITROGUANIDINE [42]

No.	Purpose	Composition (%)											
		Nitrocellulose											
			Nitrogen %	Nitrodiglycol	Nitroguanidine	Ethylphenylurethane	Diphenylurethane	Acardite	Graphite	Magnesium oxide	Potassium sulphate	Dimensions	Calorific value (kcal/kg)
1	8.8 cm anti-aircraft gun	43.5	12	18.65	30	3.75	3.25	0.5	0.1	0.25	—	?	750
2	8.8 cm anti-aircraft gun	39.5	12	16.9	30	5.0	4.25	—	0.1	0.25	4.0	?	750

TABLE 190

TUBULAR POWDER WITH SUBSTITUTES [42]

No.	Purpose	Composition (%)															
		Nitrocellulose		Nitrodiglycol	Nitroguanidine	DNT	Nitronaphthalene	Centralite	Acardite	Ethylphenylurethane	Diphenylurethane	Hydrocellulose	Graphite	Magnesium oxide	Potassium sulphate	Dimensions	Calorific value (kcal/kg)
			Nitrogen %														
1	8.8 cm anti-aircraft and other ground guns	69.7–69.9	12	14.8–15.0	—	10	2	3	—	—	—	—	0.1	0.15	—	490 × 4.9/21	690–730
2	All guns, commonly used (Universal powder)	60.55	12	25.95	—	4	2.5	3.75	—	—	—	3	0.1	0.15	—	?	730
3	Various guns	44.0	12	18.85	20.0	3.5	2.0	—	0.4	1.5	1.5	4.0	0.1	0.15	4.0	?	720

TABLE 191

TUBULAR POWDER FOR NAVAL GUNS [42]

No.	Purpose	Composition (%)															
		Nitrocellulose															
			Nitrogen %	Nitrodiglycol	Nitrotriglycol	Nitroguanidine	Nitronaphthalene	Centralite	Acardite	Ethylphenylurethane	Diphenylurethane	Butyl phthalate	Graphite	Magnesium oxide	Potassium sulphate	Dimensions	Calorific value (kcal/kg)
1	All guns, commonly used	69.38	12.2	25.27	–	–	–	5	–	–	–	–	0.1	0.25	–	?	820
2	All guns, commonly used	65.5	12.2	23.9	–	–	–	9	–	–	–	1.25	0.1	0.25	–	?	730
3	All guns, commonly used	65.7	12.2	23.95	–	–	7	2.5	0.5	–	–	–	0.1	0.25	–	?	730
4	Signal rescue charges	58.55	12.2	–	25.1	–	–	12	–	–	–	–	0.1	0.25	4	?	650
5	37 cm gun SKC/32	35.5	12.2	21.75	–	40.0	–	–	0.5	0.7	0.7	–	0.1	0.25	0.5	?	820
6	Most important guns	42.45	12.0	18.2	–	25.0	–	–	–	4.5	4.5	–	0.1	0.25	5.0	?	730

imparts a higher elasticity to the powder. This enabled the "foreign" substance to be incorporated into the powder mass while retaining its crystal form.

Powder containing nitroguanidine has certain disadvantages. It is more fragile than the ordinary solventless powder, due to the presence of nitroguanidine, i.e. a substance which is not included in the powder colloid. On the other hand it has the advantage that it does not increase the smoke to a marked degree. Small amounts of other anti-flash substances such as potassium nitrate or sometimes powdered hydrocellulose are added to this powder. The compositions of powder of this type and of other solventless powders manufactured in Germany during World War II, are summarized in Tables 187–191.

In Great Britain small amounts of sodium or potassium cryolite (potassium aluminium fluoride) were added to nitroglycerine powder containing nitroguanidine. According to Pring [47] a powder with 55% nitroguanidine and cryolite gives no flash in all calibres of cannon up to 16 in. (40 cm). Charges of this powder, however, are harder to ignite and thus require a larger quantity of blackpowder as a primer. This, in turn, increases the smokiness, since the majority of smoke in firing with smokeless powder derives from the blackpowder primer.

Other substances suggested for flashless powder instead of nitroguanidine included aminotetrazole which was, however, rejected due to its hygroscopicity, and methylene-urea.

Recently it was found that caesium salts prevent the formation of secondary flame.

SMOKELESS POWDER WITH PENTHRITE

During World War II, the German tried using penthrite as an ingredient of smokeless powder. Penthrite, in spite of being a nitric ester, does not dissolve nitrocellulose and thus retains its crystal structure in the powder mass, and causes brittleness (like nitroguanidine). The introduction of a large amount of penthrite into the powder mass was possible only when dinitrodiethyleneglycol was used, which, as is known, gives a more elastic and mechanically resistant powder. Powder containing penthrite (Nipolit) has been manufactured on a small scale. The manufacture never passed beyond pilot plant scale. The production process was the same as in other nitroglycerine powders. The composition of Nipolit is given in Table 192.

TABLE 192
THE COMPOSITION OF NIPOLIT

Ingredients	Tubes 80×27/9.1	Cords 50×9.1
Nitrocellulose (12.6–12.7% N)	34.1	29.1
Dinitrodiethyleneglycol	30	20
Penthrite	35	50
Magnesium oxide	0.05	0.05
Graphite	0.1	0.1
Centralite or urethane	0.75	0.75

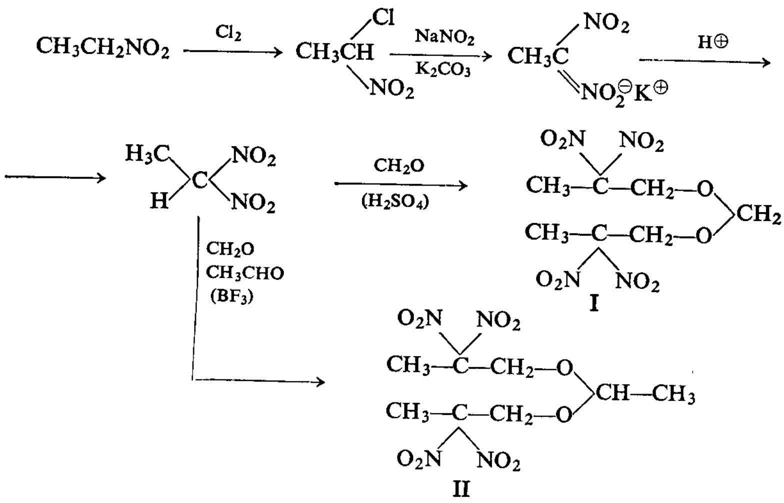
SMOKELESS POWDERS CONTAINING NITROALIPHATIC COMPOUNDS

Hexanitroethane was recommended as an ingredient of smokeless powder [48]. It is a good solvent of nitrocellulose and due to its high energy of explosion it could produce a high energy propellant.

It was believed that the German Army used smokeless powder containing hexanitroethane for the long range artillery that bombarded Paris in 1915.

The complicated and costly manufacture of hexanitroethane prevented further use of this substance as an ingredient of smokeless powder.

There is now a trend towards the use of nitroaliphatic compounds more readily available from simple nitroparaffins. Thus Aerojet-General in Sacramento, California [49] suggested using a 50/50 mixture of bis-(2,2-dinitropropyl)-formal (I) and bis-(2,2-dinitropropyl)-acetal (II) as a "nitroplasticizer". The mixture of the two compounds is liquid. The products are obtained from nitroethane through the following sequence of reactions:



The composition of the propellant was not revealed. It is only known that the propellant contains ammonium perchlorate as an oxidizer and has a very high density.

SMOKELESS POWDERS FOR ROCKETS

In the interwar period, after 1930, a number of countries (e.g. Germany, Great Britain) began to manufacture double base powder for rockets. In Great Britain (according to Wheeler, Whittaker and Pike [37]) it was manufactured in the form of tubes 2 in., 3 in. and 4.3 in. dia. The composition of German rocket powders is given in Table 193. Tubes of larger diameter were also made.

Due to the great web thickness the burning time of the powder tubes was considerable: about 3–4 sec under a pressure of about 10 kg/cm^2.

In composition, nitroglycerine powder (with a relatively low content of NG or DEGN without solvent) is the same as that commonly used without a volatile solvent for firearms; it has, however, a characteristic which calls for an examination of its use for rocket propulsion.

(1) The gases evolved on burning are intensely luminous. Non-transparent dark-coloured particles, often not visible to the naked eye, e.g. undissolved nitrocellulose, fibres or various impurities which are always present in the powder grains, adsorb this radiation more readily than the colourless or light-coloured powder mass. The temperature in the neighbourhood of these dark spots is therefore higher than that in the whole mass and even may be high enough to produce ignition of the surrounding powder. This creates the danger of irregular burning at many points inside the powder mass, causing the powder grains to crack. It also causes a sudden increase in the surface of the burning grains and a rise in pressure that may lead to the explosion of the rocket (blowing out the steel rocket case). Accidents of this kind have been noted with nitroglycerine smokeless powders of a web thickness of over 15 mm. After a certain time it was found that the addition of a darkening agent prevents the premature burning of the powder mass below the surface. Nigrosine and lamp black were used for this purpose. The darkening agent finally adopted was carbon black in the extremely fine form used in the rubber industry with a grain diameter from 0.025–0.5 μ. It is added to the powder in an amount of 0.01–0.2% by weight. It is also advisable to add some graphite, as was used formerly to facilitate the extrusion of a powder mass without a volatile solvent.

(2) Powder for rockets is usually in the form of perforated grains with a large diameter, considerably larger than that of the tubes used for cannon charges. This makes the production process for extruding the powder mass very complicated.

(3) The powder in rockets burns under much lower pressure than that in firearms (usually below 2000 lb/in^2) and its burning rate is also considerably lower. The low pressure and the low burning rate, together with the shape of the powder and of the combustion chamber, specific for rockets, lead to a reaction, totally unknown in firearms, called "resonance burning", which is characterized by certain periodic pressure oscillations. It may well be that this is caused by unevenness of the powder and the presence in it of droplets of nitroglycerine, which was discussed earlier (p. 647). Irregular burning may be alleviated by drilling radial holes in a spiral pattern along the length of the powder tube, or a non-combustible rod may be inserted into the perforation. This "stabilizing rod" is used in many current rockets.

Experience in using large charges of nitroglycerine powder has shown that powder tubes with a large diameter are unsafe to use due to the internal stresses which arise in them during cooling. While the powder is burning the tube may crack due to the local weakening of the walls and the pressure of the gases. The burning surface of the powder then increases, the pressure rises and the rocket may be blown up.

In small Soviet and German rockets a powder charge made of a bundle of small diameter powder tubes (e.g. to 20 mm) has been used. The internal stresses in these charges were not sufficiently strong to be dangerous.

In Great Britain and the U.S.A. cruciform, non-perforated powder grains have been used for rockets of heavy calibre. In these charges the mechanical stresses are far less important than in tubular charges. Another modification, consisting in the very slow cooling of the charges after extrusion and cutting up, necessitated new installations and prolonged the flow process, so a new method was introduced in which the charges were cast. This is discussed further on.

The composition of nitroglycerine powder for rocket propulsion is similar to that of conventional powder.

The composition of German rocket propellants manufactured during World War II are given in Table 193.

TABLE 193

ROCKET POWDER [42]

No.	Purpose	Composition (%)												
		Nitrocellulose		Nitrodiglycol	Acardite	Ethylphenylurethane	Diphenylurethane	Hydrocellulose	Wax E	Vaseline	Magnesium oxide	Potassium sulphate	Dimensions	Calorific value (kcal/kg)
			Nitrogen %											
1	"Universal" powder for all rocket launchers	60.0–60.2	12.6	35.3	–	1.4	1.0	1.5	0.35	0.25	0.25	0.8	?	900
2	For 30 cm rocket launcher	59.05	12.6	34.8	0.5	1.9	–	3.0	–	0.5	0.25	–	?	865

Serebryakov [50] reported the following composition for rocket powders:
J.P.N. (U.S.A.) rocket powder consists of:

Nitrocellulose (12.2% N)	51.5%
Nitroglycerine	43.0%
Diethyl phthalate	3.25%
Carbamite	1.0%
Potassium sulphate	1.25%
Wax	0.08%
Carbon black	0.2%
Moisture	0.6%

M.R.N. (U.S.A.) rocket powder consists of:

Nitrocellulose (12.2% N)	56.5%
Nitroglycerine	28.0%

Diethyl phthalate	3.0%
Aromatic nitro compounds	11.0%
Carbamite	4.5%
Wax	0.08%
Moisture	0.6%

German powder:

Nitrocellulose (12.2% N)	64.5%
DGDN	29.0%
DNT	11.0%
Centralite	3.5%
Candelilla wax	1.0%
Carbon black	0.35%
Moisture	0.5%

According to Ley [51] British smokeless powder for 2 in. rockets consisted of:

Nitroglycerine	50%
Nitrocellulose	41%
Centralite	9%

The powder was in the form of tubes about 4 cm dia. and about 1 m long.

Japanese 10–20 cm rockets were loaded with powder consisting of:

Nitroglycerine	27%
Nitronaphthalene	7%
Nitrocellulose	60%
Centralite	3%
Potassium sulphate	4%

Much attention is now paid to the mechanical properties of smokeless rocket powder [52]. This stems from the requirement for physical integrity during manufacture, storage and firing. Any imperfection, such as a crack or deformation or a stress which may lead to a crack in the course of burning can cause serious ballistic malfunction. This defective behaviour is particularly liable to occur in large double base powder grains, hot extruded under pressure.

According to Steinberger [53] the main problems, dependent on the physical properties of the propellant, are:

(1) Thermal variations. A solid propellant grain may be exposed to temperature extremes ranging from conditions of low temperature in the upper atmosphere, to tropical heat. The grain must not be too brittle at low temperature nor too soft at high temperature. The problem can be aggravated by "case-bonding" since different coefficients of expansion of the metal-case and the propellant can produce a very harmful effect.

(2) Grain collapse. This is a problem which exists in some rockets where an appreciable pressure difference can develop between the forward and aft ends of the rocket. The latter is subjected to compressive forces which can squeeze it. A propellant of high tensile strength is therefore desirable.

(3) Grain expansion. This is the problem opposite to (2). It can be serious in some rockets. The propellant must be sufficiently flexible to accomodate expansion without cracking.

Steinberger [53] suggested that propellants for case-bonded units should possess a tensile strength greater than 50 lb/in² and elongations greater than 15%. According to Boynton and Schowengardt [54] many applications require an ultimate tensile strength of 120 lb/in² and elongation of *ca.* 30%.

The difficulty in the manufacture of large grains may be overcome by substituting the classical method for the extrusion of powder by a novel technique whereby cast charges of double base propellant are produced.

CAST DOUBLE BASE PROPELLANTS

The process consists of loading a mould with granules of nitrocellulose powder and filling the interstices between the granules with a solution of a nitroglycerine plasticizer. This causes the nitrocellulose powder to swell and to gelatinize with the ingredients of the liquid phase to form a horny solid on heating the mould.

This technique seems to have been developed in various countries during World War II.

In Germany, owing to the short supply of nitroglycerine and nitrocellulose, TNT was used as the main constituent [55] (p. 681).

The composition of various more modern cast double base propellants (according to Sutton [56] and J. Taylor [57] is shown in Table 194. Table 195 gives the physico-chemical properties of propellant I.

TABLE 194

Ingredients	Propellant numbers (given by the author of this book)			
	I	II	III "OV"	IV
Nitrocellulose	45–55	47.0	58.6 (12.6% N)	60.0
Nitroglycerine	25–40	37.7	24.2	37.8
Plasticizer (mainly dimethylphthalate)	12–22	14.0	9.6	–
DNT	–	–	6.6	–
Ethyl centralite	–	1.0	1.0	0.9
Diphenylamine	1–2	–	–	0.2
Carbon black or graphite	–	0.3	0.1	0.2

TABLE 195

Constants	Figures
Adiabatic flame temperature (°F)	2600–4000
Typical sea level specific impulse, (sec)	160–220
Burning rate of 1000 lb/in² (kg/cm²) and 70°F (21°C) (in./sec)	0.22–0.3
Burning rate exponent (equation $V=k.p^n$)	0.1–0.8

The main advantage of cast propellant charges consists of the ease with which very large charges may be made without very costly equipment.

The safety of the process is higher than that of the conventional extrusion process and the labour cost is relatively low.

According to Sutton [56] the amount of additives in the cast double base charges varies from 5–30%. Their object is to improve the physical properties of the powder, facilitate manufacture, confer better stability under various storage conditions, suppress flash and inhibit ignition caused by the radiation of energy through the translucent grain. According to Sutton, an increase in the nitrocellulose content of the charge usually improves its mechanical strength.

A description of the technology of the process is given below.

Technology of casting

According to published information [52, 54, 58] two methods are in use: (1) powder casting process, and (2) slurry casting.

Powder casting process. This is the most versatile process for manufacturing double base powder charges of any size and shape.

The first step consists of making a "casting powder" composed of nitrocellulose, all the solid ingredients and a part of the non-explosive gelatinizer, such as carbamite (centralite), phthalates, etc. Solvent (alcohol–ether) is added to this mixture and threads of *ca.* 1 mm dia. are made by the usual extrusion method and cut to the length of *ca.* 1 mm. The solvent is removed by drying.

This casting powder is poured into a mould with a core of the shape required for the future charge ("grain") (Fig. 270). The mould is usually lined internally with a cellulose acetate or ethyl cellulose sheet which forms the inhibitor for the finished grain, if the grain is to burn from the inside outwards (as in most solid propellant grains used in large rockets). The thickness of the sheet of inhibitor may range from 3–12 mm. The bottom of the mould may also be covered with the same material. The mould should be provided with an equipment for the evacuation and pressurization of the assembly.

The casting powder fills *ca.* ¾ of the mould. Then the inside of the mould is evacuated to remove air and residual solvent vapours.

The interstitial spaces between the granules of the casting powder are slowly filled with the "casting solvent" composed of a mixture of plasticizers such as: nitroglycerine, diglycol dinitrate and a further quantity of carbamite (centralite) and esters. Introducing the solvent too fast can disturb the packed bed of granules. Filling can be done from the top, from the bottom or radially from the core (if perforated) and the advancing solvent front sweeps out the air, which is evacuated through a vent (at the bottom on Fig. 270).

The filled mould is sealed, sometimes pressurized and placed in an oven at moderate temperature (usually 60°C) to cure for a period ranging from 8 hr to several days.

The curing action consists of diffusion of the plasticizers into the casting powder, resulting in swelling and partial dissolution of the granules, thus consolidating the whole into a reasonably homogeneous mass. This should be tested by X-ray examination before firing.

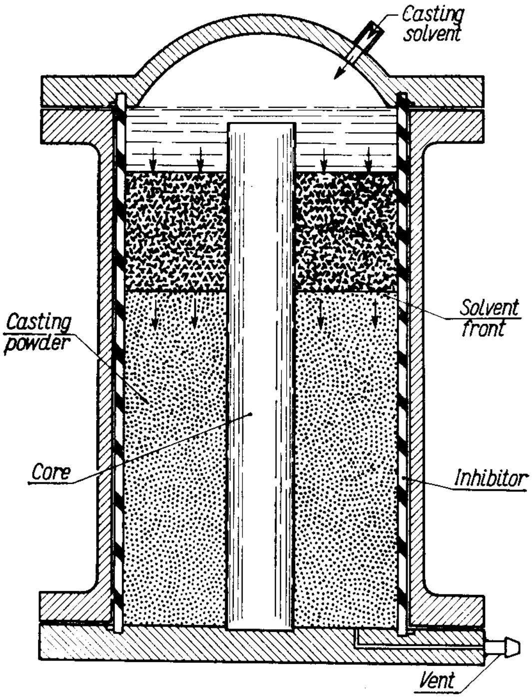


FIG. 270. Mould for casting a rocket powder grain [53].

The process has the great advantage that very large charges can be made this way. Grains up to 4 tons have been prepared.

Its main disadvantage consists in the fact that the process is slow.

Slurrying process. The main aim of this process is to avoid the necessity of making casting powder. Granular nitrocellulose is used instead, a fibrous form being inacceptable because of the high rate of swelling and solution which makes the gel insufficiently uniform.

Nitrocellulose granules, partially colloided, of sizes ranging from a few microns to a fraction of millimetres are suggested. The best known of the described methods was developed by the Hercules Powder Company [54]. It uses "densified" nitrocellulose originally developed for the lacquer industry, with an average particle size of 0.25 mm.

The basic idea of slurry casting consists of preparing the propellant in one simple mixing operation. The plasticizer is poured into a mixing pot and the solid ingredients, including the nitrocellulose, are added. The mixture is stirred for a few minutes (usually 15 min), poured into a mould or a rocket case and cured. Figure 271 gives a diagrammatic presentation of the main parts of the arrangement. When hoppers are charged and the mixers are operated, the personnel are withdrawn from the building and all is operated by remote control.

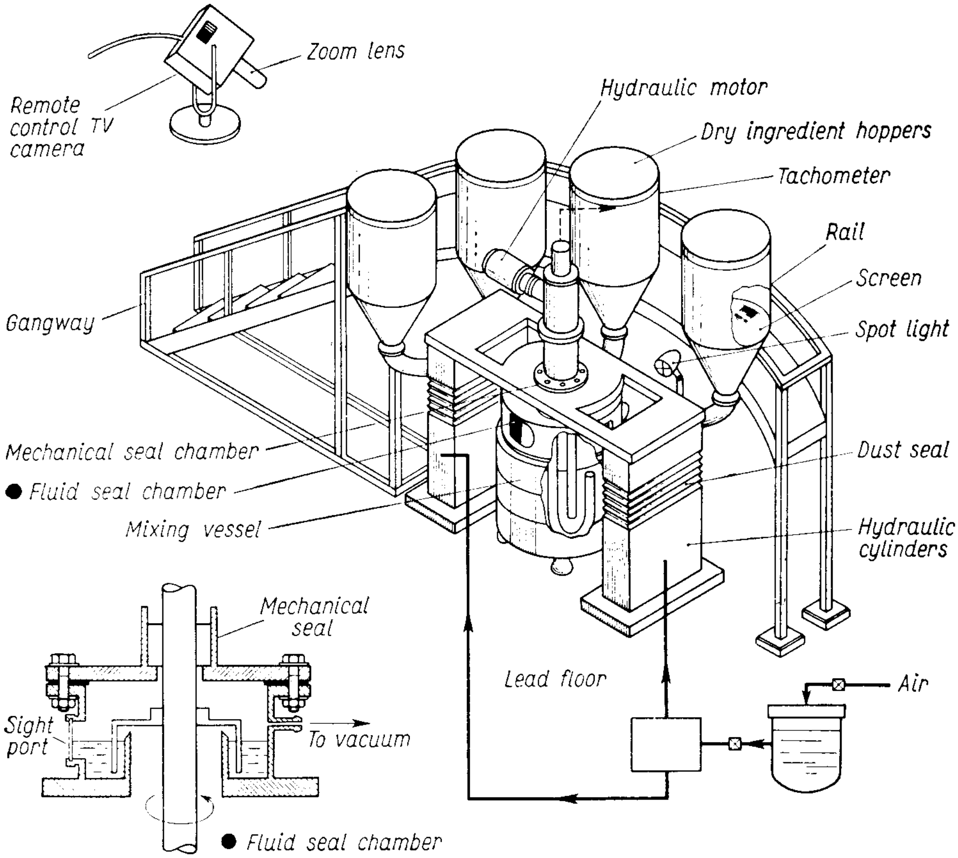


FIG. 271. Diagram of a slurry mixing arrangement at Hercules Powder Co., Bacchus Work [54].

This method can be used to make propellant charges of ammonium perchlorate, RDX, nitroglycerine and triacetine.

Physical properties of cast propellants

Steiberger [53] gives a number of diagrams which illustrate the change of mechanical properties: tensile strength, elongation and modulus of elasticity with nitrocellulose content (Figs. 272, 273 and 274). It is evident that nitrocellulose exerts a great influence on the properties of the system.

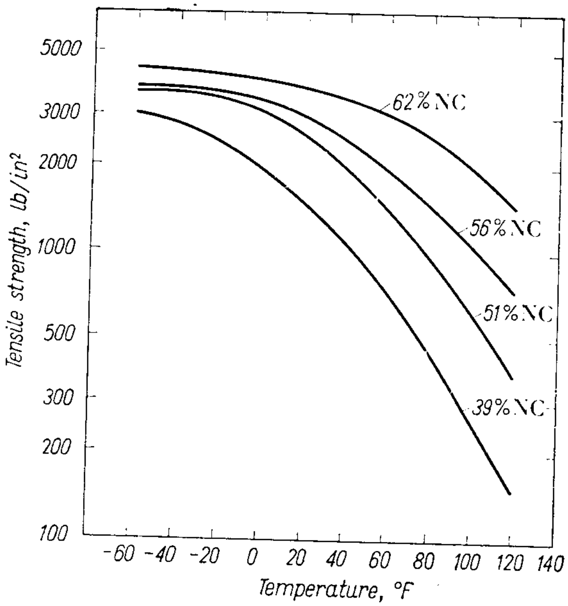


FIG. 272. Tensile strength of cast double base powder as a function of nitrocellulose content [53].

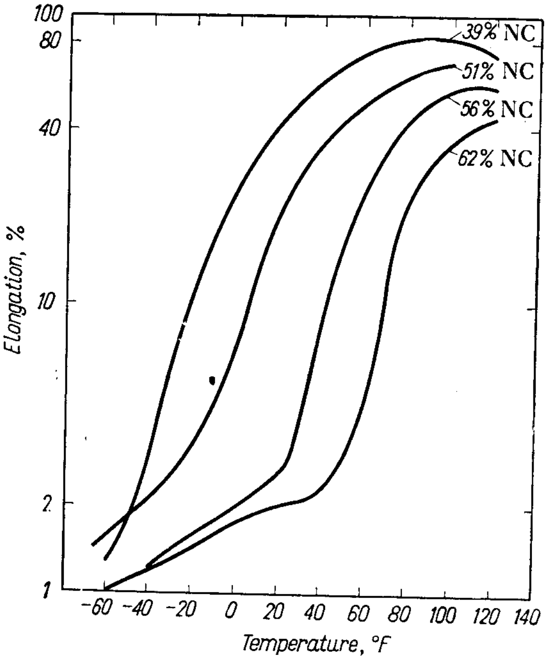


FIG. 273. Elongation of cast double base powder as a function of nitrocellulose content [53].

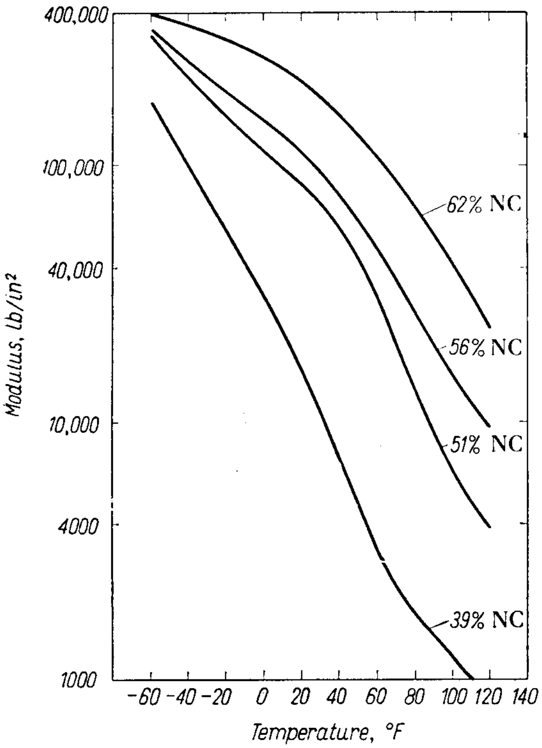
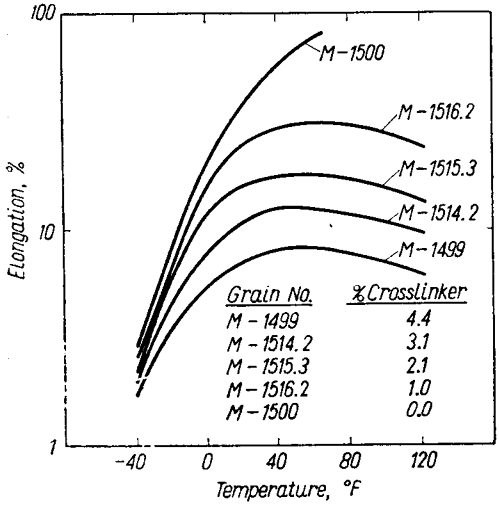


FIG. 274. Modulus of elasticity of cast double base powder as a function of nitrocellulose content [53].



Grain No.	% Crosslinker
M - 1499	4.4
M - 1514.2	3.1
M - 1515.3	2.1
M - 1516.2	1.0
M - 1500	0.0

FIG. 275. Influence of cross-linking of nitrocellulose on physical properties of cast charges [53].

Variations in the viscosity of nitrocellulose have only negligible effect on the physical properties of the propellants. On the contrary, cross-linking the nitrocellulose by adding polycarboxylic acid anhydrides, di-isocyanates or metallic salts may produce a profound influence as shown on Fig. 275. Elongation is significantly decreased especially at high temperature. The modulus is increased correspondingly, while the tensile strength is unaffected. A low degree of cross-linking may be particularly beneficial, decreasing deformation or flow at high temperature while leaving the low temperature properties unchanged.

According to Boynton and Schowengardt [54] the ultimate tensile strength of double base rocket charges should be 120 lb/in^2 and elongation *ca.* 30%. The propellant which gives these properties contains less binder than the maximum imposed by the casting powder process, but it can be produced by the slurry process.

Grosse [55] indicated that a typical NG double base powder on static testing should produce a maximum stress of 200 kg/cm^2. When the loading rate is increased to 0.23 sec and 0.15 sec until fracture, the stress is 360 and 442 kg/cm^2, respectively.

German cast propellants for rockets

Originally this powder (Giessling Pulver) consisted of:

TNT	50–52%
Nitrocellulose	28–30%
DGDN (Diethyleneglycol dinitrate)	17–18%
Centralite	0.5%
Diphenylamine	0.5%

The propellant was in the form of tube or plain grain, the latter having a diameter up to 50 cm and a length of about 100 cm.

Finely ground nitrocellulose of low viscosity was used. It was impregnated with DGDN under water in the usual way. After dehydration in a centrifuge to a moisture content of 18–22%, the blend was stirred into molten TNT. The vat was evacuated to evaporate the water and to produce a homogeneously gelatinized grain.

These propellants had rather poor physical properties produced by a high proportion of TNT: they were too brittle and unsuitable for spin stabilized rockets.

A ridged, block-shaped propellant with nine perforations was later used for 21 cm Nebelwerfer rockets. It was 12.5 cm in diameter, about 40 cm long and weighed about 6.5 kg. Its composition was:

Nitrocellulose	63%
Diethyleneglycol dinitrate	35%
Centralite	0.5%
Wax	0.2%
Graphite	1.2%

The disadvantages of smokeless powder as a rocket propellant, the difficulty in manufacturing very large charges and the high operating expenses led to a search for explosives based upon another principle: plastomers or elastomers with an oxygen carrier.

GENERAL SAFETY CONSIDERATIONS IN THE MANUFACTURE OF SMOKELESS POWDER

The safety aspects of the manufacture of smokeless powder have already been mentioned when describing manufacturing methods.

There are however some safety aspects which can be considered in general terms.

They can be classified into two main groups according to the origin of the danger:

(1) The use of combustible solvents;

(2) The sensitiveness of nitrocellulose or nitroglycerine and similar esters to thermal or mechanical factors or to electric discharge.

Solvents

A number of unexplained accidents were encountered in nitrocellulose powder factories associated with handling alcohol and particularly ether.

Thus, the simple opening of a valve closing a pipe bringing ether from a tank placed at a certain height may cause the ether to catch fire. Investigation of the origin of this phenomenon at the begining of the XXth century led to the conclusion that inflammation of the ether occurred when the static charge acquired by the solvent flowing along the pipe was discharged on contact with an earthed object.

The first experimental work on the production of static charges in liquid during its flow along insulated pipes were carried out at the end of the last century [59].

Freytag [60] collected the data on the subject obtained by various authors. Some of the figures referred to solvents used in the manufacture of powders are given in Table 196, according to Dolezalek [61].

An electric discharge from other sources can also ignite solvents.

The following accident was described in a cordite factory. A worker wearing rubber shoes wanted to clean his hands which were soiled with powder dough. He rubbed his hands together and held them towards a bucket filled with acetone standing on the concrete floor. A spark between the hands and the surface of the acetone ignited the latter.

In this instance, the worker's body became charged by the friction generated on rubbing his hands. According to Freytag [60] this kind of friction may charge the human body to a potential of 10,000–14,000 V.

Because of these accidents all tanks containing solvents and all pipes were earthed. This prevented further accidents.

Another danger associated with solvents has already been mentioned (pp. 601, 607), i.e. the explosibility of mixtures of combustible vapours with air.

These mixtures can be exploded by an electric discharge or by sparks from steel tools etc. Bronze is much safer in that respect and bronze tools should be used wherever possible. Beryllium bronze was strongly recommended at one time. However the toxic properties of beryllium limit its application.

The inflammability of gas mixtures were investigated by early workers, such as Davy, Bunsen and particularly the French School of Le Chatelier and M. Berthelot.

TABLE 196
POTENTIAL OF THE ELECTRIC CHARGE PRODUCED BY MOVING LIQUIDS ALONG METAL TUBES AT THE RATE OF 3 m/sec (DOLEZALEK [61])

Liquid	Metal	Potential (V)
Moist ether	Fe	3100
	Al	2500
	Cu	2000
	Brass	1200
	Pb	700
Dry ether	Fe	3100
	Al	2200
	Cu	3000
	Brass	1300
	Pb	2200

Investigation of the limits of flammability and of self-propagation of flame through a gaseous explosive medium became one of the main subjects of research on the combustion of gaseous mixtures.

Early results are collected in the monograph of Bone and Townend [62].

The investigations of White [63] were particularly important. He discovered that the limits of flammability depend not only on the chemical nature of the vapours but also on the direction of propagation of the flame. Figures for combustion in glass tubes 7.5 cm dia. are collected in Table 197.

TABLE 197

Vapour	Limits of propagation of flame in air	
	Upward (%)	Downward (%)
Methyl alcohol	7.05–36.5	7.45–26.5
Ethyl alcohol	3.56–18.0	3.75–11.5
Ethyl ether	1.71–48.0	1.85–6.40
Acetone	2.89–12.95	2.93–8.60
Benzene	1.41–7.45	1.46–5.55

In his later experiments White [64] found that the limits vary with the diameter of the tube, being wider in tubes of larger diameter.

Although considerable research has been carried out after these classic experiments, and a number of excellent monographs has appeared dealing with explosions of gas mixtures [65–68] little has been added to our knowledge of the limits of gas explosions.

Recent data given by Lewis and von Elbe [66] are collected in Table 198.

It is now well established that in large tanks and large compartments the limits of gas explosions are wider than in relatively narrow tubes.

Powder grains

Powder grains are sensitive to impact and friction. This is due to the sensitiveness of the main ingredients, nitrocellulose and nitroglycerine. The sensitiveness of these compounds was discussed in Vol. II.

It should be born in mind that the sensitiveness to impact and friction increases with temperature. Hence any handling of warm powder (e.g. immediately after drying) should be avoided.

Another danger is produced by the ease with which a powder (particularly warm one) can be charged with static electricity. This can be produced by the friction of warm air passing through the layer of powder grains in the course of drying. It can also be produced in the course of mixing and screening, and in the polishing drum.

The last operation should be considered particularly dangerous because of the high potential of the electric charge which can be created under prolonged friction at an elevated temperature. According to the literature [60] celluloid (which possesses properties very similar to nitrocellulose powder) can be charged to 40,000 V by simple friction.

All machinery for powder manufacture should therefore be carefully earthed.

TABLE 198

LIMITS OF VAPOUR–AIR MIXTURE INFLAMMABILITY [66]

Vapour	Limits of inflammability	
	Lower (%)	Upper (%)
Methyl alcohol	6.72	36.50
Ethyl alcohol	3.28	18.95
Amyl alcohol	1.19	–
Isoamyl alcohol	1.20	–
Diethyl ether	1.85	36.50
Acetone	2.55	12.80
Ethyl acetate	2.18	11.40

Buildings and their lay-out

In the manufacture of smokeless powder the primary danger lies not in explosion but in an outbreak of fire. For this reason the buildings usually have walls of a standard thickness, with the exception of those in which a large quantity of powder is accumulated. In drying houses, for instance, a blow-out construction, with one

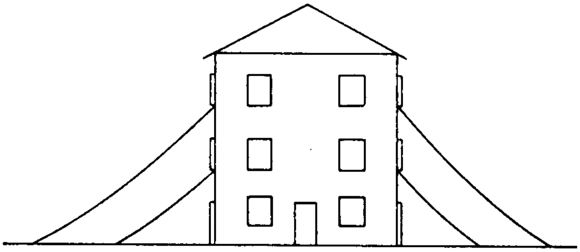


FIG. 276. A rescue ramp in a multistoreyed building.

FIG. 277. General view of a smokeless powder factory (Western Cartridge Company, Division of Olin Industries, Inc., East Alton, Illinois, U.S.A.).

light wall, may be adopted. Buildings in which there is a risk of explosions of a mixture of solvent vapours with air are of similar construction. All buildings are usually one storied, although sometimes there are installations requiring a multistoried design. These buildings are provided with emergency chutes (Fig. 276) for rapid exit from the upper floors. In some countries to permit the rapid escape of workers in case of fire, the regulations demand that no part of the premises should be further than 4.5 metres from a door. As in all factories or laboratories where explosives are dealt with, the doors open outwards.

Cement basins filled with water are placed by buildings in which particularly dangerous work is carried on. The water is heated in winter. If a workman's clothes should catch fire he can immediately jump into one of the basins. The water should be changed frequently and kept clean to prevent the risk of infection of burns.

Electric installations should be hermetically sealed and non-sparking. The bulbs should be enclosed in safety shields. Electric motors should not be installed in premises in which powder is manufactured.

The distance between the buildings should be large enough to prevent transmission of a fire from one building to another. A typical lay-out of a powder factory is given in Fig. 277.

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AUTHOR INDEX

Page numbers in parentheses denote references to Literature lists

SUBJECT INDEX

ERRATA TO VOLUMES I AND II

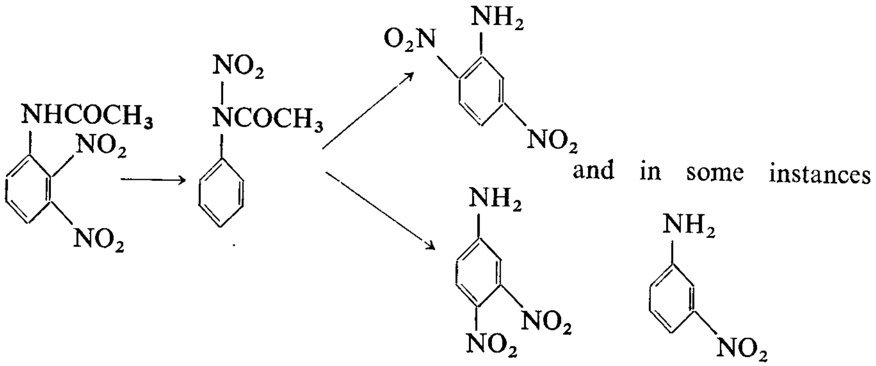
The author regrets that a few errors occurred in Volumes I and II.

Volume I

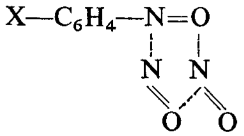
p. 15, eqn. (20) should read:

$$N_2O_4+3H_2SO_4 \rightarrow NO_2^{\oplus}+H_3O^{\oplus}+3HSO_4^{\ominus}+NO^{\oplus}$$

p. 41: the formulas should be replaced by the following:



p. 77: the bottom formula should be replaced by the following:



p. 82, lines 11–12 should read:

Wieland [13] of the formation of fulminic acid ...

p. 97, line 7 from the bottom should read:

According to Wieland [79, 79a], the reaction ...

p. 97, last line of the page should read:

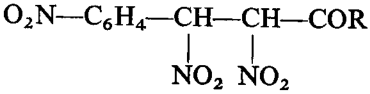
1,4-diphenylbutadiene is converted to 1,4-diphenyl-1,4-dinitrobutylene-2 (IX) [79b]:

p. 98, line 8 should read:

Subsequently Wieland [79c] found ...

p. 98, paragraph (3) should read:

(3). The phenyl group when treated with N_2O_4 underwent nitration:



$$O_2N—C_6H_4—\underset{NO_2}{CH}—\underset{NO_2}{CH}—COR$$

XVI

In such a way ...

p. 99, line 13 from the bottom should read:
Shechter and Conrad [49] ...

p. 109, line 13 should read:
On the basis of eqns. (44) and (45) ...

p. 133:
reference 12a should be corrected to 13, reference 13 should be corrected to 14, reference 14, H. Wieland and L. Semper, *Ber.* **39**, 2522 (1906) should be cancelled.

p. 135, reference 79 should read:
H. Wieland and E. Blümich, *Ann.* **424**, 75 (1921).
New references should be inserted:
79a. H. Wieland, F. Rahm and F. Reindel, *Ber.* **54**, 1770 (1921).
79b. H. Wieland and H. Stenzel, *Ber.* **40**, 4825 (1907); *Ann.* **360**, 299 (1908).
79c. H. Wieland, *Ann.* **328**, 154 (1903).

p. 176, lines 6–4 from the bottom should read:

	CCl_4	CCl_3CN
asymmetric vibr.	1506 cm^{-1}	1496 cm^{-1}
symmetric vibr.	1332 cm^{-1}	1320 cm^{-1}

p. 179, line 14 from the bottom should read:
Holder and Kline [38], Schmidt, Brown and D. Williams [40] ...

p. 618 (Author Index)
Schechter H. should be cancelled and on p. 619 items 92, 99 (134, 600) should be added to Shechter H.

Volume II

p. 165, lines 10–14 should read:

The boiling point of isopropyl nitrate is 101–102°C. It was originally believed that the substance can only be obtained from isopropyl iodide and silver nitrate [1]. Direct nitration is difficult due to oxidation at the carbon atom carrying the secondary hydroxyl group.

However a process for the continuous nitration of isopropyl alcohol in the presence of urea has been described in Imperial Chemical Industries patents [20]. Isopropyl alcohol and urea was introduced into nitric acid (over 40% HNO_3) at its boiling temperature and current of air removed unstable products. According to Desseigne [21] the method gave *ca.* 80% yield. He used nitric acid of over 50% HNO_3 at 108–110°C.

Isopropyl nitrate is becoming important as an engine starter fuel [22].

p. 165, new references should be inserted:

20. W. G. Allen and T. J. Tobin (to Imperial Chemical Industries Ltd.), Brit. Pat. 696489 (1953); see also Brit. Pats. 749734 and 749844 (1956).

21. G. Desseigne, *Mém. poudres* **37**, 97 (1955).
22. *Engineer*, London **200**, 269 (1955).

p. 180, lines 16–15 from the bottom should read:

This is the result of the symmetrical structure of PETN. PETN is completely ...

p. 429, last line on the page should read:

(a) in weight %, (b) in mole %.

Chemistry and Technology of Explosives

VOLUME 4

by

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PREFACE

Since 1964–67 when the previous three volumes of *Chemistry and Technology of Explosives* appeared, considerable progress has been made in the field of the science of explosives – the science in a broader sense which includes not only the theoretical knowledge of explosives but also their manufacture, problems of safety in the manufacturing processes and handling.

As in the previous three volumes the author limited his text to *chemistry* and *technology* of explosives. The problems of the theory of detonation and analytical ones are not discussed here and are only touched as much as it was needed to understand the properties of explosives. Thus in the 'Introduction' chapter a description is given of the relationship between the chemical structure and the parameters of the explosive properties, as this refers to the structural problems of organic substances possessing such properties.

However, the author wishes to point out that he is not giving the full review of the existing progress for some particular reasons – a general philosophy for Peace in the World and some personal reason as a former POW. He is completely against the use of explosives for military purposes and has dedicated his book to peaceful applications.

The author wishes to quote from the book by S. Fordham, *High Explosives and Propellants* (Pergamon Press): "The explosives technologist, who has usually seen and perhaps even experienced the effects of explosives is the last to want war or for his products to be used for warlike purposes. It is no accident that Nobel who founded the modern explosives industry also founded the Peace Prize associated with his name".

Once more the author would like to repeat what he said in the preface to his book in 1964–67: ". . . more explosives have been used in peace than in war. Modern civilization and modern progress would be impossible without explosives." Nevertheless, following this line of thought no mention is made in this book on shells, projectiles, fuses etc., or other parts of military weapons. However it is still difficult to distinguish between military and peaceful application of military weapons. Here are a few examples:

> Gas burning from a newly drilled oil pit in Karlin in Northern Poland in 1981 was successfully extinguished with howitzer shells; the danger of an avalanche of snow can be prevented by firing special guns with shells filled

with high explosives; firing rockets with explosives loaded with silver iodide is in use for promoting rain (Vol. III, p. 324). Silver iodide dispersed in higher layers of atmosphere by anti-aircraft rounds is in use in the U.S.S.R., according to "*TWA Ambassador*" (p. 37, May 1981).

A conscientious attempt has been made to cover the available literature on the subject, however not every paper and report has been mentioned as it was considered to be of greater value to couple a reasonably comprehensive coverage with a critical assessment of the available information and not to describe every paper. The excellent *Encyclopedia of Explosives* and related items produced by (the late) B. T. Fedoroff, O. E. Sheffield and S. M. Kaye should be consulted for the whole literature on explosives.

Also excellent reviews have appeared in Volumes of *Annual Reviews of Applied Chemistry*, Issued by Society of Chemical Industry, London, between 1950 and 1975, written by J. Taylor, E. Whitworth, W. E. Batty, I. Dunstan and a number of authors from I.C.I. Ltd.

The author apologises to the authors for any important work overlooked in the present volume.

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INTRODUCTION

(Vol. I, p. 1)

NOVEL INFORMATION ON EXPLOSIVE PROPERTIES

It has been shown that some non-explosive organic and inorganic substances can explode when subjected to the action of very high pressure. This was recorded for the first time by Bridgman [1]. Teller [2] tried to find an explanation in terms of the activation energy which should be lowered with increased pressure.

More recently Malmrud and Claesson [3] examined the behaviour of a number of compounds at a pressure of 35,000 kg/cm^2. They found that some acids, such as oxalic acid hydrate malonic, tartaric and citric acid, and other common substances such as aspirin, sucrose, polystyrene and calcium chloride, exploded when high pressure was released. A number of substances (e.g. succinic, glutaric, adipic, maleic, fumaric, phthalic acids) did not show this behaviour. According to the authors they did not explode because they required higher pressure.

The explanation given by Malmrud and Claesson is similar to that given by Bridgman. They believe that over a critical pressure, which depends on the coefficient of friction, plastic flow stress and disc thickness, the sample becomes mechanically unstable when pressure is released and is violently expelled.

Polystyrene was simultaneously carbonized which was probably caused by an increased temperature due to heating by friction.

The author of the present book is inclined to rationalize that under very high pressure considerable deformation of the crystal-net can occur and the atoms are approaching distances which produce their repulsion.

The problem arises as to whether explosives can be brought to explosion by high static pressure. So far the only published paper [4] indicated that nitromethane, perdeuteronitromethane and a few dinitroalkanes cannot explode at static pressure up to 50 kbar.

It is known that acetylenic bond possesses endothermic characteristics (Vol. III, p. 227) and it is interesting to point out that a number of acetylenic compounds were found in nature as early as 1889 [5] and 1892 [6]. Currently important are the works of E. R. H. Jones [7] and Bohlmann [8] who isolated and established the structure of numerous naturally occurring polyacetylenes and confirmed their structure by synthesis. Most of the polyacetylenes possess explosive properties.

With the advent of the development of the hydrodynamic theory of detonation, based on the concepts of Chapman [17] and Jouguet [18], it was possible to calculate the velocity of detonation. The pioneering work was done by A. Schmidt [19] and his method was improved by a number of authors. Critical reviews of the methods have been described in a number of monographs: Cook [20], Zeldovich and Kompaneets [21], Andreev and Belyaev [22], Johansson and Persson [23], Fickett and Davis [24].

The problems connected with the hydrodynamic theory of detonation are outside the scope of this book and only papers dealing with the correlation between the structure of explosives and their power will be given here. Originally the papers were directed to correlate the oxygen balance (OB) with the 'explosive power'. This was initiated by Lothrop and Hendrick (Vol. I, p. 2) and met with a well founded criticism (A. Schmidt, Vol. I, p. 2). The criticism was based on the fact that oxygen in nitro groups has a different thermochemical function than that of carboxylic and hydroxylic groups. The discussion aroused much interest in the attempt to introduce a differentiation of oxygen atoms.

The first of the kind were papers by Martin and Yallop [25a, b]. They proposed a 'corrected OB' calculated as follows:

$$\mathrm{OB} = \Omega = (z - 2x - y/2)\,100/n \pm 100\,w/n, \tag{2}$$

where: x, y, z are the respective numbers of atoms of carbon, hydrogen and oxygen in the molecule,

n – the number of atoms in the molecule,
w – summation of O atoms according to their linkages, thus:
$w = 0$ for oxygen atoms in NO_2 groups in *C*-nitro, *O*-nitro and *N*-nitro compounds,
$w = 1$ for oxygen $C{-}O{-}N$ in *O*-nitro compounds,
$w = 1.8$ for oxygen $C{=}O$ in carboxylic groups,
$w = 2.2$ for oxygen in phenols and alcohols. ± Is taken: + if the first term is +, and − if the first term is −.

The rate of detonation D was calculated from semiempirical equation (3) [25a].

$$D_{\mathrm{calc}} = 2509 + 13.25\,\Omega + 3793\,\rho + 12.81\,\rho\,\Omega \tag{3}$$

where: ρ is the density of the explosive (g/cm^3).

In another equation they introduced the value H cal/g of the heat of formation [25b].

The work of Martin and Yallop was met with criticism. Thus Price [26] concluded that OB cannot determine the heat of explosion or detonation and the rate of detonation cannot be a linear function of OB. Roth [27] pointed out that the correlation between Martin and Yallop's 'corrected OB' is successful only for a restricted group of similar explosives. The correlation breaks down for explosives with a positive OB. He concluded that "OB is a concept that can provide useful qualitative information. It should not be used for quantitative correlation except . . . for chemically similar explosives."

A number of authors: Głowiak [28], Mustafa and Zahran [29] and Pagowski [30] tried to extend the method of Martin and Yallop. In particular Pagowski's work merits attention. He attempted to correct equation (2) of Martin and Yallop suggesting the 'effective oxygen balance' B:

$$B = (z - 2x - \frac{y}{2} \pm P)\, 100/n. \tag{4}$$

P is the correction accounting for energy gains or losses from the actual chemical structure of the compound while taking into account different oxygen atoms: those which are already bonded with carbon ($C{=}O$, $C{-}O{-}N$) and those (NO_2) which are free to develop the exothermic reaction of oxidation.

For the rate of detonation Pagowski gave a semi-empirical equation (5):

$$D = 8600 \pm 32.7\, B \tag{5}$$

at $\rho = 1.6$.

According to Pagowski the calculated values of D fit well to experiments – Table 1.

TABLE 1. Experimental and calculated values of D

Explosive	D_{exp}	D_{calc}
TNT	6980	6345
Tetryl	7450	7505
EDNA (III, 18)	7920	7900
Cyclonite (RDX)	8200	8185
PETN	7820	7880

Later a remarkable semi-empirical method of calculating the detonation pressure and velocity was given by Kamlet and co-workers [31].

Kamlet and Jacobs [31a] have shown that the detonation pressure and velocity of $C{-}H{-}N{-}O$ explosives can be calculated at their initial densities above 1 g/cm³ while using the following simple empirical equations:

$$P = 15.58\, \varphi \rho^2 \tag{6}$$

$$D = 1.029\, \varphi\, (1 + 1.30\, \rho_0)^2 \tag{7}$$

$$\varphi = N M^{1/2} Q^{1/2}, \tag{8}$$

where:

P is the pressure in kbar,
D the detonation velocity in m/s,
N the number of moles of gaseous detonation products per gram of the explosive,
M the average weight of these gases in g/mol,
Q the chemical energy of the detonation reaction (enthalpy $-\Delta H_0$/pg),
$\rho =$ the initial density.

A few examples of the calculation of the velocity of detonation [25d] which give an average error of *ca.* 1% only, are given in Table 2.

TABLE 2. Experimental and calculated rates of detonation

Explosive		D_{exp}	D_{calc}	% deviation $(D_{calc} - D_{exp})$
TNT	1.64	6950	6959	+0.1
	1.445	6484	6395	−1.4
	1.30	6040	5977	−1.0
	1.00	5100	5111	+0.2
Picric acid	1.71	7350	7360	+0.1
	1.25	6070	6000	−1.2
Ammonium picrate	1.55	6850	6798	−0.8
Tetryl	1.70	7560	7681	+1.6
EDNA (III, 18)	1.562	7750	7789	+0.5
RDX (Cyclonite)	1.80	8754	8780	+0.3
	1.60	8060	8098	+0.5
	1.20	6750	6731	−0.3
HMX	1.90	9100	9117	+0.2
	1.84	9124	8913	−2.3
	1.77	8500	8671	+2.0
PETN	1.77	8600	8695	+1.1

A few examples of the calculation of Chapman-Jouguet pressure are given below – Table 3 [31c]. The Kamlet method is very useful for the rapid calculation of most important constants characterizing high explosives.

Other remarkable methods of calculating parameters of detonation have been developed by Pepekin, Lebedev and associates [32, 33]. They worked out [32] a method of calculation of heat of detonation when two factors are known: the bulk formula of the explosive and the enthalpy of formation ΔH_f^0. The following are semi-empirical equations for an explosive $C_aH_bO_cN$:

$$Q_{max} = \frac{28.9\, b + 470\, (c - b/2) + \Delta H_f^0}{MW} \tag{9}$$

TABLE 3. Calculation of pressure developed by detonation

Explosive		P_{exp} kbar	P_{calc}	% deviation ($P_{calc}-P_{exp}$)
TNT	1.62	212	197.8	−6.7
	1.30	123	127.4	+3.6
	1.14	94	97.9	+4.1
RDX	1.80	347	342.5	−1.3
	1.63	283.7	280.8	−1.0
	1.40	213	207.1	−2.8
	1.20	152	152.2	+0.1
HMX	1.90	393	380.9	−3.1
PETN	1.77	350	332.1	−5.1
	1.67	300	295.7	1.4
Tetryl	1.70	263	252.8	−3.9

where:

Q_{max} is the maximum possible heat of detonation in kcal/kg,
MW is the molecular weight of the compound.

The heat of detonation at the density ρ g/cm^3 is Q_ρ, and equation (10) makes it possible to calculate:

$$Q_\rho = Q_{max}\ [1-(0.528-0.165\rho)(1.4-\alpha)] \tag{10}$$

where: α is 'oxygen coefficient' calculated from equation (11):

$$\alpha = \frac{c}{2a + 2b/2} \tag{11}$$

When

$$\alpha \geqslant 1.4,\ Q_\rho = Q_{max}.$$

Another more complicated formula was worked out for explosives with a high content of hydrogen and low value of α, for example $\alpha < 0.4$.

The calculated figure for some common explosives are given in Table 4.

The average deviation is 2.3% and at $\rho > 1.0$ it is 1.8%.

In another paper Pepekin, Kuznetsov and Lebedev [33] worked out more complicated equations which made it possible to calculate the rate of detonation of explosives with a bulk formula $C_a\ H_b\ O_c\ N_d\ F_e$ at a given density ρ_1 g/cm^3.

The following are equations given by these authors:

$$K_{BB}\ \frac{0.135\,a\,\frac{a}{a+b} + 21\,b\,\frac{b}{a+b} + 0.4\,(c+d+e)}{\text{MW}} \tag{12}$$

TABLE 4. Calculated and experimental data for the heat of detonation

Compound		Q_{calc}	Q_{exp} kcal/kg	Q_{max}
TNT	1.00	830	860	1288
	1.60	1000	1030	
Picric acid	0.90	880	830	1282
	1.70	1030	1010	
Tetryl	0.98	980	960	1431
	1.69	1150	1160	
Nitroguanidine	0.80	970	980	1102
	1.58	1030	1060	
Cyclonite (RDX)	1.10	1160	1190	1481
	1.70	1280	1290	
Octogene	1.30	1200	1210	1477
	1.80	1300	1300	
PETN	0.90	1260	1300	1526
	1.70	1340	1350	

and

$$n = K_{BB}\ \rho_1^{1/2} \tag{13}$$

where:

K_{BB} – the coefficient of the composition of the compound,
n – the number of molecules in the products of the detonation,
ρ_1 – the density of the explosive.

The rate of detonation D m/s can be calculated from formula (14)

$$D^2 = 8.0\,(Q + R) \tag{14}$$

where Q is the heat of detonation in kcal/kg calculated from formula (10),

$$R = \left(\frac{n}{n_z}\right)^3 \rho_1{}^2 \tag{15}$$

where n_z is the number of molecules in the products of detonation.

Pressure is calculated from equation (16):

$$P = \rho_1\ D^2\ (x_1 - 1)/x_1 \tag{16}$$

where x_1 is the experimental degree of compression in the front of the detonation wave where density is ρ:

$$x_1 = \frac{\rho}{\rho_1}$$

The calculated and experimental data for D and P are collected in Table 5. Mean deviation is *ca.* 1.4%.

TABLE 5. Calculated and experimental data for D and P

Compound	ρ_1	Q	K_{BB}	x_1	D_{calc} m/s	D_{exp} m/s	P_{calc} kbar	P_{exp} kbar
TNT	1.64	1010	0.0202	1.38	6900	6940	215	220
Picric acid	1.80	1173	0.0207	1.37	7600	7700	297	
Tetryl	1.70	1150	0.0215	1.37	7480	7560	257	263
Nitroguanidine	1.70	820	0.0298	1.31	8140	8200	266	
Cyclonite (RDX)	1.802	1300	0.0260	1.34	8740	8800	349	347
Octogene (HMX)	1.903	1320	0.0260	1.33	9100	9150	390	393
PETN	1.77	1375	0.0243	1.36	8500	8370	338	350
TACOT	1.85	1044	0.0201	1.37	7310	7250	267	263

Recently Bernard [34] worked out a different formula for the rate of detonation based on his kinetic theory of detonation [35]. His equation for the correlation of the rate of detonation and the density ρ_1 in the shock wave front is as follows:

$$D_{\max} = \frac{\rho_1}{\rho_{\max}} \frac{k\,T_o}{h}\, d. \tag{17}$$

$D_{\max}$	is the experimental rate of detonation at an infinite diameter and maximum density $\rho_{\max}$,
k	the Boltzman constant,
h	the Planck constant,
T_o	the initial temperature of the explosive,
d	the mean molecular diameter.

Bernard applied his equation to a number of nitrate esters at room temperature.

Some of his results are shown in Table 6.

TABLE 6. Density in front of the shock wave and experimental rate of detonation

Substance	$D_{\max}$ m/s	$\rho_{\max}$	ρ_1
Nitroglycerine	7700	1.6	2.57
Ethylene glycol dinitrate	8000	1.49	2.78
PETN	8600	1.77	2.94
Hexanitrate of dipentaerythrit	7450	1.63	1.93
Mannitol hexanitrate	8260	1.73	2.43
Methyl nitrate	8000	1.20	2.61

A plot of log $D_{\max}$ against log ρ_1 gives a straight line.

Bernard and co-workers [51] extended his calculations to the rate of detonation of *C*-nitro, *O*-nitro and *N*-nitro compounds by using two equations:

$$D_{\infty}^{\rho_{\max}} = \frac{\rho_1}{\rho_{\max}} \frac{k\,T_o}{h} \left(\frac{6\,M}{\pi\,N\,\rho_{\max}}\right)^{1/3} \tag{17a}$$

and

$$D^2 = C_o\,(M/n) \tag{17b}$$

where:

h	is the Planck constant,
M	denotes the mean molecular mass of the products,
N	Avogadro number,
C_o	concentration of molecules on the surface of the explosive,
n	number of the nitro groups in the molecule,
a	exponent varying from 1.5 to 2.

A characteristic feature of the calculation by Bernard is that he does not use the enthalpy of detonation but considers that the density ρ_1 in the shock front, that is, the compression by the shock wave is decisive for the rate of detonation. The groups 'explosofores', such as NO_2, N_3 are particularly strongly compressed. Thus $\rho_1/\rho_{\max}$ for dinitrobenzene is 1.40 and for picric acid is 1.88. For azides it is approaching 1.7.

Two more papers should be mentioned: that by Aizenshtadt [52] and one recently given by Rothstein and Petersen [53]. The latter authors like Bernard [34, 51] point out that a simple empirical linear relationship exists between the detonation velocity at theoretical maximum density and a factor *F* which solely depends upon chemical composition and structure.

Thus:

$$D' = D_o + (\rho_{TM} - \rho_o) \times 3.0, \tag{18}$$

where

D'	is calculated rate of detonation,
D_o	experimental rate of detonation,
ρ_{TM}	theoretical maximum density,
ρ_o	experimental density.

Factor *F* can be calculated:

$$F = 100 \times \left[\frac{n(\mathrm{O}) + n(\mathrm{N}) - \frac{n(\mathrm{H})}{2n(\mathrm{O})} + \frac{\mathrm{A}}{3} - \frac{n(B)}{1.75} - \frac{n(D)}{4} - \frac{n(E)}{5}}{\mathrm{MW}}\right] - G \tag{19}$$

where $G = 0.4$ for liquid and $G = 0$ for solid explosives. $A = 1$ if the compound is aromatic, otherwise $A = 0$ and MW = molecular weight.

The other expressions:

$n(\mathrm{O})$ = number of oxygen atoms,
$n(\mathrm{N})$ = number of nitrogen atoms,
$n(\mathrm{H})$ = number of hydrogen atoms,
$n(B)$ = number of oxygen atoms in excess of those already available to form CO_2 and H_2O,
$n(C)$ = number of oxygen atoms double bonded to carbon as in $C{=}O$,
$n(D)$ = number of oxygen atoms singly bonded directly to carbon in $C{-}O{-}R$ linkage where $R = \mathrm{H}, \mathrm{NH_4}$ or C.
$n(E)$ = number of nitrate groups either as nitrate-esters or nitrate salts.

The relation between D' and F can be expressed by the linear equation

$$D' = \frac{F - 0.26}{0.55}. \tag{20}$$

The deviations between the calculated and experimental values in 95% of explosives is of the order of 5%. Some of the results are given in Table 7.

TABLE 7. Calculated and experimental data of D. Calculated values of the factor *F*

Substance	*TM*	D (calc)	*F*	D_0 (exp)	Deviation %
TNT	1.65	6960	3.93	6670	−4
TNB	1.64	7270	4.26	7270	0
Picric acid	1.76	7500	4.31	7360	−2
HNB	2.0	9500	5.27	9110	−4
Tetryl	1.73	7910	4.54	7780	−2
Nitroguanidine	1.72	8160	4.81	8270	+1
EDNA	1.71	8230	4.83	8310	+1
Cyclonite (RDX)	1.83	8850	5.18	8950	+1
Octogene (HMX)	1.90	9140	5.24	9050	−1
Nitroglycerine	1.60	7700	4.35	7440	−3
DGDN	1.38	6760	3.97	6750	0
PETN	1.77	8290	4.71	8090	−2
DINA	1.67	8000	4.63	7950	−1
TACOT	1.85	7250	4.14	7050	−3

It appears that the calculation of important parameters of detonation is still in progress and further improvements with two basic methods:

(1) taking into account the enthalpy of detonation,
(2) taking into consideration the kinetic theory of detonation.

The problems are tackled in a few monographs: the earlier ones: [54–60] and more recent by Fickett and Davis [24] and Mader [61].

A more detailed discussion of the problems of the theory of high explosives are outside the scope of the present book.

SENSITIVITY OF EXPLOSIVES TO IMPACT

The experimental finding of Wöhler and Wenzelberg (Vol. I, p. 3) gives a general estimation of the sensitivity of nitroaromatic explosives to impact as a function of the character and number of substituents to the benzene ring. On the other hand T. Urbański [36] expressed the view in 1933 that the sensitivity of solid explosives to impact is a complicated function of a few factors, among which the most important are:

(a) sensitivity to high temperature,
(b) sensitivity to friction.

This was based on two observed factors:

(1) similarity of the curves of the sensitivity of mixtures of explosives to impact and sensitivity to temperature,
(2) the shape of the curves of sensitivity of solid mixtures to impact indicates that the sensitivity of mixtures is greater than that of the components due to the friction of particles of two different solid substances. In turn, the friction can obviously generate a high temperature (Bowden and Tabor [37]).

The related curves are given in Vol. III, pp. 250, 251, 262 and reproduced now in Fig. 1. Both curves (*T*-sensitivity to elevated temperature, *M*-sensitivity to impact) are clearly composed of two parts: I and II. (Curve *T* was established by determining the temperature of ignition of the samples of 5 g in test tubes placed in wood alloy at 150°C by increasing the temperature of the alloy at the rate of 10°C/min. The sensitivity to impact is expressed in ordinates as the work in kg/cm² produces 50% of explosion). The sensitivity to impact is manifest by a shape where fraction I of the curve *M* indicates the increase of the sensitivity of compound *A* by adding a less sensitive compound *B*. This is rationalized in terms of the friction between two foreign solid particles.

The sensitivity of mixtures to impact through friction is particularly noticeable in examples of mixtures of TNT with hard crystals of ammonium nitrate (Fig. 70, Vol. III, p. 262).

Papers have been published on the increase of sensitivity to impact by adding gritty compound, Ubbelohde *et al.* [38] and recently Scullion and McCormack [39].

Bowden and Yoffe [40] have developed the well known concept of 'hot spots' and that the initiation of explosion stems from 'hot spots' created by thermal factors and crystal hardness and shape. Small bubbles of air included in

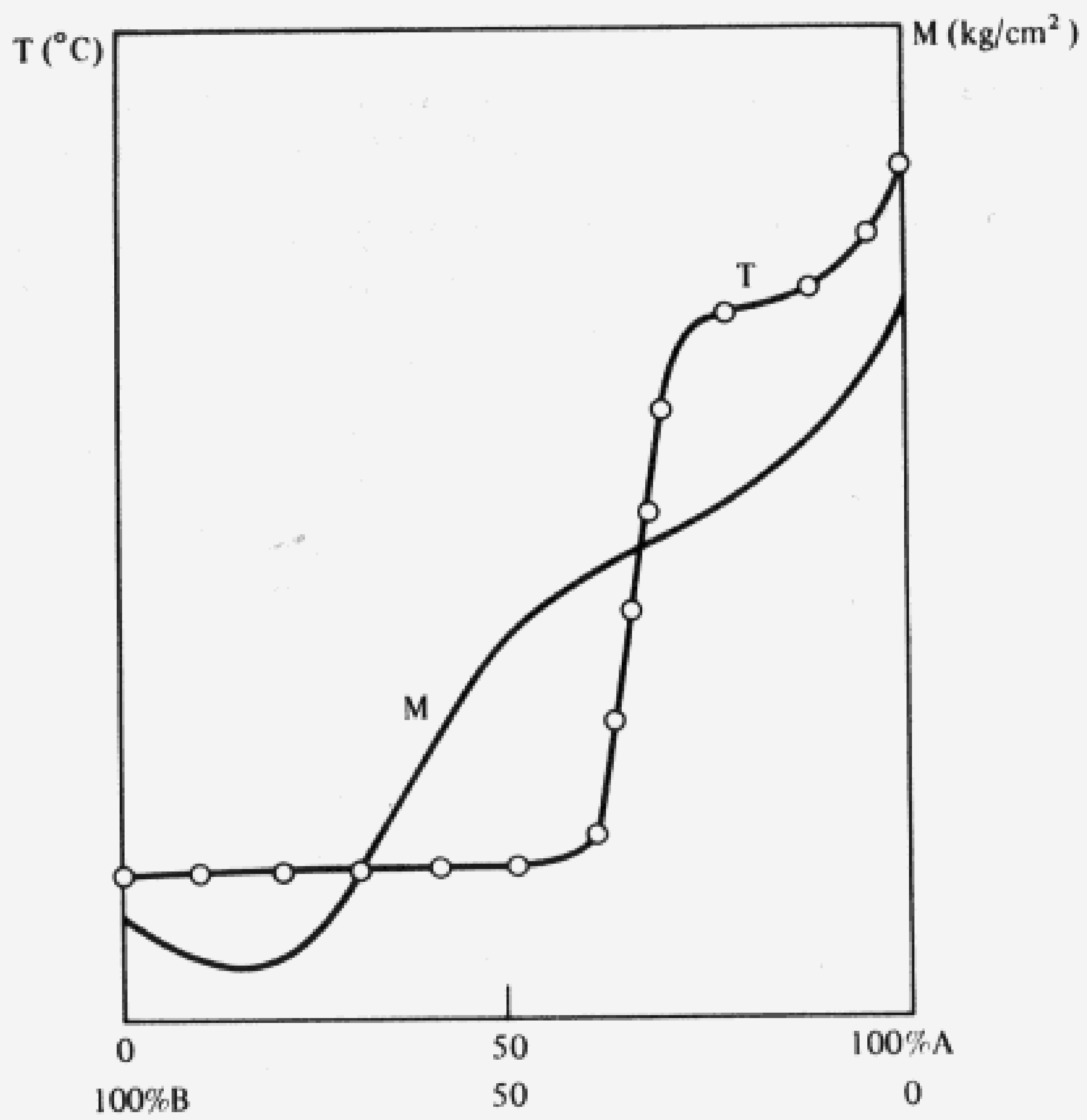

FIG. 1. Sensitivity to impact (*M*) and initiation temperatures (*T*) of mixtures of two explosive components: *A* and *B*. (According to T. Urbański [36]).

liquid explosives (e.g. nitroglycerine) also increase the sensitivity to impact through the adiabatic compression of air and a rapid increase in temperature. See also Lovecy [41].

Kamlet [42, 43] also agrees with the thermal character of the sensitivity to impact. He developed an ingenious method of calculating the sensitivity of explosives to impact. For similar explosives he found a linear relationship between logarithmic 50% impact heights and values of oxygen balance OB_{100}. The latter value is calculated for C—H—N—O explosives from the equation:

$$OB_{100} = \frac{100(2n_O - n_H - 2n_C - 2n_{COO})}{MW} \qquad (21)$$

where n_O, n_H, n_C represent the number of atoms of the respective elements in the molecule and n_{COO} is the number of carboxylic groups.

Fifty per cent impact heights on a logarithmic scale give a straight line.

A few figures are given (Table 8) for typical nitroaromatic compounds [42] and nitramines [43].

TABLE 8. Sensitivity of explosives to impact

Explosive	OB_{100}	*h* 50% (cm)
TNT	−3.08	160
TNB	−1.46	100
Picric acid	−0.44	87
Stiphnic acid	+0.41	43
RDX (Cyclonite)	0	24
HMX	0	26
EDNA	−1.33	34

Cherville and associates [44] have examined a number of explosives in a mass spectrograph. Particularly important and reproducible were results at 77K. The formation of NO_2 was readily established in the spectrograms. The authors introduced a concept of the radiochemical yield G_{NO_2} of the formation of NO_2. A considerable difference exists between the values of G_{NO_2} of nitramines and nitroaromatics. They correlated the values of G_{NO_2} with those of the sensitivity of explosives to impact, friction and high temperature (temperature of initiation t_i at the rate of heating 5°C/min): Table 9.

TABLE 9. Sensitivity of explosives to impact and friction

Explosive	Sensitivity to impact kgm	Sensitivity to friction kgf	Difference between t_i and temp. of melting point t_m $t_i - t_m$	G_{NO_2}
PETN	0.31	4.5	79	3.8
RDX	0.45	11.5	56	0.9
Octogene	0.52	10	50	0.8
Tetryl	1.1	27% at 36 kgf	111	0.006
Picric	3	7% at 36 kgf	178	0.001
TNT	48% at 5 kgm	29.5	209	0.001
Nitroguanidine	no explosion	no explosion	no inflammation	0

A very important contribution to the knowledge of the sensitivity of explosives to impact has been given by Delpuech and Cherville [45]. They came to the conclusion that the basic criterion of sensitivity of explosives lies in the distribution of electrons in their ground state and the comparison with that in the excited state. With the advent of quantum mechanical methods, and particularly that of I.N.D.O. [46] they were able to calculate the distribution of electrons in explosives, thus introducing a new and original criterion of sensitivity of explosives. For quantitative estimation they introduced a parameter $\Delta C^\circ/l$, where

ΔC° is the dissymmetry of the distribution of electrons in the ground state,
l the length of the bond $C-NO_2$, $N-NO_2$ or $O-NO_2$.

The following are a few figures thus calculated (Table 10). Higher sensitivity of explosives is manifested by a higher $\Delta C^{\circ}/l$. The data for excited state $\Delta C^{\times}/l$ were calculated with the method C.N.D.O-S/C.I. [47].

TABLE 10. Sensitivity of explosives to impact

Explosive	Bond*	C°	$\frac{C^{\circ}}{l}$	$\frac{C^{\times}}{l}$
DNB	$C(1)-NO_2$	0.539	0.363	0.308
TNB	$C(5)-NO_2$	0.575	0.391	0.303
RDX	$N(1)-NO_2$	1.044	0.764	0.343
HMX (δ)	$N(1)-NO_2$	0.937	0.673	0.345
EDNA	$N-NO_2$	0.880	0.676	0.499
Tetryl	$N-NO_2$	0.841	0.624	0.478
PETN	$O-NO_2$	0.878	0.645	0.417

* The numbers in brackets indicate the position of atoms of C and N in the molecule as given in their formulae based on crystallographic analysis (Vol. I, 181; II, 372, 385).

The relative change δ from ΔC° to $\Delta C^{\times}$ can be expressed by equation (22)

$$\delta = \frac{100\,(\Delta C^{\times} - \Delta C^{\circ})}{\Delta C^{\circ}} \tag{22}$$

Delpuech and Cherville [45b] suggest using values of $\Delta C^{\times}/l$ and δ as data indicating the tendency of explosives to decompose under impact. This would be particularly advisable with new explosives which although their structure is known, possess unknown properties.

While examining the shape of the curve of the sensitivity to impact of TNT at different temperatures (Vol. I, p. 320, Fig. 74). T. Urbański [48] advanced an hypothesis that the increase of sensitivity is due to the increase of entropy (S) and therefore decrease of free energy $G = H - TS$. A critical change is at the melting point of TNT – *ca.* 80°C which is well known, is manifested by a rapid increase of entropy (Fig. 2). Cruchaud [79] drew attention to the electric phenomena which accompany the shock and friction produced by the impact. Charging with static electricity is an important factor influencing the explosion according to this author.

Attention is drawn to two monographs dealing with the initiation of explosives by impact: solid explosives by Afanasyev and Bobolev [49] and liquid by Dubovik and Bobolev [50]. The authors based their views on the considerable work carried out by Khariton, Andreev, Belyaev, Kholevo, Sukhikh, Avanesov, Bolkhovitinov, Baum and their own experiments. The authors agree with the thermal nature of the sensitivity of explosives to impact. However most of the problems raised by the authors of the monographs are outside the scope of the present book.

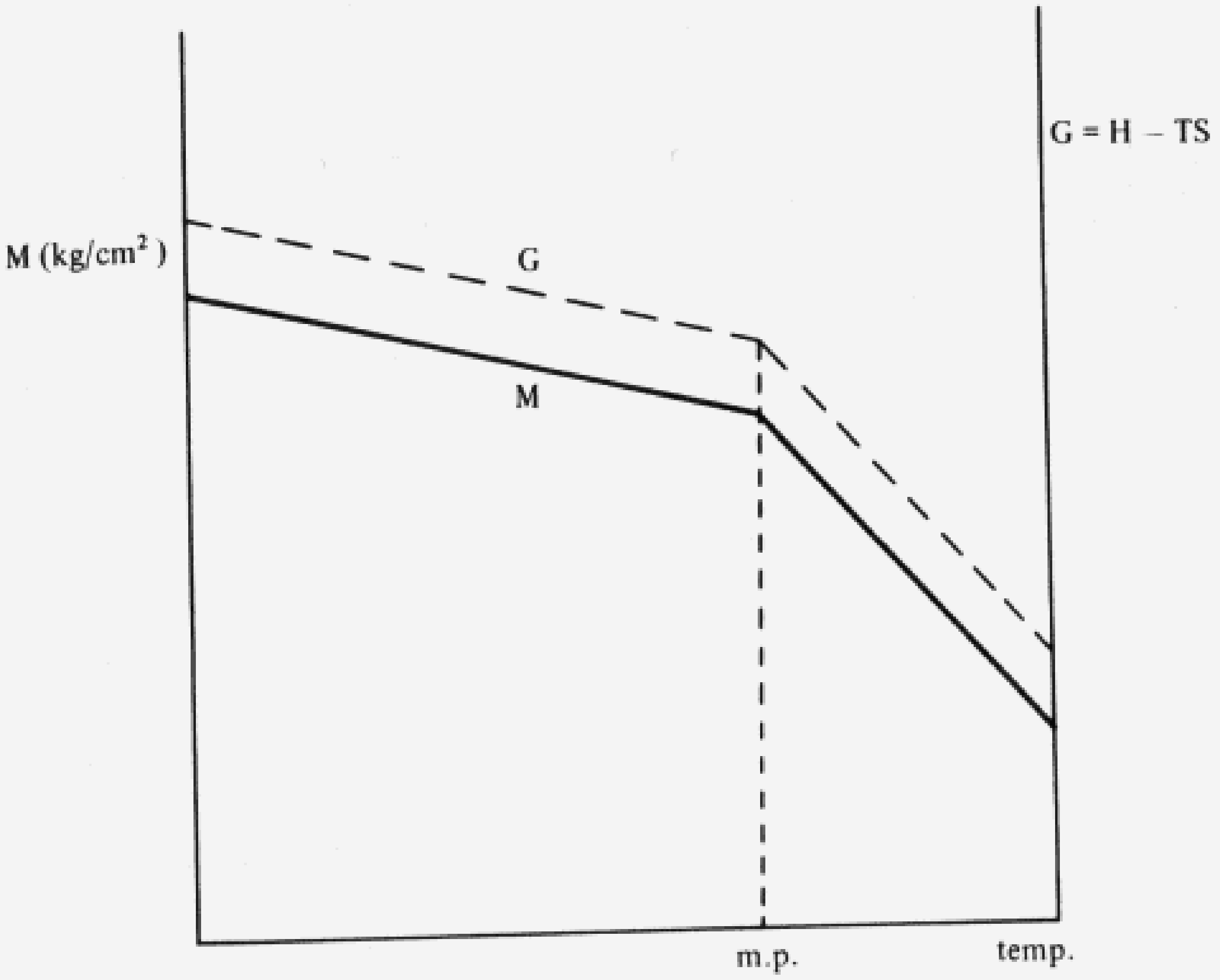

FIG. 2. Sensitivity to impact of TNT (M) and Gibbs free energy (G) as a function of temperature. Melting point: m.p. (According to T. Urbański [48]).

Sensitivity of high explosives (*HE*) *to initiation* by an initiating explosive ('gap sensitivity', 'initiability') is less defined than the sensitivity to impact and cannot be expressed in absolute units. The sensitivity of *HE* to initiation is usually determined:

(1) by the amount of the initiating explosive in the detonator (this method is also used to determine the 'initiating strength' of primary explosives),
(2) by transmitting the detonation from one charge to another through air or other medium (water or a sheet of metal or a polymer) of different thickness,
(3) by determining the critical diameter, that is the minimum diameter which is able to transmit the detonation.

It is well known that the *HE* can be arranged in the sense of decreasing sensitivity to detonation: *O*-nitro, *N*-nitro and *C*-nitro compounds.

Cachia and Whitbread [63] described a ‘gap’ test of different explosives and determined the minimum gap thickness that inhibits detonation.

Recently Ahrens [64] reviewed the problem of determination of the sensitiveness of explosives to initiation.

Sensitivity to friction is also less defined than the sensitivity to impact and can be expressed only by figures comparative to a standard. By decreasing sensitivity the explosives can be arranged as follows [65]:

initiating explosives (with exclusion of azides),
O-nitro compounds,
N-nitro compounds and metal azides,
C-nitro compounds.

The sensitivity of explosives to heating, naked flame, impact and friction is decisive in the international rules for railway traffic ‘RID’ (Réglement International Concernant le Transport des Marchandises Dangereuses) [65]. Analogous rules ‘ADR’ are concerned with international motor traffic [66].

Important reviews have appeared on the sensitivity and initiation of explosives [67, 68].

Action of Ultrasonic Waves and Laser Pulse

Early work on the action of ultrasonic waves on explosives indicated that such sensitive substances as nitrogen iodide could explode [73, 74] but that silver fulminate could not be brought to detonation [74].

Some experiments by Wolfke [69] have shown that high intensity waves were required to bring mercury fulminate to detonation. Negative results were obtained by Renaud [75] who pointed out that the positive results of Marinesco [74] were due to the mechanical action of pushing crystals by the oscillator. This query was recently solved by Leiber [76] who stated that the detonation of nitroglycerine by ultrasonic waves can occur provided that the explosive contains bubbles and the nature of the effect is mainly thermal bringing the temperature to 300–500°C through the adiabatic pressure of the order of 33 bar.

Mizushima and Nishiyama [77] examined the action of laser and found that compressed explosives can be brought to decomposition by a giant laser pulse. Loose explosives cannot detonate. They examined initiating explosives, PETN, RDX, TNT and Tetryl.

Action of Irradiation

Numerous publications particularly in recent years have been dedicated to the sensitivity of explosives to various forms of irradiation.

Bowden and Yoffe [70] reviewed the literature and their own work on the decomposition of initiating explosives by irradiation with electrons, neutrons, fission products, α-particles, X-rays and γ-rays.

Recently two abundant reviews appeared in the *Encyclopedia of Explosives* edited by Kaye and Herman [71, 72].

Thus Avrami [71] reviewed radiation effects on explosives, propellants and pyrotechnics. Here are some of the main conclusions taken from the work of Avrami and numerous authors: initiating explosives are decomposed under irradiation with α-particles, neutrons, γ-radiation, electron irradiation and underground testing. Among the reviewed papers Avrami reported his own work on the influence of Co^{60} gamma radiation on the detonation velocity of explosives: they all show a fall in velocity after irradiation. Cyclonite (EDX) appears to be particularly sensitive, less sensitive are PETN and HMX. Aromatic compounds such as TNT and Tetryl seem to be still less sensitive.

A good stability is shown by heat resistant explosives: TACOT, DATB (Diaminotrinitro-) and TATB (Triaminotrinitrobenzene) (Chapter VII).

Helf [72] described the technique of radiation gauging in energetic materials.

A remarkable paper has been published by Cherville and co-workers [80]. They examined the behaviour of a few secondary explosives to the irradiation from Co^{60} and introduced the value G_{NO_2}: the quantity of NO_2 by irradiation. They found the values of G_{NO_2} being correlated to the ability of explosives to detonate. The following are the figures for G_{NO_2}:

PETN	3.80
Hexogene, Cyclonite (RDX)	0.90
Octogene (HMX)	0.80
Tetryl	0.006
Picric acid	0.001
TNT	0.001
Nitroguanidine	0

Influence of High Temperature

The behaviour (including the decomposition) of explosives at high temperature is one of their important characteristics. With the advent of DSC (differential scanning calorimeter) high precision can be reached of the examination of endo- and exothermic changes in substances with the increase of temperature. This was reviewed by Collins and Haws [81]. The pioneering work on DSC by Tucholski in 1932–33 [82] should be recalled (see also Vol. I, p. 525).

Two Soviet monographs appeared [83, 84] both dedicated to thermal decomposition and burning of explosives, and a review by Maycock [85].

INCREASING THE STRENGTH OF EXPLOSIVES BY ADDING METALS

A popular method of increasing the strength of explosives is by adding aluminium and less frequently calcium silicide, ferro-silicon, silicon (Vol. III, p. 266).

The following figures illustrate the action of aluminium on the calorific value of RDX (Cyclonite) given by Belaev [86]:

RDX + Al	0% Al	cal. val.	1200 kcal/kg
	5%		1380
	10		1420
	15		1520
	20		1690
	33		1890

Recently the addition of Boron or its compound with hydrogen, for example, 'ortho-borane' ($C_2H_{12}B_{10}$) was investigated by Pepekin, Makhov and Apin [87]. They examined mixtures of PETN and Cyclonite with boron or ortho-borane. The calorific value of Cyclonite–Boron reached a maximum (1890 kcal/kg) with *ca.* 16% B. PETN with *ca.* 22% reached a value of *ca.* 2050 kcal/kg.

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CHAPTER 1

NITRATION AND NITRATING AGENTS

(Vol. I, p. 4)

A considerable number of papers were dedicated to the problem of nitration in the years following the publication of Vol. I.

Among nitrating agents the most important still remain nitric acid–sulphuric acid mixtures, but some other very efficient nitrating agents related to nitric acid have been found and are in use, mainly on a laboratory scale.

NITRIC ACID (Vol. I, p. 6)

Considerable attention is currently being paid to nitric acid (and nitrogen dioxide) because of their wide use, not only for nitration, but also as oxidizing agents in rocket propellant systems. A review has recently been published by Addison [1].

Pure nitric acid free of nitrogen dioxide, so called white fuming nitric acid (WFNA), is in use as an oxidizer and for nitration of some compounds (e.g. hexamethylene tetramine [hexamine], Vol. III, p. 87).

However WFNA is relatively unstable and with time develops a certain amount of dinitrogen tetroxide. More stable for rocket propulsion is red fuming nitric acid (RFNA) which contains *ca.* 14 wt% N_2O_4. It is formed from WFNA or from nitric acid with added N_2O_4. RFNA is the equilibrium product formed from both extremes of the concentration range:

$$\begin{array}{lcccccl} HNO_3 & \longrightarrow & HNO_3 & + N_2O_4 & + H_2O & \longleftarrow & HNO_3 + N_2O_4 \\ \text{WFNA} & & 84.5\% & 14\% & 1.5\% & & \text{(in excess,} \\ & & & & & & \text{subject to} \\ & & & \text{RFNA} & & & \text{evaporation).} \end{array} \tag{1}$$

RFNA is more reactive than WFNA, N_2O_4 being a *sui generis* catalyst of the oxidation reactions. Subsequently RFNA is more recommended in rocket fuel than WFNA, but should be avoided in most nitration reactions. Dinitrogen tetroxide (usually given in analytical data as NO_2) is present in spent acids containing nitric and sulphuric acids and is formed in the course of nitration as a result of the oxidation of the nitrated substances. The content of NO_2 in the spent acid can be as high as 5%. Commercial 'fuming nitric acid' ('anhydrous nitric acid') usually contains less than 1% NO_2 and is used for the nitration of hexamine.

Pure nitric acid (WFNA) can be obtained by distillation of nitric acid from a mixture of concentrated nitric acid (d 1.50 at 25°C) and concentrated sulphuric acid, under reduced pressure at room temperature. A white crystalline solid results with the following properties [1]:

m.p. – 41.6°C
b.p. + 82.6°C
d – 1.549 at 0°C
viscosity 10.92 cP at 0°C
dielectric constant 50 ± 10 at 14°C
surface tension 43.5 dy/cm at 0°C
specific conductivity 3.77×10^{-2} ohm^{-1} cm^{-1}.

The latter two figures are high due to hydrogen bonding (Vol. I, p. 7, Fig. 1).

The data in Fig. 1a (Vol. I, p. 7) should be slightly altered on the basis of more recent measurements by micro-wave spectroscopy [2, 3]. They are now given in Fig. 3.

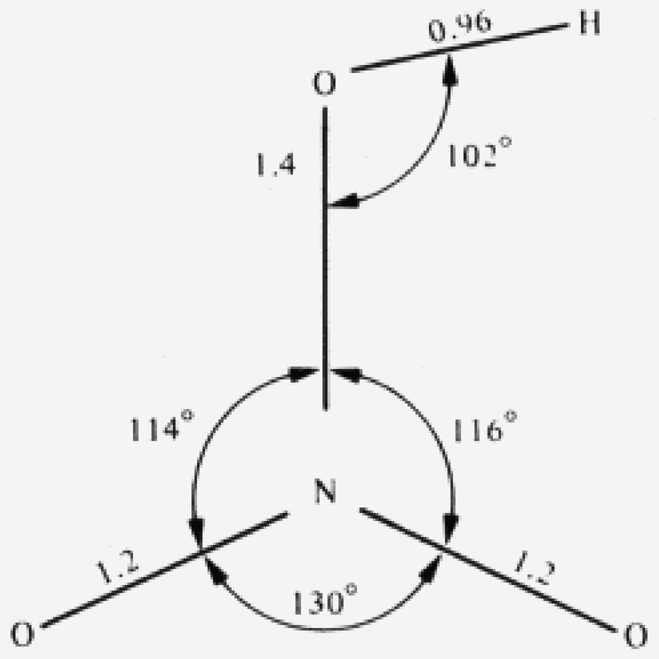


FIG. 3. Structure of the molecule of nitric acid [2, 3].

It is well known that nitric acid forms an azeotropic solution with water. It contains 68.5 wt% HNO_3 and boils at 122°C under standard atmospheric pressure.

Cryoscopic measurements (Vol. I, pp. 15–16) have shown that only a little over 3% of pure nitric acid is dissociated at –40°C according to the equation:

$$2HNO_3 \rightleftharpoons \underset{1.2}{NO_2^+} + \underset{1.7}{NO_3^-} + \underset{0.5\ \text{wt\%.}}{H_2O} \qquad (2)$$

Water is in the form of the nitric acid hydrate.

A few more spectroscopic data for nitric acid should be added to those previously given (Vol. I, p. 22). Vitse [31d] has found bands in nitric acid: 1680, 1300 and 930 cm^{-1} assigned to NO_2 and band 3200 cm^{-1} to OH stretching vibrations.

It is now generally accepted that the nitronium ion NO_2^+ is the main nitrating agent. Although most industrial nitrations are carried out by nitric acid–sulphuric acid mixtures, some compounds can be nitrated with nitric acid alone (production of tetryl, Vol. III, p. 42). Some products, such as PETN (Vol. II, p. 185) are usually obtained by nitration with nitric acid alone and Cyclonite (if made by nitration) is produced exclusively with nitric acid free of N_2O_4 (Vol. III, p. 87).

Although the nitronium ion is the nitrating agent, there are known examples when nitration can occur in media in which the concentration of NO_2^+ is too small to be detected spectroscopically (Vol. I, pp. 25, 48). This was pointed out by Bunton and Halevi [4] who succeeded in nitrating aromatic compounds with 40–60% aqueous nitric acid. Bunton and co-workers [5, 6] showed that the nitronium ion was an intermediate in both oxygen-exchange and aromatic nitration in the sense of reactions:

$$2HNO_3 \rightleftharpoons H_2NO_3^+ + NO_3^-, \qquad (3)$$

$$H_2NO_3^+ \rightleftharpoons NO_2^+ + H_2O. \qquad (4)$$

Hydrated nitronium ion (nitracidium ion) $H_2NO_3^+$ is a source of the nitrating agent NO_2^+.

It was reported [7] that nitration of 1,5-dinitro-naphthalene can occur with 70% nitric acid to yield trinitro-naphthalenes.

The problem of nitration with aqueous nitric acid was reviewed by Hanson and associates [8]. They confirmed the idea of nitracidium ion being a nitrating agent and pointed out that attention should be paid to the presence of nitrous acid in the system, as nitration with dilate nitric acid can proceed through the nitrosation by nitrous acid formed as the result of oxidation–reduction. T. Urbański and Kutkiewicz [9] (Vol. I, p. 85) found that 8-hydroxyquinoline can be nitrated by boiling with 0.5% nitric acid to yield 5,7-dinitro-8-hydroxyquinoline. It was also found that 8-hydroxy-5-nitroquinoline yielded the same dinitro derivative.

As far as the mononitration of phenol and the formation of 8-hydroxy-5-nitroquinoline can be explained in terms of the conventional mechanism of nitrosation followed by the oxidation of nitroso to the nitro group (p. 23), this mechanism could not explain the formation 5,7-dinitro-8-hydroxyquinoline from mononitro compound. The mononitrophenols cannot be nitrosated with nitrous acid and subsequently the formation of the second nitro group cannot occur through nitrosation. Nevertheless, the reaction of formation of the dinitro compound from the mononitro product is preceded by the oxidation and evolution of NO_2. This would apparently suggest that nitrosation (as shown above) is not possible with 8-hydroxy-5-nitroquinoline.

Also Ross and co-workers [87] pointed out that the accepted scheme of nitration of phenol in 56.2% sulphuric acid through nitrosation prior to nitration, is inconsistent with the results and expressed the view that another route should exist.

The author of the present book suggests the solution of the problem of nitration of phenols with dilute nitric acid in a two-fold way:

(1) Through oxidation (which always accompanies nitration and particularly the nitration of phenols) NO_2 is evolved and the well known reaction occurs:

$$2\,NO_2 + H_2O \longrightarrow HNO_3 + HNO_2. \qquad \textbf{(5a)}$$

(2) The dilute nitric acid originally present in the solution and also formed in reaction (5a) can given rise to NO_2^+ in a readily oxidizable medium according to scheme (5b) rationalized by the author [112]:

$$NO_3^- \longrightarrow NO_2^+ + O^{2-} \qquad \textbf{(5b)}$$

Reaction (5b) can take place in readily oxidizable mediums such as phenols and aromatic amines.

NITRIC AND SULPHURIC ACID

Mixtures of nitric and sulphuric acids contain nitronium sulphates which have been described by Ingold and associates, Woolf and Emeléus (Vol. I, p. 19). Revallier and co-workers [10] have found by Raman spectroscopy and vapour pressure measurements, that compounds made by acting with SO_3 on nitric acid are salts of nitronium ion (NO_2^+) and sulphate anions. Vitse [11] established the structure of the compound $N_2O_5.4SO_3$ as nitronium ion salt by X-ray crystallography. The salts of pyrosulphuric acid (Vol. I, p. 12) can be present only in a mixture of nitric acid with oleum or SO_3. They are described in the paragraph on nitronium salts (p. 27). The presence of NO_2^+ in various solutions was discussed in Vol. I, pp. 14–49.

The basicity of nitric acid in the sense of the dissociation $NO_2OH \rightleftharpoons NO_2^+ + OH^-$ in concentrated sulphuric acid was recently studied by Marziano *et al.* [12]: the ionization ratio NO_2^+/HNO_3 of nitric and 80–96% sulphuric acids has been evaluated by Raman and ultraviolet spectroscopy. The function pK_a of nitric acid as a base was calculated $pK_a = -15.2$.

As far as the activity of the nitrating mixture (Vol. I, p. 29) is concerned, a novel approach to the problem was recently developed by Marziano and associates [13]. In a series of papers on thermodynamic analysis of nitric acid with sulphuric or perchloric acid these authors introduced a new function of the activity coefficient M_C:

$$M_C = \log \frac{f_B\, f_{H^+}}{F_{BH^+}}$$

where f_B is the activity coefficient of the nitrated substance, f_{H^+} activity coefficient of the proton H^+.

Effects of Adding Salts on Nitration in Sulphuric Acid

A few authors have examined the effect of adding salts on the rate of nitration in sulphuric acid.

Thus Surfleet and Wyatt [14] studied the nitration of benzenesulphonic acid in sulphuric acid and found that the addition of hydrogen sulphates of various metals increases the nitration rate. The most marked effect occurred with calcium and barium hydrogen sulphates. An explanation of the effect was sought in terms of the Brönsted salt-effect theory. It was suggested that the main influence of ionic solutes is in the activity coefficient of the nitrated substance (f_B) since the activity coefficients of the other two species, the nitronium ion ($f_{NO_2^+}$) and the similarly charged transition complex ($f_{\ddagger}^{+}$) as a ratio in the Brönsted equation and would be approximately equally affected by changes in the ionic environment. The view was expressed that reactions involving only ionic species would exhibit small salt effects.

Bonner and Brown [15] expressed the view that the increase in reaction rate due to added salts is similar to the increase initially resulting from the addition of water to anhydrous sulphuric acid, attaining the maximum at *ca*. 90% acid. They supported it by examining the rates of nitration of trimethylphenylammonium ion and 1-chloro-4-nitrobenzene. When ammonium sulphate was added, the rate increased more than X20 their value in the anhydrous acid. On the nitration of cellulose with nitric acid in the presence of inorganic salts (see Vol. II, p. 346).

Nitric Acid and Trifluoromethane Sulphonic Acid

A very interesting nitrating mixture has been reported by Coon, Blucher and Hill [16]. It was composed of nitric acid and trifluoromethane sulphonic acid:

$CF_3.SO_3H$. It contains nitronium salt: $NO_2^+\ CF_3SO_3^-$. The major difference between the aromatic nitration with this and other nitronium salt is an extremely high reaction rate.

The nitration of toluene with such a mixture is described in the chapter dedicated to the nitration of aromatic hydrocarbons.

Nitric Acid and Hydrofluoric Acid

NMR spectroscopy revealed [17] that NO_2^+ is also formed by acting with HF on nitric acid, viz.:

$$HNO_3 + 2HF \longrightarrow NO_2^+ + H_3O^- + 2F^-. \quad (6)$$

Earlier the presence of NO_2^+ in nitric acid–hydrofluoric acid solution was postulated by Vorozhtsov Jr and his School [18]. Vorozhtsov Jr and associates [19] found that nitric acid–hydrofluoric acid solution can produce both: the nitration and fluorization of aromatic compounds through an ipso-attack (see p. 50) of both NO_2^+ and F^-.

Nitric and Phosphoric Acid

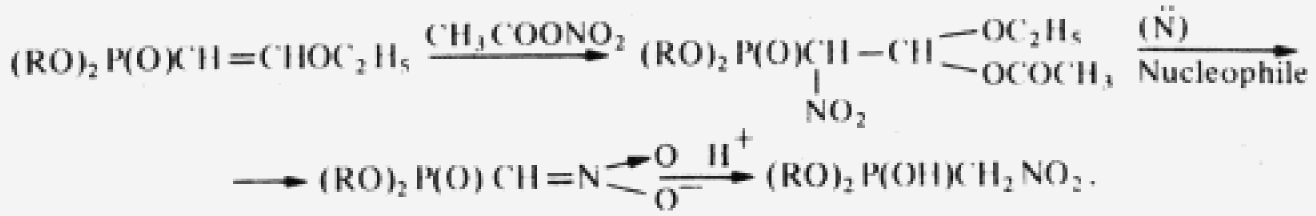
It is admitted that anhydrous solution of nitric and phosphoric acids contains nitronium ion.

So far nitric–phosphoric acid mixtures have been mainly of theoretical interest (Vol. II, p. 341). However recently a few attempts have been reported on the nitration of toluene with nitric–phosphoric acid mixtures in order to reduce the proportion of *o*-nitrotoluene and subsequently to increase the yield of para isomer (Harris [20]).

Nitric Acid and Acetic Anhydride

Nitric acid and acetic anhydride mixture is often used as a nitrating agent on a laboratory scale. It is possible that nitronium ion is present in such solutions [21]. According to A. Fischer and associates [22, 23] nitric acid–acetic anhydride mixtures contain nitronium acetate. Nitric acid–acetic anhydride yield not only nitro compounds but can also produce an acetylation through the oxidation and subsequent acetylation of the side chain [23]. Thus *o*-xylene subjected to the action of nitric acid–acetic anhydride at 0°C gave 16% 3-nitro- and 33% 4-nitroxylene and 51% 3,4-dimethylphenyl acetate. The authors suggested it as being the result of the presence of oxonium ion $CH_3COO^+NO_2$. Nucleophilic attack on a ring carbon leads to acetoxylation.

Very often nitration with nitric acid–acetic anhydride solution is referred to as nitration with acetyl nitrate (Vol. I, p. 44). Petrov and co-workers [24] experimented with nitric acid and acetic anhydride with a small quantity of sulphuric acid at 35°C on ethoxyvinylphosphates. The ester was hydrolysed to yield a nitromethane derivative:



$$(RO)_2P(O)CH{=}CHOC_2H_5 \xrightarrow{CH_3COONO_2} (RO)_2P(O)\underset{\displaystyle NO_2}{\underset{|}{CH}}-CH\begin{smallmatrix}-OC_2H_5\\ -OCOCH_3\end{smallmatrix} \xrightarrow[\text{Nucleophile}]{(\ddot{N})} \quad (7)$$

$$\longrightarrow (RO)_2P(O)\,CH{=}N\begin{smallmatrix}\nearrow O\\ \searrow O^-\end{smallmatrix} \xrightarrow{H^+} (RO)_2P(OH)CH_2NO_2.$$

Literature on the practical use of nitric acid–acetic anhydride includes also some warnings on explosion hazards associated with the use of mixtures of fuming (97%) nitric acid with acetic anhydride. Thus Brown and Watt [25] demonstrated that mixtures of nitric acid with acetic anhydride containing more than 50% by weight of nitric acid can undergo a spontaneous explosion.

Dingle and Pryde [26] extended this warning also to mixtures containing less than 50% nitric acid. Particularly dangerous is the addition of a small quantity of water or some mineral acids to such a mixture. A mixture containing 6% nitric acid in acetic anhydride with 1.7% concentrated hydrochloric acid was found to self-heat at 20°C and to fume-off vigorously at 60°C with gas evolution.

Nitric Acid with Cerium Ammonium Nitrate or Tallium Nitrate

Considerable interest has been shown recently in the use of cerium (IV) salts as oxidizing agents. Cerium (IV) ammonium nitrate can also be a nitrating agent [125]. It can also act in the presence of acetic acid [119]. In the presence of nitric acid [120] it can form nitrate esters from the methyl group, viz.:

$$-CH_3 \longrightarrow -CH_2ONO_2$$

(see Chapter X).

Tallium (III) nitrate can also be used as a nitrating agent [119].

NITRONIUM CATION (NO_2^+) AND ITS SALTS

Crystalline nitronium salts were first obtained as early as 1871 by Weber [27] (see also Vol. I, p. 12). He gave the composition $N_2O_5.4SO_3.3H_2O$ and $N_2O_5.4SO_3.H_2O$. Several similar salts have been obtained by a number of authors [10, 28–30]. The most important contribution to the knowledge of stoichiometry of $N_2O_5.SO_3$ and $N_2O_5.SO_3.H_2O$ complex-salts has been made by Vitse [31].

All these salts possess ionic structure comprising cation NO_2^+ bonded in various proportions to HSO_4^-, $HS_2O_7^-$, $S_2O_7^{2-}$ etc.

Some of the salts possess a great stability if protected from moisture. Thus Werner compound $N_2O_5.4SO_3.H_2O$ has the structure $NO_2^+\ HS_2O_7^-$ and m.p. 105.6°C [10a]. The compound $8N_2O_5.20SO_3.7H_2O$ with the structure $(NO_2^+)_{16}S_2O_7{}^{2-}(HS_2O_7^-)_4(HSO_4^-)_{10}$ has m.p. 119.8°C. Its crystal structure was determined by X-ray analysis [11] as already mentioned (p. 28).

Other salts of nitronium ion and sulphuric acid have been previously described (Vol. I, p. 19). Ingold and co-workers (Vol. I, p. 19) obtained crystalline nitronium perchlorate which was relatively stable, but decomposed on storage and was not further investigated.

R. J. Thomas, Anzilotti and Hennion [32] reported that boron trifluoride could play the same part as sulphuric acid in the nitration of aromatics. Olah and co-workers [33, 40] prepared and successfully applied a number of stable salts of nitronium ion in a relatively simple way:

$$NO_2^+\ X \text{ where } X = BF_4,\ AsF_6,\ PF_6$$

and

$$(NO_2^+)_2\ Y \text{ when } Y = SiF_6{}^{2-}.$$

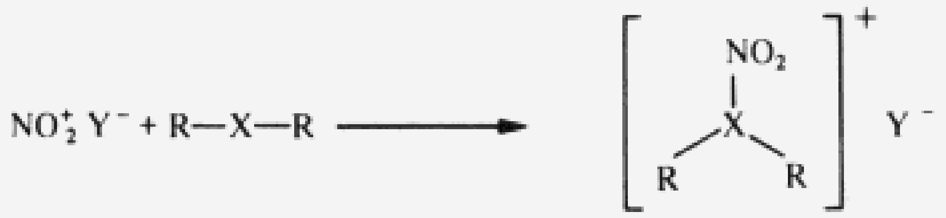
Particularly important is nitronium tetrafluoroborate obtained by adding anhydrous HF to nitric acid in a solvent such as nitromethane or methylene chloride and then saturating the solution with boron trifluoride (8):

$$HNO_3 + HF + 2BF_3 \longrightarrow NO_2^+BF_4^- + BF_3.H_2O. \tag{8}$$

An almost quantitative yield of stable nitronium salts $NO_2^+BF_4^-$ can be obtained in that way [34] and it is now commercially available [35]. It is a colourless, crystalline very stable compound which decomposes above 170°C into NO_2F and BF_3 without subliming. It is a very strong nitrating agent [36].

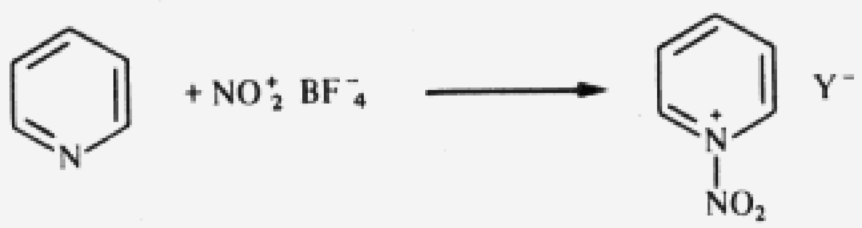
Among other compounds nitric acid–boron trifluoride $HNO_3.2BF_3$ complex (m.p. 53°C) obtained by Revallier and associates [37] proved by Raman spectroscopy to possess the structure of nitronium salt $NO_2^+(BF_3)_2OH^-$ [38].

Nitronium ion is able to form nitroxonium and pyridinium ions with ethers and pyridine or collidine respectively by acting on ethers and pyridine or collidine respectively with nitronium tetrafluoroborate [39, 40d]:



(9)

$Y = PF_6^-,\ BF_4^-$
$X = O, S; R = \text{Alkyl}, H$



(10)

The nitroxonium and nitropyridinium (or nitrocollidinium) ions are efficient nitrating agents. They also can form *O*-nitro compounds.

Nitronium hexafluorophosphate ($NO_2^+\ PF_6^-$) is also a strong nitrating agent according to Olah and Lin [40b]. It can nitrate alkanes at 25°C to a small yield of nitro compounds (2–5% for ethane to butane). Nitronium tetrafluoroborate in fluorosulphuric acid (FSO_3H) possesses strong nitrating properties. It can nitrate *m*-dinitrobenzene to *sym*-trinitrobenzene with a yield of 66% [40c].

Among the salts of nitronium ions a very active nitrating agent is nitronium trifluoromethyl sulphate ($NO_2^+\ CF_3SO_3^-$) as already mentioned [16].

Nagakura and Tanaka [41] explained a great reactivity of NO_2^+ by calculating its lowest vacant orbital and the highest occupied orbital of benzene. The figures are −11.0 and −9.24 eV respectively. Other electrophilic reagents, such as Br^+ and Cl^+ are less reactive. They gave values of −11.8 and −13.0 eV respectively.

Nitronium salts are usually applied in an aprotic solvent [35]. Such is tetramethylene sulphone ('Sulfolan') used by Olah [40]. However, Giaccio and Marcus [42] suggested acetic acid as a solvent. This, however, reacts with nitronium tetrafluoroborate on standing at room temperature to yield acetyl nitrate:

$$CH_3COOH + NO_2^+BF_4^- \rightleftharpoons CH_3COONO_2 + HF + BF_3. \tag{11}$$

The nitrating action of acetyl nitrate differs from that of nitronium tetrafluoroborate [40]. Also the stability of acetyl nitrate is not satisfactory.

Dinitrogen Pentoxide (N_2O_5) (Vol. I, p. 105)

Dinitrogen pentoxide (nitric anhydride) can be a source of the nitronium ion. As previously mentioned Titov suggested (Vol. I, p. 106) that dinitrogen pentoxide undergoes a heterolytic dissociation:

$$N_2O_5 \rightleftharpoons NO_2^+ + NO_3^-. \tag{12}$$

The infra-red bands of the ionic form at liquid nitrogen temperature have been examined by Teranishi and Decius [43] and substantiated by Hisatsune and co-workers [44] who also examined Raman spectra. They found a temperature dependence of the structure of solid N_2O_5 which changed the covalent structure $O_2N-O-NO_2$ into ionic at temperatures from −175° to −80°C.

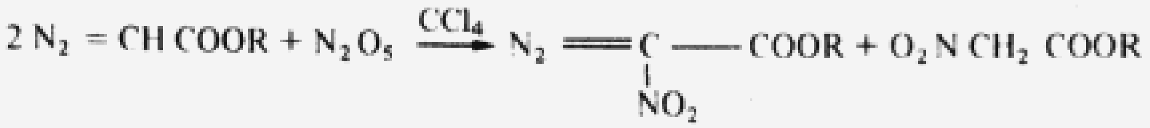
The covalent structure is characterized by a bent of the central N—O—N group.

Dinitrogen pentoxide readily forms nitronium salts. As mentioned, Weber [27] and other authors [28–31] obtained a number of sulphates of NO_2^+. Bachman and Dever [45] prepared a complex with BF_3 which most likely possesses the structure $NO_2^+ \; BF_3ONO_2^-$. Kuhn and Olah [33] obtained nitronium tetrafluoroborate by adding anhydrous HF as a solvent to N_2O_5 and BF_3:

$$N_2O_5 + HF + BF_3 \longrightarrow NO_2^+ \, BF_4^- + HNO_3. \qquad \textbf{(13)}$$

T. Urbański used N_2O_5 in vapour phase or in a solution in nitric acid to nitrate cellulose (Vol. II, p. 348) and starch (Vol. II, p. 430).

N_2O_5 was successfully used by Schöllkopf and associates [46] to nitrate aliphatic diazocompounds to obtain eventually nitrodiazomethane [46b] and dinitrodiazomethane [46c]. As the first step esters of diazoacetic acid were nitrated with half a mole of N_2O_5 in carbon tetrachloride at −20 to 30°C:



$$2\,N_2{=}CH\,COOR + N_2O_5 \xrightarrow{CCl_4} N_2{=}\underset{\underset{NO_2}{|}}{C}{-}COOR + O_2N\,CH_2\,COOR$$

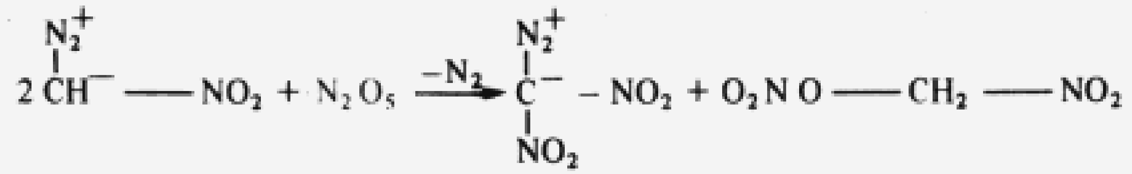
$(R = C_2H_5$ or ter$-C_4H_9)$ **(14)**

$$N_2{=}\underset{\underset{NO_2}{|}}{C}{-}COOR \xrightarrow{CF_3COOH} N_2{=}\underset{\underset{NO_2}{|}}{CH} + CO_2 + ROH$$

I **II**

Nitrodiazoester (I) is relatively acid-stable, but the COOR group can be cleaved off by acting with trifluoroacetic acid in ether to obtain nitrodiazomethane (II) $O_2N{-}CH\;N_2^+$ m.p. 55°C. It is a substance which is sensitive to impact and explodes on heating.

Nitrodiazomethane was nitrated [46c] with N_2O_5 in dichloromethane at −30°C to yield dinitrodiazomethane (III) and a nitromethyl nitrate ester (IV)



$$2\,\overset{\overset{N_2^+}{|}}{CH^-}{-}NO_2 + N_2O_5 \xrightarrow{-N_2} \underset{\underset{NO_2}{|}}{\overset{\overset{N_2^+}{|}}{C^-}}{-}NO_2 + O_2N\,O{-}CH_2{-}NO_2 \qquad \textbf{(15)}$$

III **IV**

III is an explosive substance with m.p. 65°C (with decomposition).

N_2O_5 possesses marked oxidizing properties [47]: a small yield of CO_2 was formed by acting with N_2O_5 on CO. Baryshnikova and Titov [123] have found an interesting reaction of N_2O_5 on aromatic compounds which consists in both nitration and oxidation. Thus chlorobenzene was transformed into chloronitrophenols.

Dinitrogen Tetroxide and Nitrogen Dioxide (Vol. I, p. 90)

The increasing importance of dinitrogen tetroxide brought to light a number of new facts on the properties of the substance.

Some physical constants are [1]:

freezing point −11.2°C
b.p. 21.15°C
density 1.470–1.515 g/cm^3 between +10° and −10°C
viscosity 0.468–0.599 cP between +10° and −10°C
dielectric constant 2.42
surface tension 26.5 dyn/cm at 20°C
specific conductivity 10^{-12} ohm^{-1} cm^{-1}.

An extensive review of the properties of dinitrogen tetroxide has been given by Riebsomer [47]. The addition of N_2O_4 to olefins was reviewed by Shechter [48] and free radical reactions of NO_2 by Sosnovsky [48a].

The N—N bond in dinitrogen tetroxide can readily be split above room temperature. The case of breaking N—N bond is due to its low enthalpy: $-\Delta H$ of N—N in N_2O_4 is 14.6 kcal/mol and similarly in N_2O_3 is 10.2 kcal/mol. [49].

The N—N bond is mainly σ in nature, not of pure π character according to Green and Linnett [50]. This was based on a calculation by LCAO MO method and was contradictory to earlier views. The bond N—N seems to be of an unusual kind, not fully understood, as the two NO_2 units do not rotate with respect to each other in spite of the length of the bond.

The views of Green and Linnett were subjected to criticism by R. D. Brown and Harcourt [113]. The latter pointed out that Green and Linnett had overlooked the significant effect of σ-electron delocalization upon N—N and N—C bonds. Brown and Harcourt proposed a new electronic structure with '$\sigma + \pi$' model.

A review recently appeared [126] on the spectrum of NO_2 in gas phase. The spectrum is rich and complex and was examined by modern techniques. The study is outside the scope of the present book.

N_2O_4 is miscible with many organic liquids and is a solvent of many solid organic substances.

Ammonium nitrate is insoluble in N_2O_4 but alkylammonium nitrates dissolve readily [1].

Nitrogen dioxide at high temperature (*ca.* 620°C) was subjected to homolytic dissociation into nitric oxide and oxygen atom. The same occurred upon irradiation with 313 and 316 nm light [51, 52].

The heterolytic dissociation can be represented in two ways:

$$N_2O_4 \rightleftharpoons NO_2^+ + NO_2^- \qquad (16)$$

$$N_2O_4 \rightleftharpoons NO^+ + NO_3^- \qquad (17)$$

and there is also an irreversible heterolytic oxygen exchange:

$$NO_2^+ + NO_2^- \longrightarrow NO^+ + NO_3^-. \qquad (18)$$

However the species NO_2^+ and NO_2^- have not been identified as free ions in liquid N_2O_4. They exist as the ion pair $[NO_2^+ \; NO_2^-]$. In the presence of an electron-pair acceptor, complexes are formed which contain the nitronium ion. This happens in the presence of Lewis acid halides used for the first time ($AlCl_3$) by Schaarschmid (Vol. I, p. 103). Boron trifluoride reacts with N_2O_4 to form $N_2O_4.BF_3$ [53, 54] and $N_2O_4.2BF_3$. Their structures were suggested as being $NO_2^+ \; BF_3NO_2^-$ and $NO_2^+ \; [N(OBF_3)_2]^-$ respectively. These complexes possess only a moderate nitrating ability, a fact which casts some doubt on whether they possess the structure with nitronium ion. It is known that N_2O_4 in nitric acid is almost fully ionized into NO^+ and NO_3^-. In view of the absence of NO_2^+ the complex $N_2O_4.BF_3$ may have the structure of a nitrosonium salt $NO^+ \; BF_3NO_3^-$. Indeed it shows an ability to nitrosate and to diazotize [53] and spectroscopic examination [56] showed only a relatively weak band at 1400 cm^{-1} and a strong one at *ca.* 2340 cm^{-1}.

It is suggested [40] that an equilibrium exists between nitronium and nitrosonium forms of the complex $N_2O_4.BF_3$ i.e.

$$NO_2^+ \; [BF_3 \; NO_2]^- \longrightarrow NO^+ \; [BF_3NO_3]^-. \qquad (19)$$

A solution N_2O_4 + HF should be considered as a potential nitrating agent [57].

Dinitrogen tetroxide can give additional complexes with compounds possessing an ether bond. They were examined by Shechter *et al.* and described in his review paper [48].

Here are the most important of the compounds:

1.	$2(C_2H_5)_2O \cdot N_2O_4$	m.p. −74.8°C
2.	$2(C_5H_{10}O) \cdot N_2O_4$ (Tetrahydropyren)	m.p. −56.8°C
3.	$C_4H_8O \cdot N_2O_4$	m.p. −20.5°C
	$2C_4H_8O \cdot N_2O_4$ (Tetrahydrofurane)	m.p. (indefinite)
4.	$O(CH_2CH_2)_2O \cdot N_2O_4$	m.p. +45.2°C

Davies and C. B. Thomas [58] reported an interesting instance of nitration of arylthallium (III) aromatic complexes with nitrogen dioxide at room temperature. Tallium (III) fluoroacetate was used as the agent metallating an aromatic ring which can react with NO_2:

$$\text{Alk } C_6H_5 \; Tl(OOCCF_3)_2 \xrightarrow{NO_2} \text{Alk } C_6H_4NO_2. \qquad (20)$$

A remarkable feature of the reaction is the high proportion of *p*-nitro products. More details are given in the chapter on the nitration of toluene.

Dinitrogen tetroxide in vapour phase can be used as an energetic nitrating agent (Vol. I, pp. 92–105). The nitration of aromatics can be facilitated by irradiation with ultraviolet light. The claim of Gorislavets (Vol. I, p. 105) was substantiated by Bunbury [59].

As far as nitration with liquid N_2O_4 is concerned, attention should be paid to the danger of keeping solutions of alkanes with N_2O_4.

T. Urbański and Falęcki [60] reported a spontaneous explosion when a solution of N_2O_4 in *n*-alkanes was kept for a few days at room temperature. This was most likely a consequence of the formation of branched reaction chains through free radicals.

In addition to the use of dinitrogen tetroxide as an oxidizer in rocket propellant systems, and as a potential nitrating agent is is also used as a cooling liquid in nuclear energy reactors under the name of 'Nitrin' [61].

Dinitrogen Tetroxide–Nitric Acid

The two liquids: HNO_3 and N_2O_4 are not miscible in all proportions. At room temperature (20°C) an immiscibility region extends between *ca.* 54 and 92 wt% of N_2O_4. The critical solution temperature is 60.9°C at a composition 68.2 wt% N_2O_4. The phase diagram is shown in Fig. 4 [62, 63].

A solid compound $(HNO_3)_2 \; N_2O_4$ exists, it contains 42.2% N_2O_4. It gives an eutectic m.p. −65°C at 25.6% N_2O_4 [64]. The compound gives maximum values of density and viscosity [65]. Spectroscopic examination shows [1] that the species present in HNO_3–N_2O_4 mixtures are as follows:

$$NO^+, NO_2^+, NO_3^-, H_2O, HNO_3, NO_2, N_2O_4.$$

The mixtures HNO_3–N_2O_4 are highly corrosive and attack metals (steel, aluminium or chromium, nickel). Corrosion can be inhibited by the addition of fluorine compounds, notably HF or PF_6 [1]. The addition of 0.7 wt% of HF reduces the corrosion by a factor over 100 and the mixture of 44% N_2O_4 and 56% HNO_3 with 0.7–1.0% HF termed 'standard HDA' is in current use as a rocket oxidant fuel.

When HF is added to the nitric acid–dinitrogen tetroxide mixture, the following are reactions:

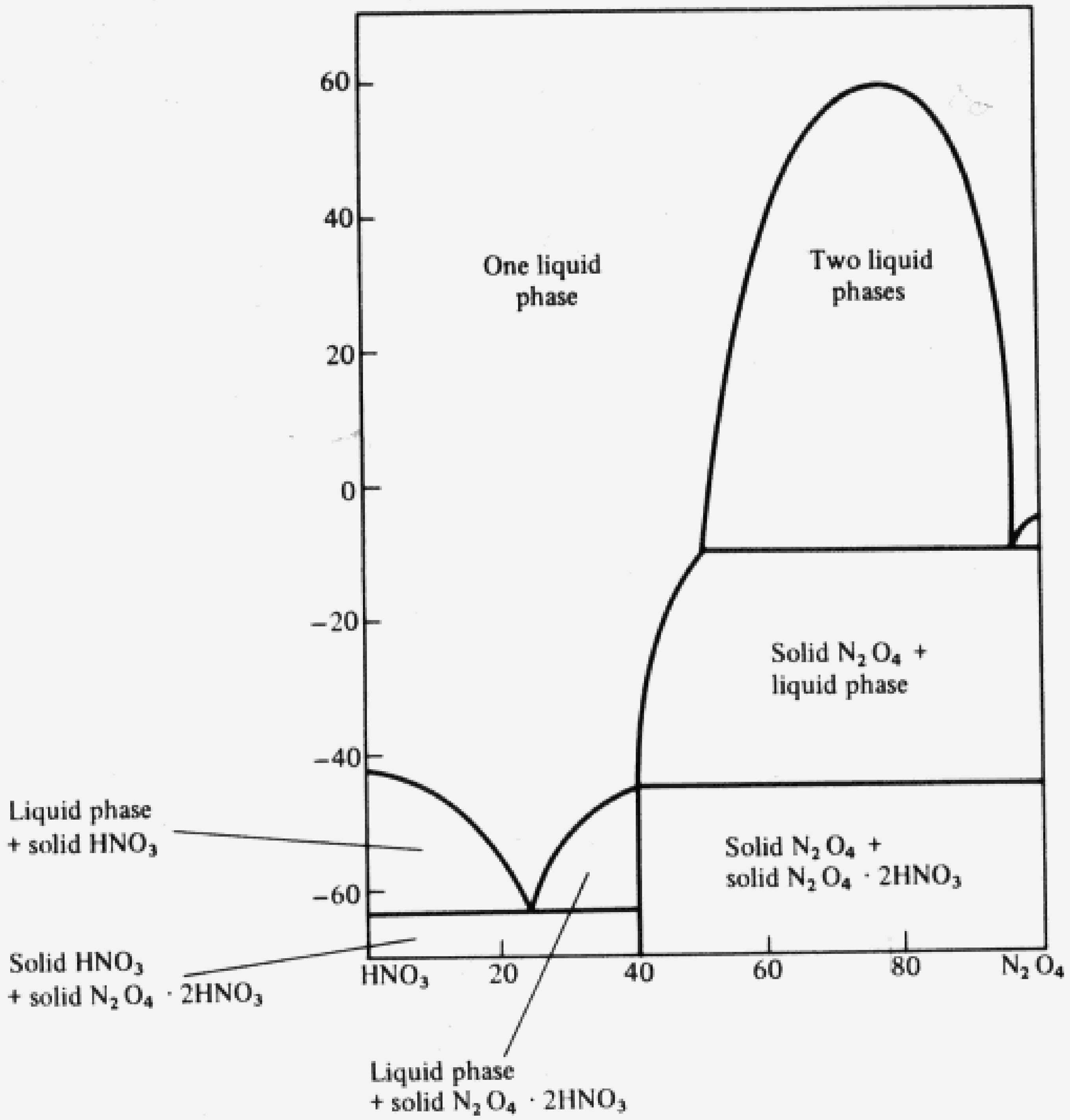


FIG. 4. Phase system $HNO_3 + N_2O_4$. (C. C. Addison [1], reproduced with permission of the American Chemical Society).

$$2\,HF + HNO_3 \longrightarrow NO_2^+ + H_3O^+ + 2F^- \qquad \textbf{(21a)}$$

$$HF + F^- \longrightarrow HF_2^- \qquad \textbf{(21b)}$$

$$N_2O_4 + HF \longrightarrow NOF + HNO_3 \qquad \textbf{(21c)}$$

$$NOF + H_3O^+ \longrightarrow NO^+ + HF + H_2O \qquad \textbf{(21d)}$$

In the presence of sulphuric acid N_2O_4 reacts as follows (Vol. I, p. 102):

$$N_2O_4 + 3H_3SO_4 \rightleftharpoons NO_2^+ + NO^+ + H_3O^+ + 3HSO_4. \qquad \textbf{(22)}$$

This was substantiated by Raman spectroscopy and cryometry.

FRIEDEL-CRAFTS NITRATING AGENTS (Vol. I, p. 103)

The use of Friedel-Crafts catalysts in nitrating systems was originally suggested by Schaarschmidt (Vol. I, p. 103) and Topchiev (Vol. I, p. 46). Currently it is related to the concept of 'Superacids' [66, 67]. The term 'superacid' refers to acid systems which show acidity stronger than 100% sulphuric acid function H_0 [68] lower than −10.60. A superacid is usually formed by Lewis Acid and a mineral acid.

As already pointed out N_2O_4 can form complexes such as BF_3 with Friedel-Crafts catalyst.

Most mixtures of Friedel-Crafts catalysts are non-homogeneous. However, Olah [37] has found that a homogeneous system can be obtained with $TiCl_4$, BF_3, PF_5 and AsF_5 while using tetramethylene sulphone 'Sulfolan' as a solvent. Nitronium fluoride or chloride can then be formed, e.g.

$$2N_2O_4 + TiCl_4 \longrightarrow NO_2Cl + 2NOCl + TiO_2. \qquad \textbf{(23)}$$

Olah [33, 40] drew attention to a number of nitrating agents, such as nitronium halides (usually referred to as nitryl halides): NO_2X (X = F, Cl, Br). Nitronium chloride and fluoride were reported as nitrating agents in Vol. I, pp. 58, 107; Vol. II, p. 355 and Vol. I, p. 109 respectively. Nitronium chloride is usually prepared by reacting nitric acid with chlorosulphonic acid [69]. Nitronium bromide is unstable and was not isolated [33, 40]. According to Aynsley, Heatherington and Robinson (Vol. I, p. 109) nitronium fluoride is a more powerful nitrating agent than nitronium chloride. Infra red and Raman spectra of nitronium fluoride were examined [70].

Nitronium halides should be regarded as acyl halides and are able to take part in Friedel-Crafts acylation, which in this case is nitration, according to scheme:

$$ArH + NO_2X \longrightarrow ArNO_2 + HX. \qquad \textbf{(24)}$$

In the presence of aluminium halides nitronium halides react forming complex nitronium salts [33, 40]:

$$NO_2X + AlX_3 \rightleftharpoons NO_2^+\,AlX_4^- \qquad \textbf{(25)}$$

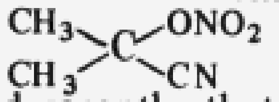
Solid Superacid Catalysts

Olah [40c] has drawn attention to the fact that the first solid acid catalyst was suggested by Kameo, Nishimura and Manabe [71]. They used polystyrenesulphonic acid with nitric acid, but the system was unstable, as the catalyst was degraded by the strong acid. Olah and associates [72] developed a nitrating agent from *n*-butyl nitrate and acetone cyanohydrine nitrate by adding a per-fluorinated resinesulphonic acid (nafion–H). It provides an exceptionally clean way of preparing nitroaromatic compounds. Nitro compounds can be isolated by a simple filtration of the catalyst, without the need of any aqueous basic washing or workup. All by-products are removed during the reaction, as they are volatile. By way of azeotropic removal of water, the nitration can be brought to a very high yield.

ALKYL NITRATES AND BORON TRIFLUORIDE

Alkyl nitrates in sulphuric acid have already been used as nitrating agents (Vol. I, p. 122). Poly(phosphoric) acid [73] and Lewis acid halides [74–76] were also used with alkyl nitrates. Olah and Lin [77] nitrated a number of aromatic compounds with methyl nitrate and BF_3 in nitromethane solution. Only mononitration took place.

Spectroscopic examination of the nitrating solutions (infra red and Raman spectroscopy) did not show the presence of a detectable concentration of NO_2^+ ion. This does not exclude the possibility of nitrating aromatics (as has already been discussed pp. 23–24). Either the system $NO_2^+\ BF_4^-$ or a polarized complex $CH_3ONO_2 \longrightarrow BF_3$ is the nitrating agent.

Narang and M. J. Thompson [78] suggested using acetonecyanhydrine nitrate (ACN)  $(CH_3)_2C(ONO_2)CN$ and BF_3 as a nitrating agent. Olah and co-workers [124] reported recently that aromatic compounds can be nitrated with silver nitrate in acetonitrile solution in the presence of boron trifluoride at 25°C. With *p*-xylene the yield is up to 91% of mononitro compound. (See also Vol. I, p. 46).

NITRIC ACID AND MERCURY SALTS (Vol. I, p. 110)

Among different metal salts catalysing the nitration of aromatic systems, mercury salts occupy an exceptional position (perhaps tallium would also play a certain part, see p. 27).

A review on mercuric salts in nitration was given by Titov and Laptev [79]. Japanese authors: Tsutsumi and Iwata [80], Osawa and co-workers [81] have found that mercuric oxide and mercuric nitrate were catalysts of nitration with nitric acid. Komoto and co-workers [82] found that mercuric acetate catalysed nitration of toluene with nitric and acetic acid at 80°C.

Stock and T. L. Wright [83] came to the conclusion that nitration occurred in three steps:

(1) mercuration,
(2) nitrosodemercuration by the nitrosonium ion (NO^+) which exists in the nitrating mixture and is more energetic than the nitronium ion (NO_2^+) which does not produce the demercuration and only deprotonation,
(3) oxidation of the nitroso to nitro compound.

This can be depicted by a scheme established for toluene:

$$CH_3\,C_6H_5 + Hg(OAc)_2 \longrightarrow CH_3\,C_6H_4\,Hg(OAc) + HOAc \qquad (26)$$

$$\big\downarrow NO^+ \text{ (demercuration)}$$

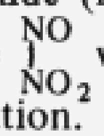
$$CH_3\,C_6H_4NO + Hg\,OAc^+ \qquad (27)$$

$$CH_3\,C_6H_4\,NO + H\,NO_3 \longrightarrow CH_3\,C_6H_4NO_2 + HNO_2. \qquad (28)$$

Inorganic Nitrate Salts and Trifluoroacetic Acid (Vol. I, p. 46)

Nitric acid salts in the presence of other acids have been previously described (Vol. I, p. 46). It was recently reported by Crivello [125] that metal nitrates in trifluoroacetic anhydride (TFAA) can nitrate aromatic compounds at room temperature in very good yields. Thus ammonium nitrate with TFAA nitrated benzene to nitrobenzene with a yield of 95%.

NITROUS ACID (Vol. I, p. 116)

Dinitrogen trioxide (nitrous anhydride) was found to have m.p. −100.7°C [84]. Its structure  $ON{-}NO_2$ was confirmed by Anderson and Mason [84] through N^{14} NMR examination.

Nitration with nitrous acid can proceed in three ways:

(1) through the addition to double bonds (Schechter [48]),
(2) through the nitrosation which is the first step of the reaction followed by the oxidation of the nitroso product,
(3) through the formation of nitric acid from the nitrogen dioxide built from nitrous acid:

$$HONO \longrightarrow N_2O_3 \longrightarrow NO{+}NO_2 \xrightarrow{[O]} 2NO_2. \qquad (29)$$

The known reaction of NO_2 with water yields equimolar proportions of HNO_3 and HNO_2. The latter can again furnish NO_2 according to (29) and finally NO_2^+ according to (5a) and (5b).

Nitrous salts in strong acids are subjected to dissociation with the formation of nitrosonium ion NO^+:

$$HONO + H_3O^+ \longrightarrow NO^+ + 2H_2O. \qquad (30)$$

The nitrosonium ion can be subjected to oxidation with the release of NO_2 and further formation of HNO_3 and HNO_2.

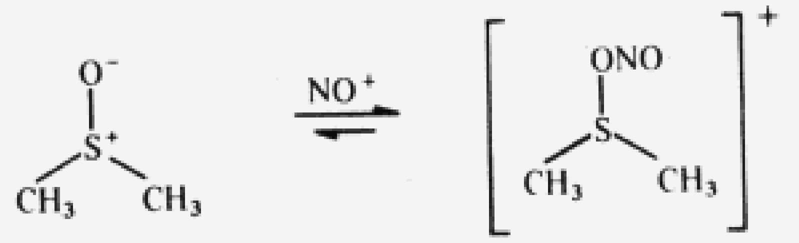
The presence of nitrosonium ion has been spectroscopically established by Singer and Vamplew [85] in aqueous (58%) perchloric acid. It showed strong bands 260 and 420 nm, and molecular HONO gave weak maxima of 340 and 390 nm. The equilibrium constant of the reaction (30) was determined by Turney and Wright [86].

It was stated by T. Urbański and Kutkiewicz [9] that 8-hydroxyquinoline could be nitrated by boiling with a dilute (*ca.* 0.3%) solution of $NaNO_2$ in 10% hydrochloric acid to yield 5,7-dinitro-8-hydroxyquinoline. If the reaction passes through the nitrosation it cannot give a dinitro product, as the nitrosation can introduce only one nitroso group. Still more convincing is the fact the 8-hydroxy-5-nitroquinoline when heated to *ca.* 90°C with *ca.* 0.4% solution of sodium nitrite in 10% hydrochloric acid produced 5,7-dinitro-8-hydroxyquinoline with 60% yield. It is known that a mononitrophenol (and thus the 8-hydroxy-5-nitroquinoline) cannot be nitrosated. Subsequently the formation of the dinitro compound is the result of nitric acid formed from NO_2 and yielding NO_2^+ according to the scheme rationalized already – reactions (5a) and (5b) (p. 24).

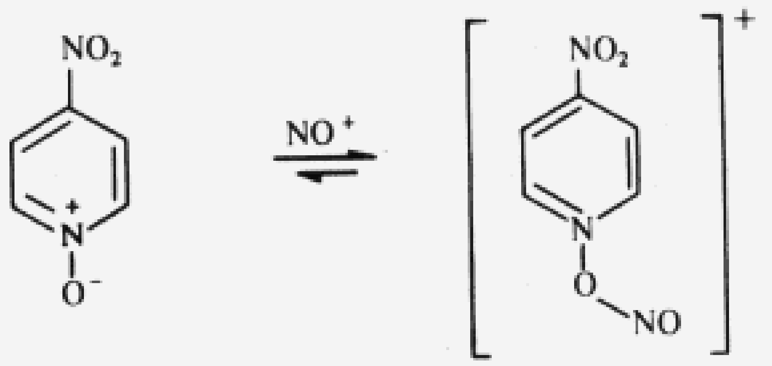
The view that the nitration of phenol is inconsistent with the commonly accepted prior nitrosation scheme was also expressed by Ross and co-workers [87].

A few more examples of nitration by nitrous acid should be mentioned: the nitration of *m*-fluoro-*N*-dimethylaniline [88], nitration of phenothiazine-3 [89] and phenothiazine-5-oxide [90]. They also should be rationalized by formulae (5a) and (5b).

Recently Olah and associates [91], [40c] obtained *S*- and *N*-nitrito onium ion salts (31) and (32), and found them to be electrophilic nitrating agents:



(31)



(32)

The addition of N_2O_3 to a double bond $C{=}C$ was given in Vol. I, p. 96. Recently Hauff, Traillon and Perrot [92] described the addition of nitrous anhydride to α, β-unsaturated ketones of the chalcone type to yield pseudonitrosites, which were reduced with $LiAlH_4$ to a number of amines.

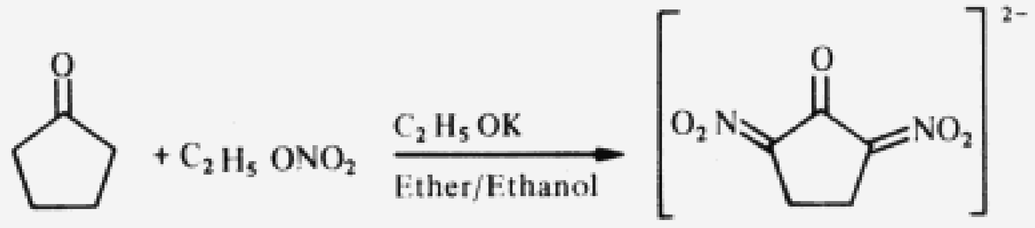
NITROSYL CHLORIDE

Nitrosyl chloride, NOCl (b.p. −5.5°C, m.p. −64.5°C) is the acid chloride of nitrous acid. As is known, it is evolved from 'aqua regia' together with chlorine and can be formed from NO and chlorine in the presence of charcoal as a catalyst at 40–50°C.

Nitrosyl chloride can be added to a double bond to yield dichlorides, dichloronitroso compounds and also chloronitro compounds of the type $Cl-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-NO_2$ through the secondary reaction of oxidation [114–117].

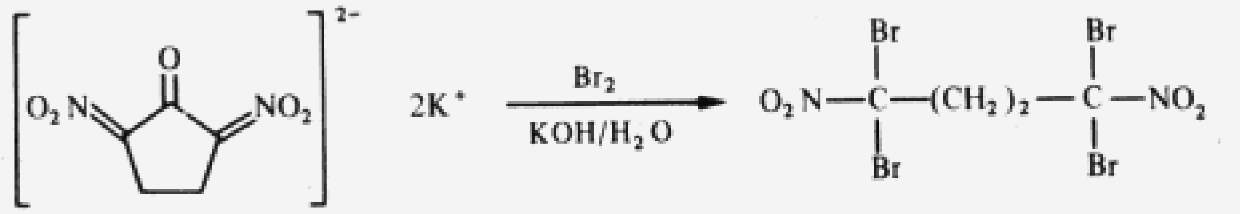
NITRATE ESTERS IN ALKALINE MEDIUM (Vol. I, p. 122)

The nitration of active methylene compounds by the action of nitrate esters under basic conditions is a general and convenient method for introducing a nitro group in α-position to the activated group. The pioneering work of Thiele [93] and Wislicenus [94] should be added to the previously (Vol. I) mentioned papers. Also the work of Wieland and associates [95] should be mentioned as producing the dipotassium salt of dinitro cyclic ketones, according to equation (33):



(33)

The authors claimed 75% yield, but Feuer and co-workers [96] obtained only 10% yield with the formation of tarry by-products. They also carried out a ring opening reaction which is already known [97]



(34)

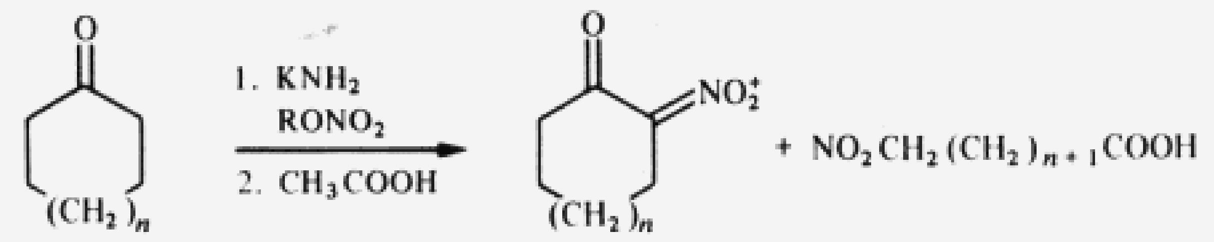
Kornblum [98] reviewed earlier papers on the nitration of ketones and nitriles.

Feuer [99] carried out a considerable amount of work on nitration with nitrate esters and introduced a number of improvements. The basic features of his method consist in:

(a) using a stronger base than potassium ethoxide,
(b) using an aprotic solvent.

Thus he reacted on compounds with an active methylene group with a basic reagent such as sodium or potassium amide and liquid ammonia as a solvent. He summarized his earlier work in a review paper [99].

A few examples should be mentioned here. Feuer and co-workers [100] nitrated cyclopentanone, hexanone and heptanone with an excess of amylnitrate (3–3.5 eqv.) in the presence of potassium amide (3–3.5 eqv.) in liquid ammonia at −33°C obtained dinitro-dipotassium salts of the type as in equation (33) with yields of 94, 94.5 and 85% respectively. With 2 eqv. of alkyl nitrate and 1 eqv. of KNH_2 mononitration occurred with a simultaneous ring opening to ω-nitrocarboxylic ester [100, 101]:

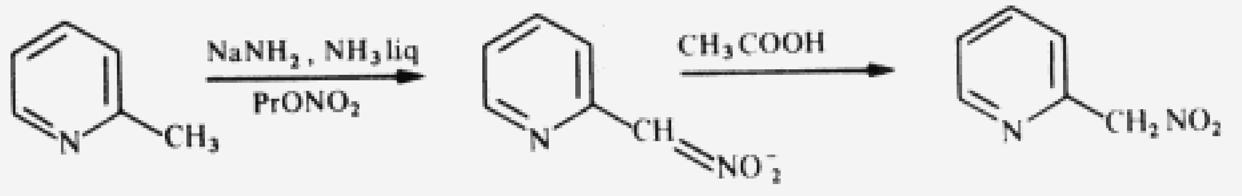


(35)

In the case of cyclooctanone the yields were: 60% mononitropotassium salt and 21% nitroester.

While experimenting with esters of the homologues of acetic acid $RCH_2COO.C_2H_5$ with the same nitrating agent Feuer and Monter [102] obtained not only the nitro product $R\underset{NO_2}{C}HCOOC_2H_5$ but also nitroalkanes of the type RCH_2NO_2 sometimes with a high yield (48% when $R = C_6H_5$). If $R = O_2NC_6H_5$, the nitration does not take place due to the high acidity of the nitrated compound.

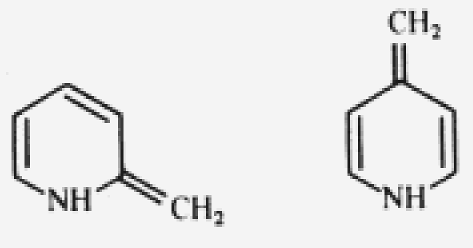
An interesting application of the method of nitration of active methylene group is the nitration of methyl group in α- and γ-picoline [103], for example:



(36).

(92%) (58%)

This should be rationalized (according to the author of the present book) in terms of the reactivity of tautomeric forms of α- and γ-picolins:



α γ

Also Feuer and Friedman [104] in a similar way obtained phenylnitromethane derivatives with a yield of 40–55% by experimenting with amyl nitrate and KNH_2 in liquid ammonia at −33°C on *o*- and *p*-substituted toluene $RC_6H_4CH_3$, on condition that the substituent is an electron attracting group, for example $R = CN, SO_2\,C_6H_5$ etc.

The same method of nitration was used to nitrate compounds with active CH groups: arylidene [105] and aldimines [106] i.e. compounds of the structure $RCH = N{-}NH\,C_6H_5$ and $RN = CH\,CH_2R$ respectively. Nitro compounds $R\underset{NO_2}{C} = N\,NH\,C_6H_5$ (yield 91%) $RN = \underset{NO_2}{C}\,CH_2R$ (yield 40–70%) respectively were obtained.

Feuer and co-workers [107] obtained nitroalkylphosphonate esters. $R\underset{NO_2}{C}H\,P(O)(OR)_2$ from the alkylesters $R\,CH_2P(O)(OR)_2$ by using a modification of his method while potassium amide in liquid ammonia proved to be unsuitable to nitrate. More energetic agents, such as butyllithium in THF or Li-diisopropylamide in THF were applied at −60°C and gave a yield of 27–41%.

Recently, Petrov and co-workers also [121, 122] published a number of papers on the nitration of active methylene groups with nitrate esters.

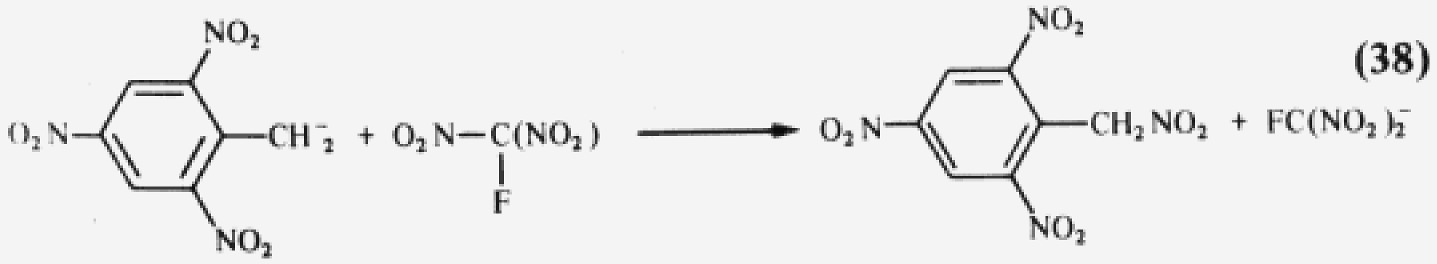
ALIPHATIC NITRO COMPOUNDS

Tetranitromethane (TNM) continued being used as a nitrating agent. An extensive review of the properties of TNM including nitration was given by Perekalin and Altukhov [118]. The property of TNM as a nitrating agent is based on the fact that one of the four nitro groups of this compound can readily be split off. The properties of TNM are described in Chapter VIII.

Penczek, Jagur-Grodzinski and Szwarc [108] described the mechanism of the nitration of 1,1-diphenylethylene with tetranitromethane. As the first step an undefined charge–transfer complex (CT) is formed which dissociates into ions reacting to yield 1,1-diphenyl-2-nitroethylene:

$$\begin{aligned}&(C\,H_5)_2\,C = CH_2 + C(NO_2)_4 \longrightarrow (CT) \longrightarrow (C\,H_5)_2\,C^+\,CH_2NO_2 + \\&(NO_2)_3\,C^- \longrightarrow (C\,H_5)_2\,C = CH\,NO_2 + (NO_2)_3CH.\end{aligned} \tag{37}$$

Sitzman, Kaplan and Angers [109] used fluorotrinitromethane [110] to nitrate the methyl group in 2,4,6-trinitrotoluene. The reaction was carried out in *ca.* 14% aqueous NaOH at 0–5°C followed by quenching with hydrochloric acid:

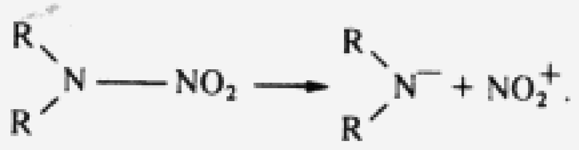


(38)

NITRAMINES (Vol. I, p. 125)

Nitroguanidine in sulphuric acid has been found to be a nitrating agent. T. Urbański and Zyłowski [111] extended this observation to other nitramines, such as nitrourea, dimethyldinitroxamide and cyclonite. They nitrated anthraquinone dissolved in sulphuric acid by adding nitramines to the solution at room temperature and keeping the solution for a few hours. With cyclonite and dimethyldinitrooxamide the yield of 1,5-dinitroanthraquinone was 34 and 77% respectively. When nitroguanidine and nitrourea were used, the solution was heated to 100–120°C and the yield of the dinitro derivative was 67%.

The reaction suggested the formation of the nitronium ion:



(39)

Nitration with cyclonite in sulphuric acid confirms the suggestion of Šimeček (Vol. III, p. 81) that the decomposition of cyclonite in sulphuric acid yields nitronium ions.

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CHAPTER 2

NITRATION OF AROMATIC SYSTEMS

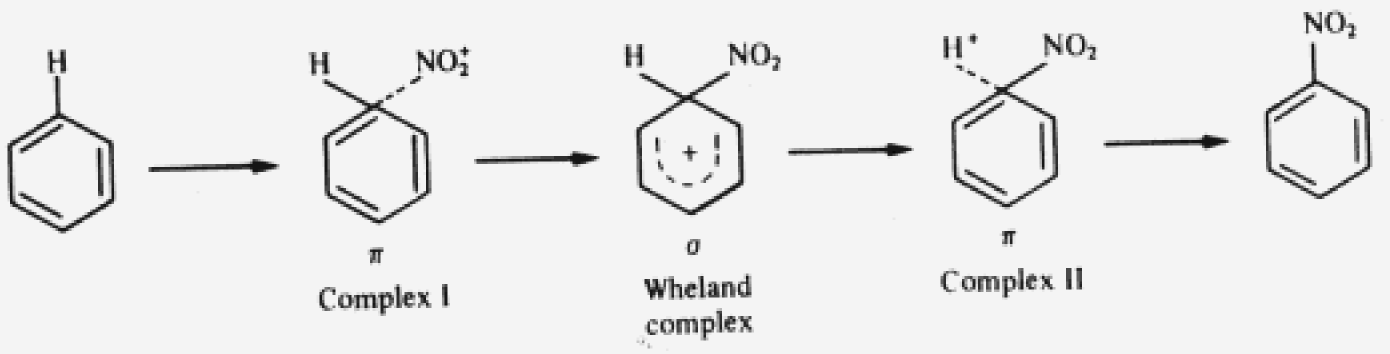
A considerable number of excellent monographs and review papers have been published on the nitration of aromatic systems and all references can be found therein [1–8]. Only main outlines will be given here.

It is now generally accepted that the nitration of aromatics proceeds stepwise. A stepwise process of substitution (known now as electrophilic substitution) was first suggested in 1901 by Lapworth [9] then by Pfeiffer and Wizinger [10], Melander (Vol. I, p. 38) but only later the idea was rationalized by a number of authors almost simultaneously due to the advent of spectroscopy and improvements of preparatory methods of new reagents.

A reference should be made to the paper by Nagakura and Tanaka [11] on the calculated reactivity of the nitronium ion NO_2^+ and aromatic hydrocarbons. They suggested the formation:

1. of an aromatic cation which is a π complex,
2. Wheland transition state with the formation of a σ complex.

This can be depicted at present by scheme (1):



(1)

A simplified energy diagram is presented in Fig. 5 based on that of Olah and associates [12, 13]. In a similar way R. D. Brown [14] considered that an electrophilic substitution begins by the formation of unstable charge–transfer complexes. R. Taylor [15] observed anomalously high and solvent dependent o/p ratios for the nitration of biphenyl and rationalized it that a π-complex between NO_2^+ and biphenyl is formed initially and rearranges to a more stable σ-complex at the *ortho* position of one of the aromatic rings of biphenyl. The final experimental proof for stable Wheland σ-complexes being formed as intermediates of the nitration was given by Olah and co-workers [12] when they isolated benzaltrifluoride-nitronium boron tetrafluoride

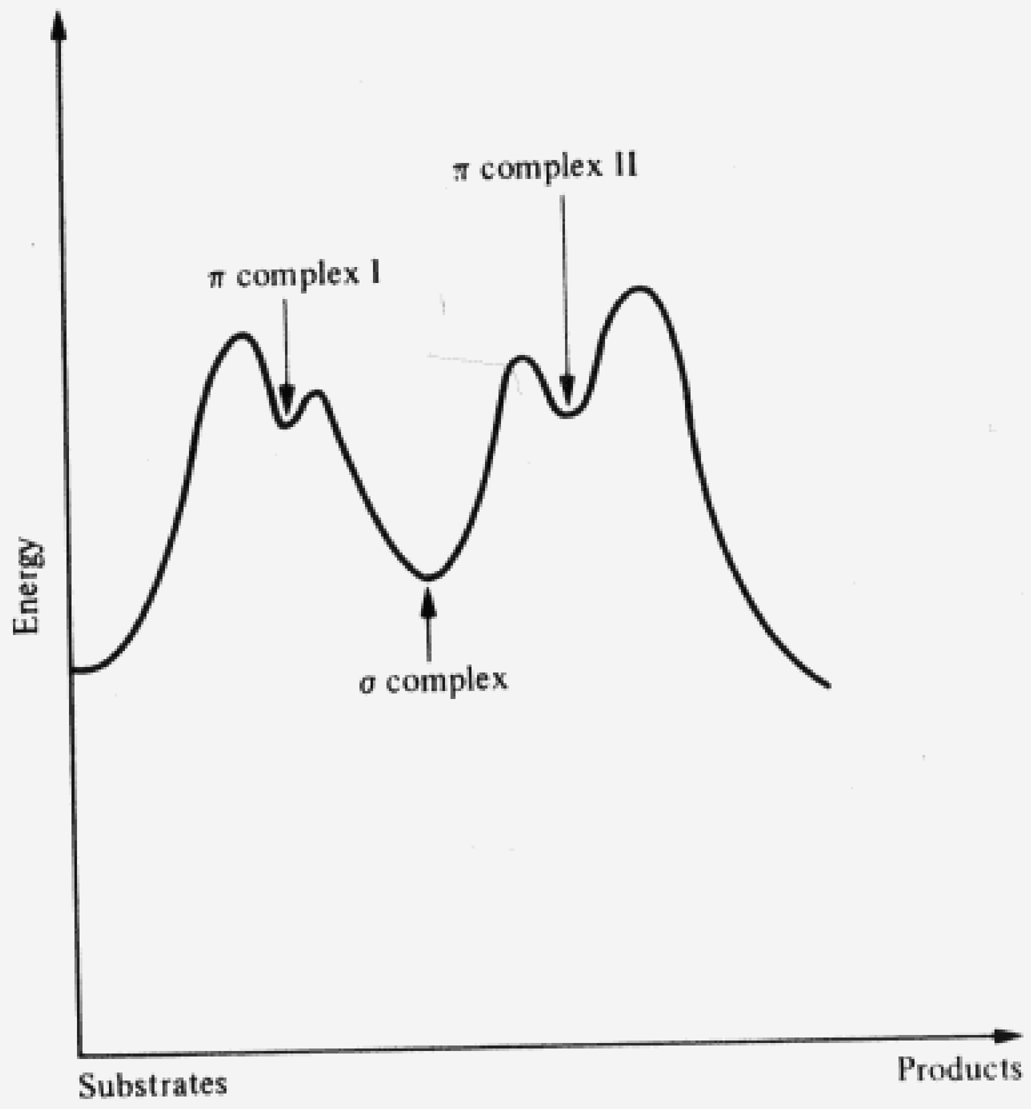
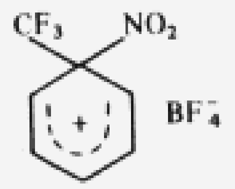
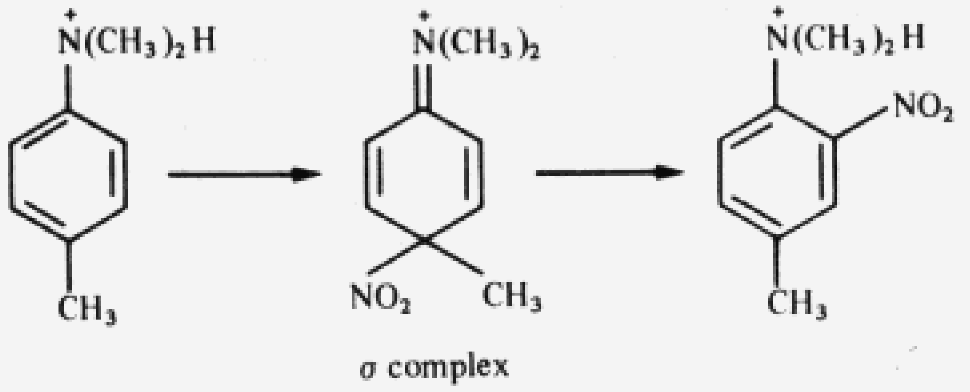


FIG. 5. Simplified energy diagram of the nitration of aromatics with nitronium ion.



by acting on benzaltrifluoride ($C_6H_5CF_3$) with nitronium fluoride (NO_2F) and boron trifluoride at −120° to −100°C, a yellow coloured complex stable up to −50°C resulted. Olah and associates [13] pointed out that the Wheland structure is not a transition state (as σ complexes) but a relatively stable intermediate.

Recently Fujiwara and co-workers [16] found that the nitration of *N,N*-dimethyl-*p*-toluidine in 70–77% sulphuric acid proceeds by a formation of the σ complex through the *ipso*-attack (on *ipso*-nitration see p. 50) and after that the ion is rearranged to the nitro compound (2):



(2)

Ridd considered that the amino group in the nitrated compound stabilizes the σ-complex.

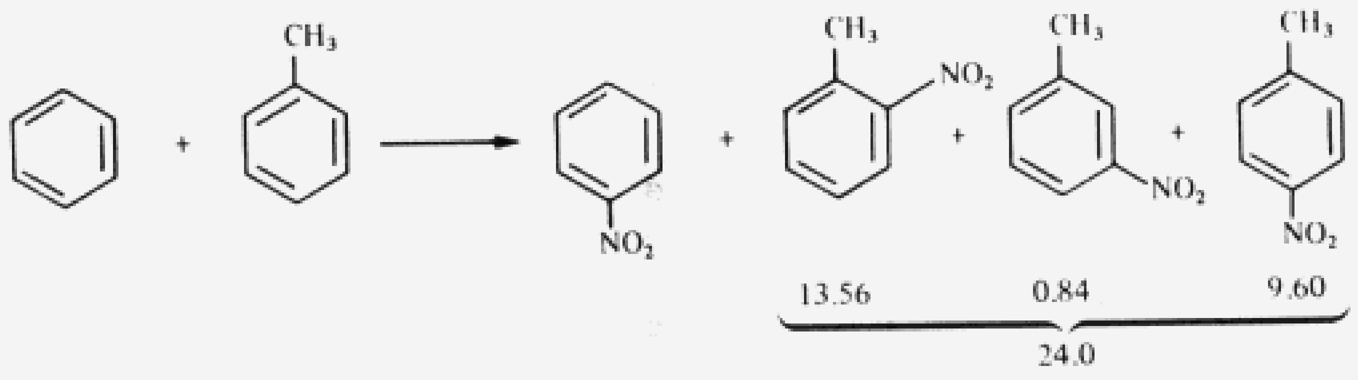
INFLUENCE OF SUBSTITUENTS ON NITRATION

Very important from both theoretical and practical points of view were experiments on the influence of substituents on the rate and the yield of nitration. For that purpose the method of competitive nitration was used. It was originally developed by Wibaut [17] to study the rate of nitration with nitric acid–acetic anhydride of toluene, chlorobenzene and bromobenzene in relation to benzene. The experiments established a higher rate of nitration of toluene and a lower rate of chloro- and bromobenzene:

$$C_6H_5CH_3 > C_6H_6 > C_6H_5Cl > C_6H_5Br.$$

Thus it was stated that the methyl group activates the aromatic ring, whereas chloride and bromine deactivate it.

The method of competitive nitration was extensively used by Ingold and co-workers [18] and by a number of other authors. Very spectacular are the results of the relative rates of nitration of benzene and toluene obtained by Cohn and co-workers [19]. The nitration was carried out with nitric acid in nitromethane. They gave relative reactivities of each position of toluene:



(3)

Thus the relative rate of the substitution of toluene is 24.0 (benzene being postulated as 1.0).

The following is an example of the calculation of 'partial rate factors'.

The rate constant of the substitution of toluene k_T is: $k_T = 2k_o + 2k_m + k_p$, where k_o and k_m are the rate constants of one of the *o*- and *m*-positions respectively and k_p the rate constant of the *p*-position. If the rate constant of one of the positions of benzene is k_b, the total rate constant of benzene k_B is equal to $6k_b$. From this can be written:

$$\frac{k_T}{k_B} = (2k_o + 2k_m + k_p)/6k_b = 24. \quad \textbf{(4)}$$

The fraction of each isomer, for example the rate at the *ortho* position relative to the total rate of the substituted benzene can be calculated:

$$\text{fraction of } o\text{-product} = 2k_o/(2k_o + 2k_m + k_p) = \frac{13.56}{24} = 0.565. \quad \textbf{(5)}$$

From equations (4) and (5) the rate of nitration can be calculated of a single position in toluene to that of in benzene:

$$2k_o + 2k_m + k_p = 144\,k_b \quad \textbf{(6a)}$$

and

$$2k_o + 2k_m + k_p = \frac{2k_o}{0.565}, \quad \textbf{(6b)}$$

hence:

$$144\,k_b = \frac{2k_o}{0.565} \quad \textbf{(6c)}$$

and

$$\frac{k_o}{k_b} = 41 \quad \textbf{(6d)}$$

The value k_o/k_b is called partial rate factor in *ortho* substitutions and expressed now by symbol f_o or o_f. Similarly the partial rate factors for the other positions in toluene can be calculated:

$$\text{for } meta \text{ positions } f_m \text{ or } m_f = k_m/k_b = 2.5, \quad \textbf{(7)}$$

$$\text{for } para \text{ position } f_p \text{ or } p_f = k_p/k_b = 58 \quad \textbf{(8)}$$

Bird and Ingold [20] have given the following comparative figures for the nitration of toluene and chlorobenzene with nitric acid in nitromethane at 25°C – Table 11.

For partial rate factors of different hydrocarbons and under different nitration conditions see [4].

The figures of the rate constants k for the reactions of *m*- and *p*-substituted benzene derivatives have been taken for Hammett equation [21]:

TABLE 11. Isomer distribution and partial rate factors of the nitration of toluene and chlorobenzene

	Relative rates k/k_b	% Isomer distribution			Partial rate factors		
		o	m	p	o_f	m_f	p_f
Toluene	21	61.7	1.9	36.4	38.9	1.3	45.8
Chlorobenzene	0.031	29.6	0.9	69.5	0.028	0.00084	0.130

$$\log k/k_B = \rho \cdot \sigma \qquad (9)$$

where:

ρ is the measure of the sensitivity of the substance to ring substitution
$\rho = 1$ in benzoic acid,
σ is characteristic to the substituent.
For nitration $\rho = -6.0$

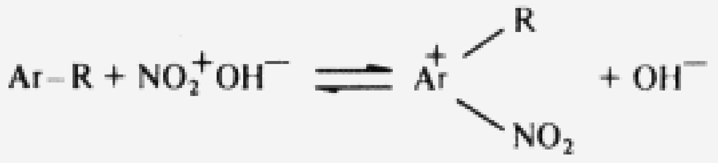
A plot of log k/k_B against σ was given by Stock [22] and reproduced here – Fig. 6.

A particular instance of nitration is *ipso*-nitration.

IPSO-NITRATION

The aromatic electrophilic substitution is usually represented by replacing a hydrogen atom with an electrophilic agent. However it was recently shown that the electrophilic attack is not restricted to aromatic carbon bonded with hydrogen. This is the case in *ipso*-nitration where the attack occurs at a substituted aromatic ring carbon. The *ipso*-reaction was placed in focus by Perrin and Skinner [23] in 1971 and two excellent review papers appeared on the subject: by Myhre [24] and by Hahn and associates [25].

A general trend of *ipso*-nitration can be depicted by scheme (10):



$$\mathrm{Ar{-}R} + \mathrm{NO_2^+OH^-} \rightleftharpoons \overset{+}{\mathrm{Ar}}\begin{smallmatrix}\diagup \mathrm{R} \\ \diagdown \mathrm{NO_2}\end{smallmatrix} + \mathrm{OH^-} \qquad (10)$$

Ipso ion
(Nitroarenium ion)

The reaction is characterized by its reversibility. The *ipso* ion is able to further react and can be used as a valuable intermediate. By using the rate data existing in the literature [26] Myhre [24] calculated the partial rate factors of the nitration of toluene as shown in formula I. Fischer and Wright [27]: they found that the nitration of toluene at low temperature with acetic acid–acetic an-

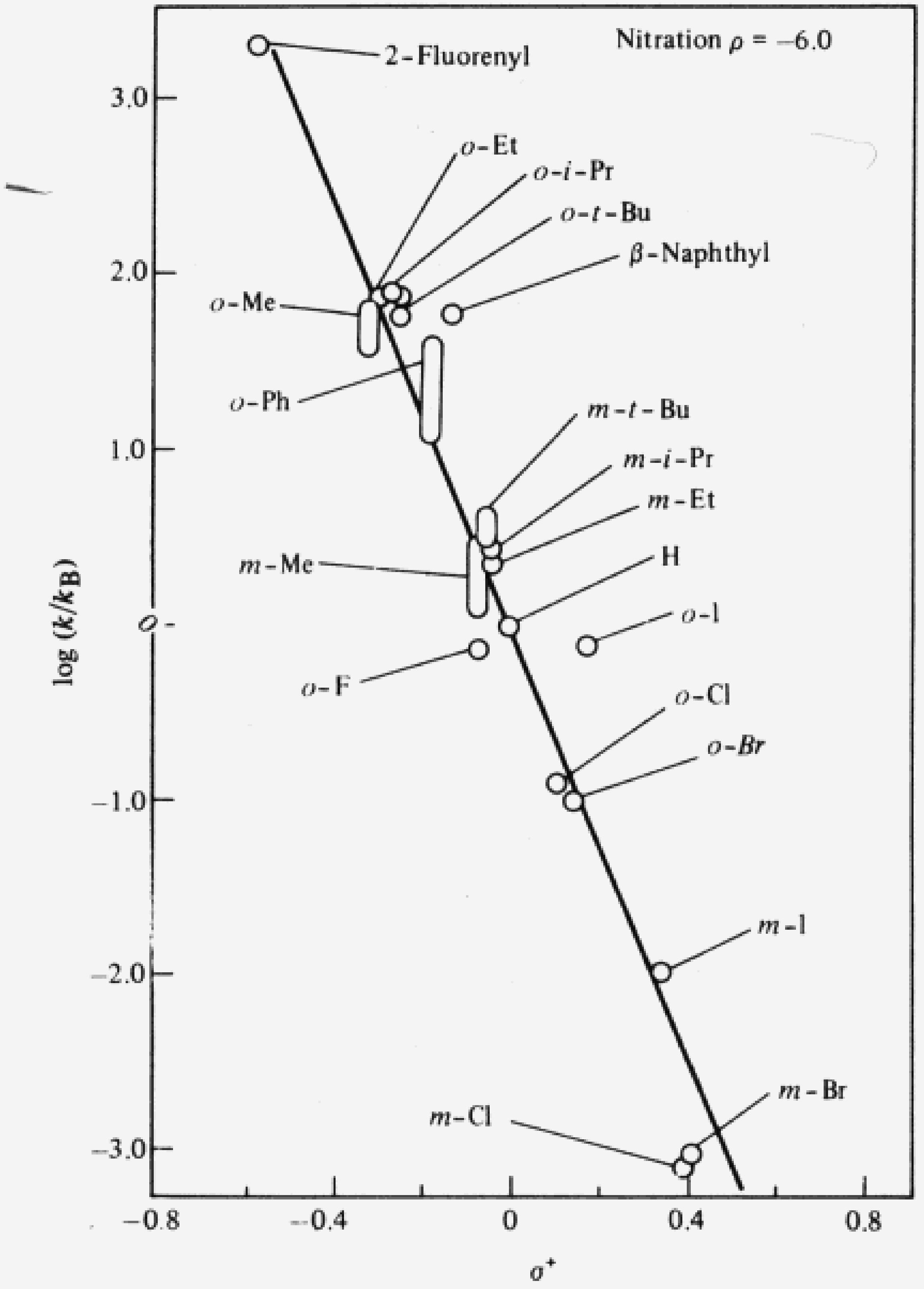
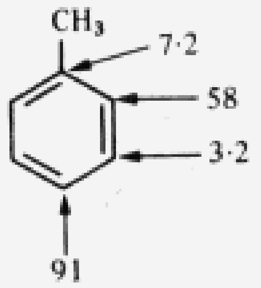


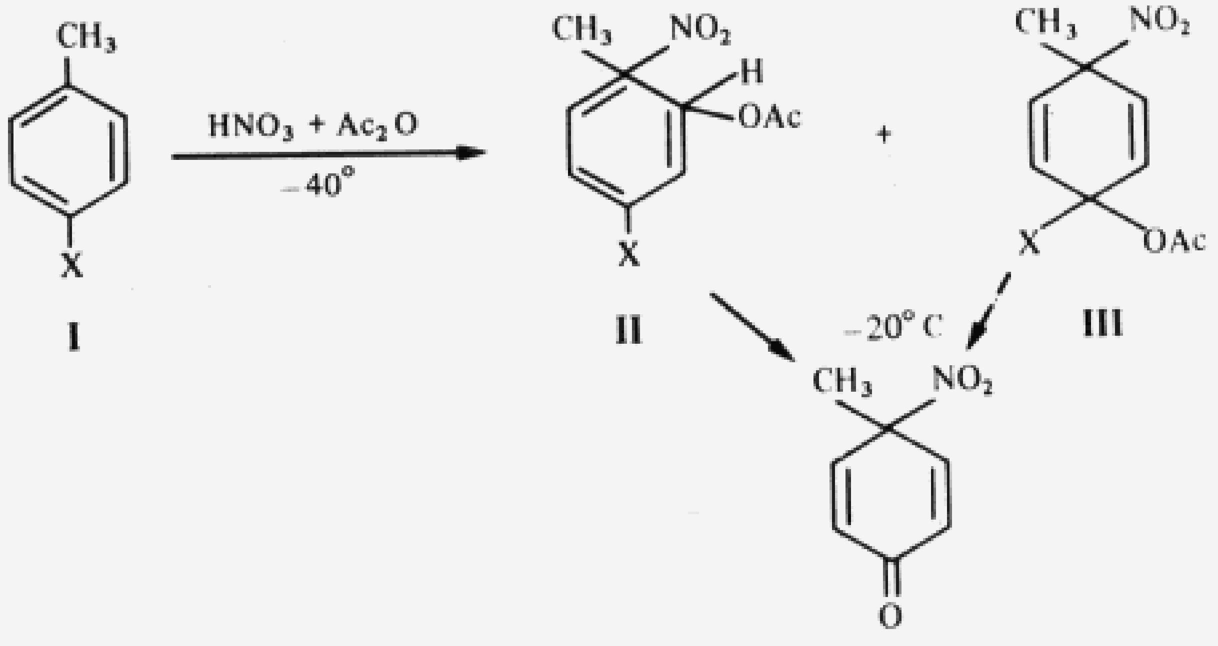
FIG. 6. Log k/k_B against σ^+ according to Stock [22].

hydride–nitric acid solution in *ipso* position is more than twice faster than in *meta* position:



Thus, surprisingly enough, position 1 is more reactive than *meta*.

While reacting–*p*–halogenotoluenes (I) with nitric acid–acetic anhydride at –40°C Fischer and co-workers [28] obtained two isomers: *ortho* II and *para* III of nitrocyclohexandienylacetates. In the instance of X = F, the overall yield was 100% and the ratio $o/p = 25/75$.



I II III IV (11)

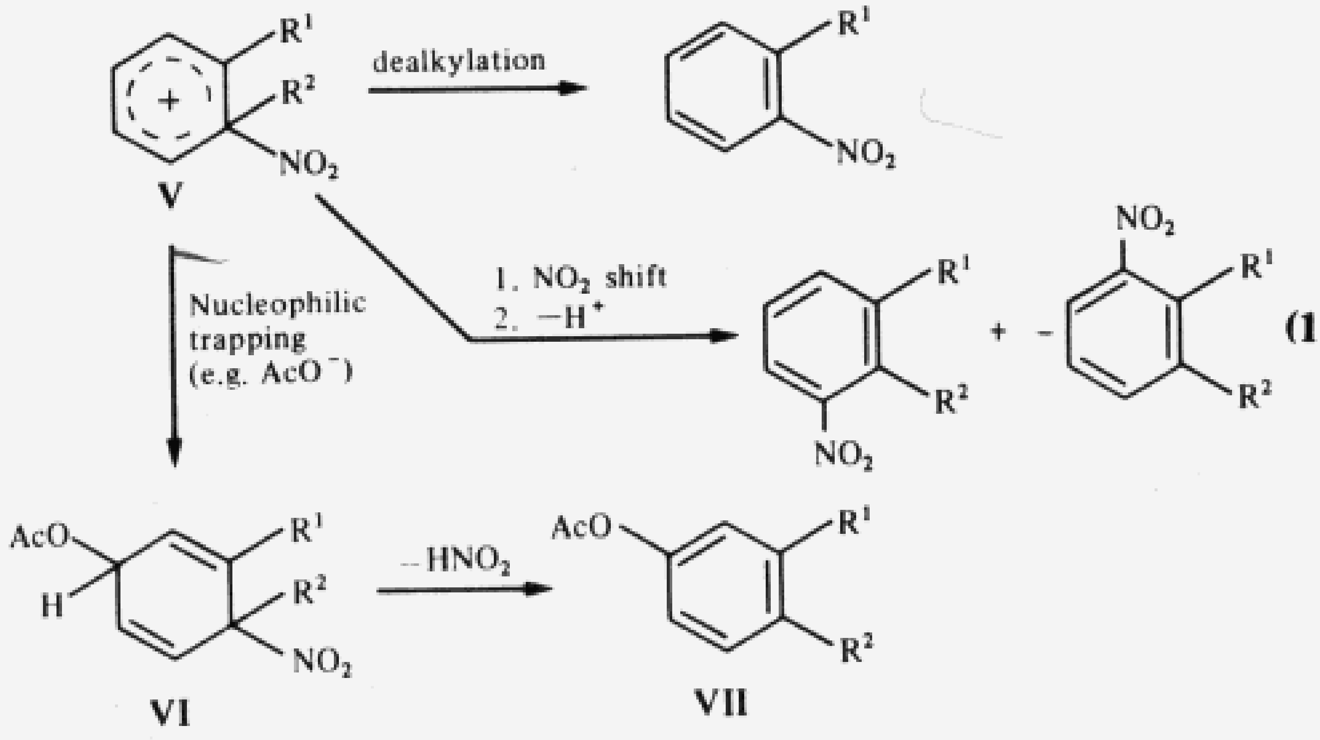
On warming to –20°C both isomers were converted to 4-methyl-4-nitrocyclahexa-2,5-dienone (IV). Barnes and associates [29] reported that they prepared several 4-alkyl-4-nitrocyclohexa-2,5-dienones in good yield up to 85% by low temperature –40° to 0°C nitration of the appropriate 4-alkylphenylacetates with 90% nitric acid or acetyl nitrate in acetic anhydride.

Nitration of a number of 4-substituted toluenes with a formation of *ipso*-compounds, their transformation and Hammett equation for *ipso*-nitration was also described [30].

The transformation of *ipso*-products leading to different compounds was summarized by Galley and Hahn [31]. The nitroarenium ion cyclohexadienyl cation (V) derived from *ipso* attack can undergo the reactions:

(1) dealkylation [32],

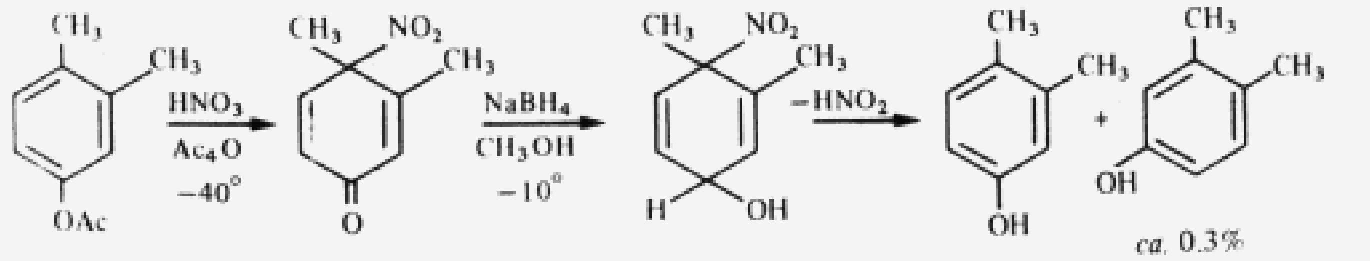
(2) nitro group migration, followed by deprotonation [33, 34],
(3) nucleophilic trapping which may be followed by HNO$_2$ elimination [35] (12).



(12)

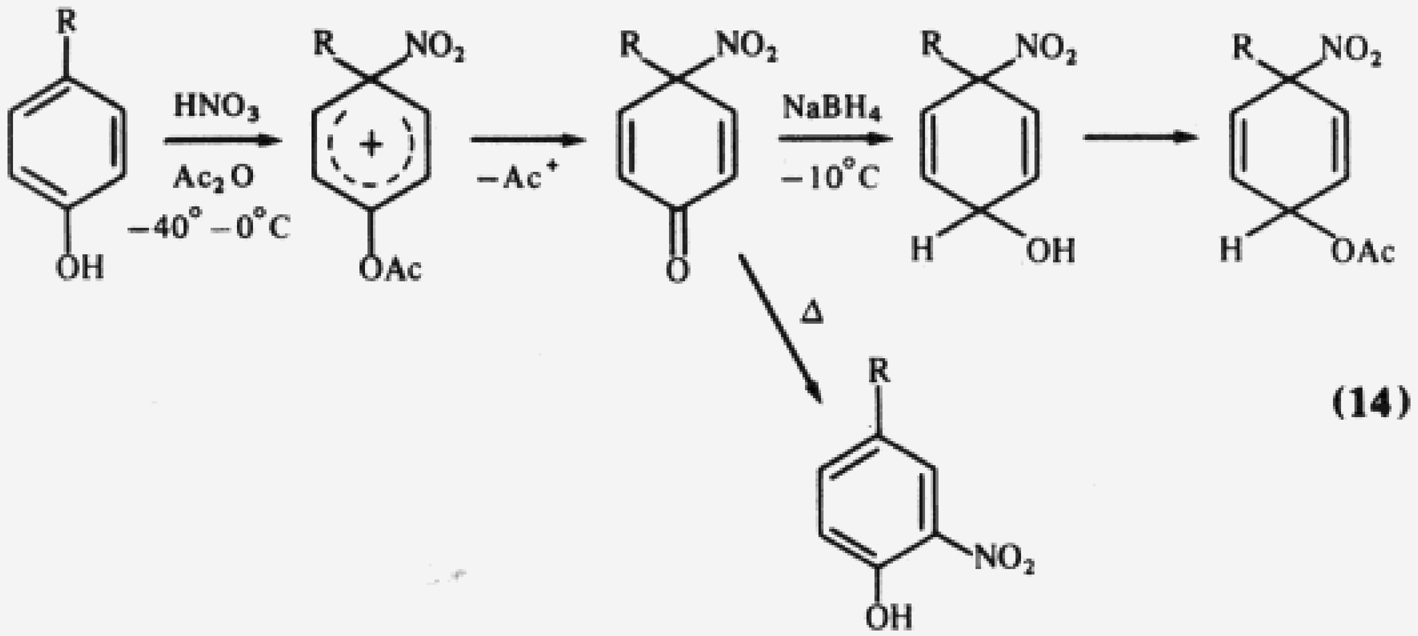
The formation of acetoxy compounds VII which was originally thought to be a result of electrophilic substitution [36] has been shown to occur as an addition–elimination reaction through the *ipso*-attack [37]. The formation of cyclohexadienyl derivatives of type VI provide a rational explanation of some non-conventional aromatic substitutions [38].

Recently Myhre and co-workers [39, 40] described the nitration of a number of 4-alkylphenol acetates to yield 4-alkyl-4-cyclahexadienones. Reduction of these dienones with sodium borohydride gave 4-alkyl-nitrocyclohexadienols which can be converted to nitrophenols. Here an interesting intramolecular migration of a hydroxyl group was recorded [39]:



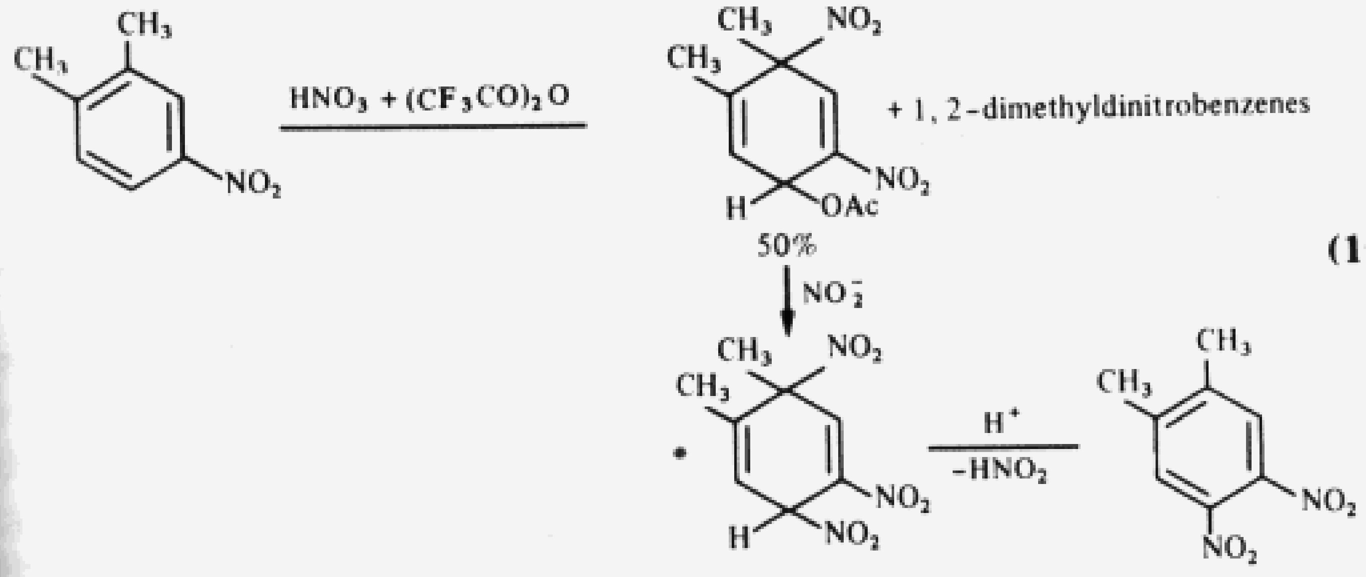
(13)

The influence of the temperature of nitration of 4-alkyl-phenol acetates was examined by the same authors [40] and simultaneously and independently by Schofield and associates [41]. The latter examined the thermal migration of the nitro group:



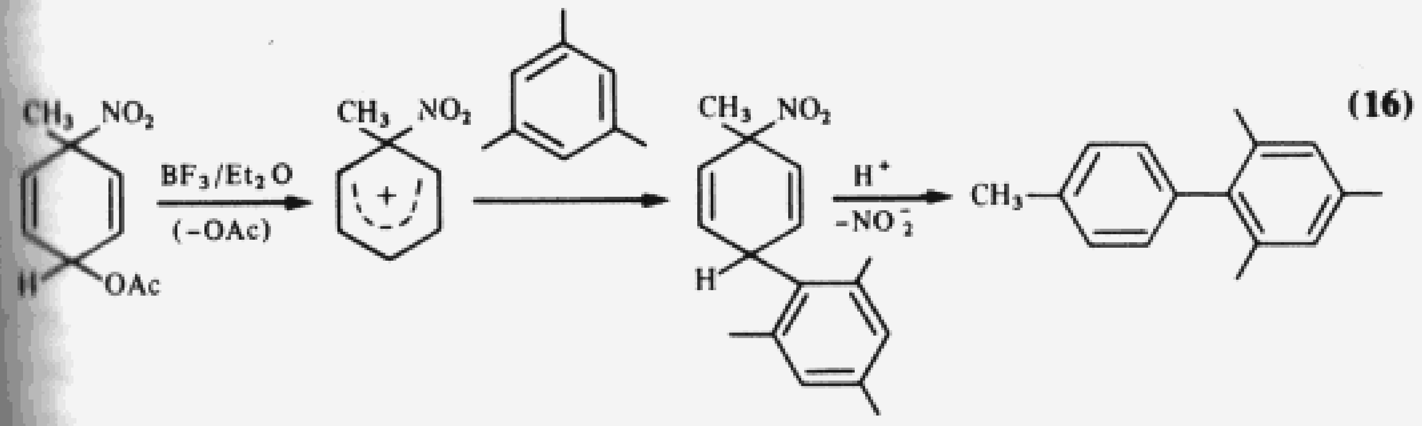
(14)

An interesting reaction of the nitration of 1,2-dimethyl-4-nitrobenzene in a mixture of nitric acid with trifluoroacetic anhydride was reported by Fischer and Iyer [42]. 4,5-Dimethyl-2,4-dinitrocyclohexa-2,5-dienyl acetate was originally formed. It reacted with nucleophiles, such as NO_2^- to yield eventually 1,2-dimethyl-4,5-dinitrobenzene:



(15)

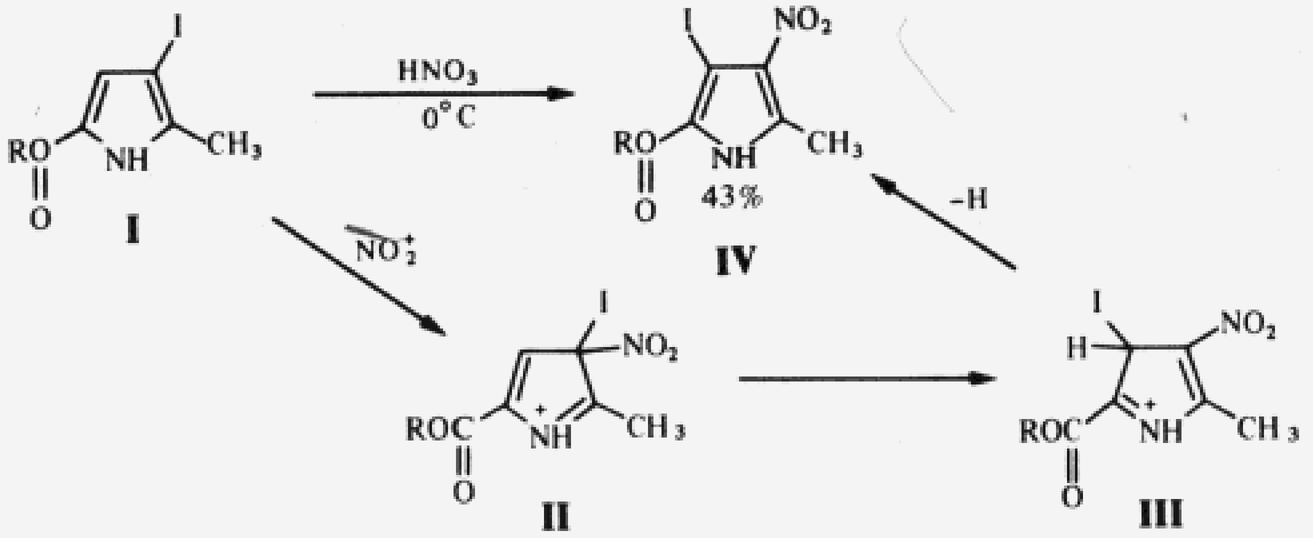
One of the possible practical applications of nitro cyclohexandienyl acetate is coupling it with some aromatics to obtain diphenyl derivatives [43]:



(16)

An interesting *ipso*-nitration of nitrofurane derivative was reported [44]. gem-Nitro compound is formed and $\begin{matrix}NO_2\\NO_2\end{matrix}\!\!>\!C\!<$ is converted to $O = C<$.

Some recent investigations of the nitration of heterocyclic aromatic systems, such as derivatives of pyrrol should be mentioned, as they seem to support the idea of the additional mechanism of NO_2^+ in the sense of *ipso*-reaction. Thus, Sonnet [45] described the reaction:



(17)

He explains it in terms of the formation of intermediate *ipso*-addition product II which is transformed into III through the migration of iodine atom (17). The loss of the proton from III yielded eventually IV.

AROMATIC RADICAL CATION

Dynamic nuclear polarization of aromatics in the course of nitration was suggested [92] and recently Ridd and Sandal [93] gave evidence of it on the nitration of *N,N*-dimethylaniline in sulphuric acid and stated a strong polarization of 15N nuclei rationalized in terms of the formation of the radical pair $[ArH^{+\bullet}NO_2^{\bullet}]$ from the preformed radicals $ArH^{+\bullet}$ and $NO_2^{\bullet}$.

REVERSIBILITY OF AROMATIC NITRATION

It is generally accepted that the C-nitration of the aromatic system is an irreversible process. The problem has already been discussed in Vol. I, p. 41 and the conclusion was that the C-nitration group can migrate if this meets with steric hinderance, for example, the nitro group in *ortho* position to adjacent group or groups. It was also substantiated by T. Urbański and Ostrowski (Vol. I, p. 41) but the conclusion was that the mobility of the nitro group cannot be regarded as the proof of the reversibility of the C-nitration.

However, the problem was recently revived. It was recalled that Frisch, Silverman and Bogart [46] pointed out the lability of *o*-nitro group in 4-amino-3-nitroveratrole. This compound in acid condition can be transformed into 4-

amino-5-nitroveratrole when heated with acetic–phosphoric acid mixture, but the fact has not been further examined.

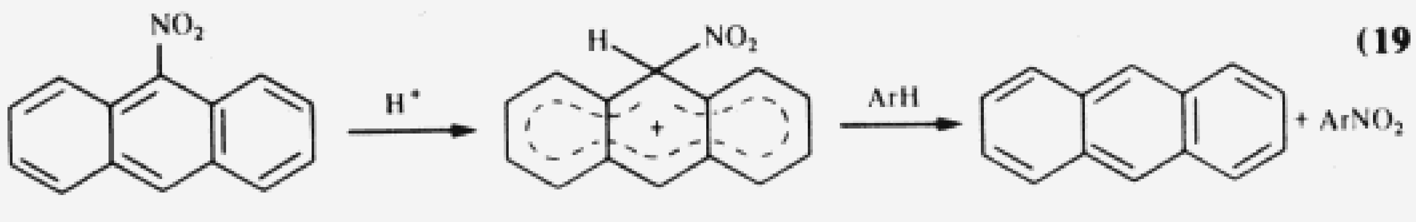
Later Gore [47] found that 9-nitroanthracene when heated with sulphuric and trichloroacetic acid to 95°C, after 15 min revealed a considerable amount of nitric acid *ca.* 80% and anthraquinone *ca.* 20%. This author suggests a scheme:

$$ArNO_2 \rightleftharpoons [ArHNO_2]^+ \rightleftharpoons ArH + NO_2^+ \qquad \textbf{(18)}$$

but when nitrobenzene was added he failed to find dinitrobenzenes.

The author comes to the conclusion that 'normal aromatic nitration' should continue to be regarded as essentially irreversible, but can be reversed in certain cases when the nitro group is in a steric hindered position.

Cerfontain and Telder [48] acquired an indication of the possible reversibility of aromatic nitration of anthracene-9-d, and finally Olah and associates [49] obtained evidence of the reversibility of the nitration of 9-nitroanthracene and pentamethylnitrobenzene when they found that these substances catalysed by superacids can yield nitrobenzene, nitrotoluene and nitromesytylene when reacted with benzene, toluene and mesitylene respectively. They suggested the mechanism as follows:



(19)

It should however be borne in mind that positions 9 and 10 in anthracene are not typically aromatic. They are manifested by a higher reactivity than positions α and β as established by MO calculation [50]. In addition 9-nitroanthracene shows a non-planar structure with the nitro group out of plane [51] as pointed out by Cerfontain and Telder [48]. This is very similar to the position of the nitro group in *o*-dinitrobenzene and all derivatives of benzene with two *ortho* nitro groups. It is well known that the nitro groups in *o*-dinitrobenzene are not planar and there is no conjugation of double bonds in this compound. The fact is also reflected in ultraviolet-absorption spectrum of *o*-dinitrobenzene which deviates from those of *m*- and *p*-dinitrobenzenes (Vol. I, p. 169, Table 20).

The degenerate rearrangement was studied by Mamatyuk and associates [52]. They showed that the rearrangement takes place through successive intermolecular 1,2-migration of the nitro group.

The conclusion should be drawn that the reversibility of nitration can occur when a nitro group in *ortho* position is displaced through steric hindrance (aromatics with two nitro groups in *ortho* position, or a nitro group is in *ortho* position to a bulky substituent, e.g. *t*-butyl group) and the nitro group is no longer planar to the aromatic ring. This is also the case for 9-nitroanthracene.

Another example of the migration of a nitro group through an *ipso*-nitro form was described by Myhre [33], Hahn and co-workers [34].

NITRATION UNDER THE INFLUENCE OF GAMMA RADIATION

(Vol. I, p. 126)

Several papers appeared after the pioneer work of Minc and co-workers (Vol. I, p. 126). Papers by Chernova and co-workers [53] and Sugimoto and co-workers [54] have shown that even dilute nitric acid (0.1–1.7 N) can nitrate aromatic compounds when subjected to gamma radiation from Co^{60}. Benzene yielded nitrobenzene and *p*-nitrophenol as the result of free radical reactions.

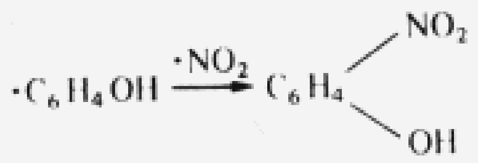
Nitric acid is decomposed by radical mechanism according to equation [55]:

$$HNO_3 \rightsquigarrow HNO_3^* \longrightarrow \cdot OH + \cdot NO_2 \qquad \textbf{(20)}$$

As a result of the formation of free radicals OH and NO_2 the following are reactions which can be rationalized through the diagrams (21) [54]:

$$C_6H_6 \longrightarrow C_6H_5^{\cdot} \xrightarrow{\cdot NO_2} C_6H_5NO_2 \qquad \textbf{(21a)}$$

$$C_6H_5^{\cdot} \xrightarrow{\cdot OH} [C_6H_5OH] \xrightarrow{\cdot OH} \cdot C_6H_4OH + H_2O \qquad \textbf{(21b)}$$



$$\cdot C_6H_4OH \xrightarrow{\cdot NO_2} C_6H_4\begin{matrix} NO_2 \\ OH \end{matrix} \qquad \textbf{(21c)}$$

The yield of these reactions was found to be $G = 0.47–0.96$ G value is the number of molecules produced by the radiation energy of 100 eV. The yield is small when $G < 1$.

Falęcki, Minc and T. Urbański [56] examined the action of liquid N_2O_4 at room temperature on *n*-hexane when subjected to irradiation with Co^{60}, and obtained 1% yield of 1-nitrohexane along with a considerable amount of carboxylic acids and some nitrate esters.

Lee, Chung and Albright [57] examined the nitration of propane with nitric acid vapours at 425–430°C when propane to nitric acid ratios were 6:1 and 10:1. Gamma irradiation with 195,000 roentgens per hour from Co^{60} source of propane gas did not significantly increase the yield of the nitration, except when oxygen was added to the reactants. Also the irradiation of liquid propane prior to the reaction increased the yield by 10–15% relative percentages. The products distribution (nitromethane, nitroethane, 1-nitropropane and 2-nitropropane) was unaffected by radiation.

A number of papers were dedicated to the nitration of aromatics by gamma radiation of the aromatics present in aqueous solutions of sodium nitrate [58–61]. Broszkiewicz [59] found that sodium nitrate in the presence of oxygen yielded *o*-nitrophenol from benzene (yield $G = 41$). Chernova and Orekhova [58] obtained nitrobenzene (yield $G = 0.2$) when irradiation was carried out in an atmosphere of nitrogen.

Nowak [62] examined the influence of radiation on the system dodecane – 30% TBP tributyl phosphate – nitric acid used as extractants of burned up nuclear fuel and found that nitro compounds were formed even at low concentrations of nitric acid. Nitroso and carbonyl compounds were also formed.

INDIRECT METHODS OF INTRODUCING A NITRO GROUP

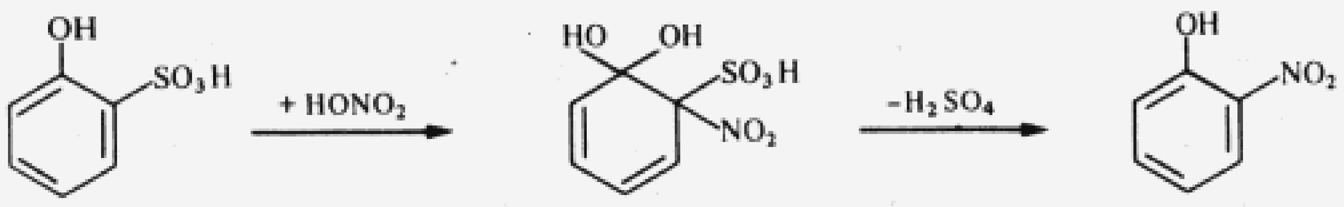
Substitution of Sulphonic Group (Vol. I, p. 126)

In addition to the work of Marqueyrol, Carré and Loriette (Vol. I, p. 500), and Pascal (Vol. I, p. 501), two more papers should be mentioned: by King [63], Olsen and Goldstein [64]. King pointed out the importance of the presence of phenol-2,4-disulphonic acid and *p*-phenolsulphonic acid in the sulphonated phenol, whereas Olsen and Goldstein suggested that the nitration of sulphonated phenol involves, in the first stage, the introduction of nitro groups into the aromatic ring. In the light of more recent investigations by T. Urbański and Leśniak [65a], it was found that two processes run simultaneously:

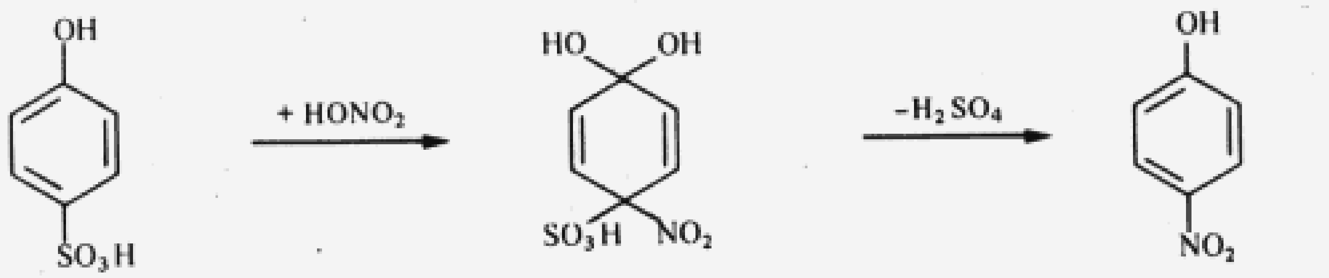
(1) introduction of a nitro group into phenol–sulphonic acid,
(2) substitution of the sulphonic group.

This was established by the chromatopolarographic method of Kemula [65b].

Also it was rationalized [65] that by reacting nitric acid on *o*- and *p*-phenolsulphonic acid coloured quinoid intermediate additions products are transformed into nitrophenol:



(22a)



(22b)

Substitution of Diazo Group

The well known reaction of Sandmeyer [66a] was suggested by Waters [66b] in terms of free radical intermediates generated by electron transfer. Russell [66c] rationalized the reaction with a stable nitroaromatic anion where copper metal serves as the electron donor and cuprous ion as the electron acceptor (23):

$$\begin{gathered}
\mathrm{ArN_2^+ + Cu \longrightarrow Cu^+ + [ArN_2^{\bullet}] \longrightarrow N_2 + Ar^{\bullet}} \\
\mathrm{Ar^{\bullet} + NO_2^- \longrightarrow ArNO_2^{\bullet -}} \qquad (23) \\
\mathrm{ArNO_2^{\bullet -} + Cu^+ \longrightarrow ArNO_2 + Cu.}
\end{gathered}$$

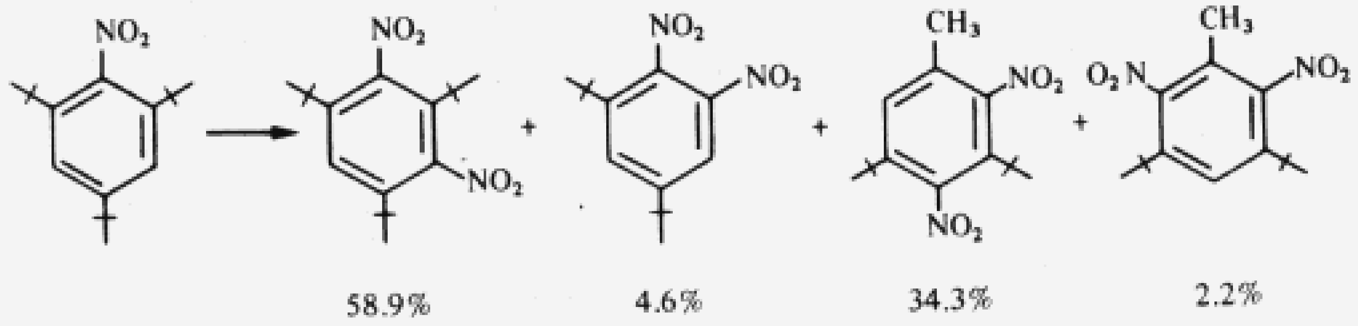
Substitution of Halogen (Vol. I, p. 127)

The reaction of Kornblum (Vol. I, p. 127) became a much more convenient method of making longer chain nitroalkanes.

In halogen derivatives of benzene, halogen can be replaced by the nitro group under the action of nitric acid. The first paper on the subject by Zinke [67] should be mentioned.

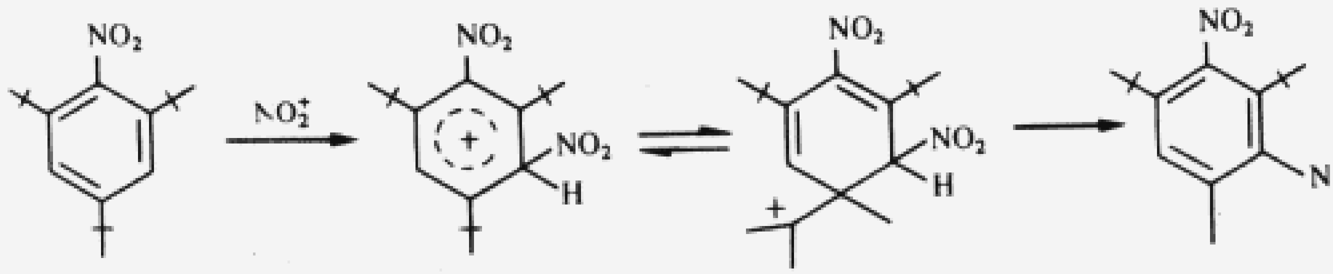
Substitution of t-Butyl Group

The nitration of 2,4,6-tri-*t*-butylnitro benzene leads to several unexpected products as shown by Myhre and Beng [68] (24):



(24)

In addition to the replacement of *t*-butyl by the nitro group a transformation of *t*-butyl into the methyl group was established. This is rationalized in terms of the reactions:



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INTRODUCING THE NITRO GROUP BY OXIDATION (Vol. I, p. 131)

Oxidation of Primary Amino Group

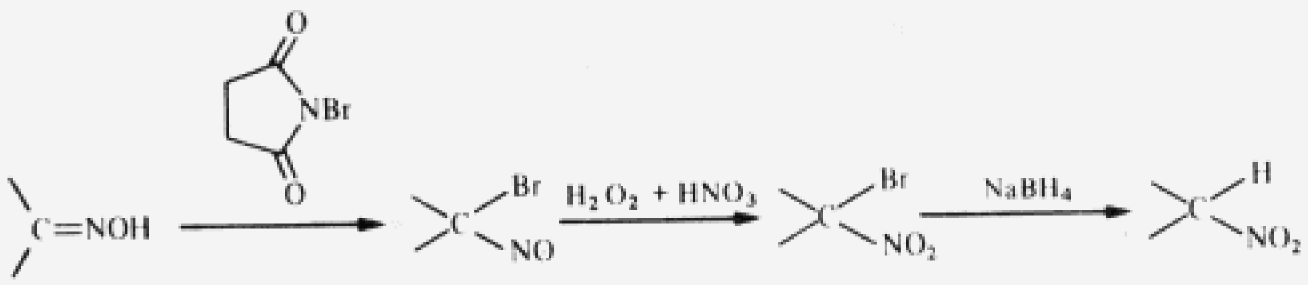
Oxidation of primary amino group in aromatic compounds by peroxytrifluoro acetic acid has been reported by Clarke and Steele [69]. The yield was 90%.

A much spectacular achievement was recently obtained by Nielsen and co-workers [70]. By oxidizing the primary amino group attached to a benzene ring bearing a number of nitro groups, polynitrobenzenes were obtained. Thus, by oxidizing 2,3,4,6-tetranitroaniline and pontanitroaniline they obtained penta-nitro- and hexanitrobenzene respectively. They used peroxy disulphuric acid (98% hydrogen peroxide in sulphuric acid or oleum at 25°C) as an oxidizing agent.

Further use of this oxidant to produce a number of polynitro aromatics was reported by Nielsen and co-workers [71] in their remarkable paper. The authors also reviewed work on the other oxidants used to pass from HN_2 to NO_2 : Caro acid, peracetic, permaleic, *m*-chloroperbenzoic and perbenzoic acids. They pointed out that the power of the oxidant is proportional to the acid strength of deoxy peracid. Peracetic and *m*-chloroperbenzoic acids are suitable for the oxidation of aliphatic primary amines, whereas peracetic, peroxytrifluoroacetic and peroxymaleic acids are best for the oxidation of ring substituted anilines. Potassium persulphate in sulphuric acid was also used successfully [71].

Oxidation of Oximes

Iffland and co-workers [72] described an original method of forming nitro derivatives of alicyclic compounds by the oxidation of oximes:



(26)

The first step was the bromination of the oxime with bromocuccinimide to yield a bromonitroso compound on which the oxidation of hydrogen peroxide with nitric acid was transformed into bromonitro compound. The latter by acting with sodium borohydride furnished a secondary nitro compound with a yield of 33–80%. The method was particularly suitable for the formation of nitro derivatives of nitro cycloalkanes. The method is unsuitable for aromatic ketoximes and aldoximes. However, Barnes and Patterson [73] extended the method to aldoximes by using ozone as an oxidizing agent on gem-chloronitroso compounds. The removal of chlorine was accomplished by palladium. Piotrowska, Sas and Winiarski [74] used the Adams catalyst for the removal of chlorine.

Emmons and Paganò [75] succeeded in oxidizing oximes of alicyclic ketones with trifluoro peracetic acid to yield nitrocyclopentan and nitrocyclohexane with the yield of 60–62%. Oximes of steroids were oxidized with nitric acid–hydrogen peroxide to yield gem-dinitro derivative which under hydrogenation on platinum gave nitrosteroids with the nitro group in positions 3, 4, 6, 7 and 17 [76].

DIFFUSION CONTROL IN NITRATION

The importance of diffusion in chemical kinetics was pointed out by Eyring in 1936 [77], and subjected to a wide description by Glasstone, Laidler and Eyring [78]. The applicability of the principles of the diffusion control in various reactions and the nitration among them was recently reviewed by Ridd [79].

For reaction in solution the analysis of diffusion control is usually based on the concept of a molecular encounter. When two solute molecules come together in a solution they are effectively held within a cage of solvent molecules and make a number of collisions with each other within this cage. Such a set of repeated collisions is termed an encounter. The lifetime of each encounter is very short, 10^{-10} to 10^{-8} sec.

While considering the influence of the encounter rate on chemical reactivity a microscopic and macroscopic diffusion control should be mentioned. In microscopic diffusion control, the reactants exist together in a homogeneous solution and the reaction occurs on every encounter.

The term macroscopic diffusion control describes processes in which the rate of the reaction is determined by the rate of mixing of the reactant solutions.

According to Ridd [79] the clearest evidence for microscopic diffusion control in nitration comes from the kinetic studies of Coombes, Moodie and Schofield [80] with low concentration of nitric acid in 68.3% sulphuric acid as a solvent. In this medium the concentration of nitronium ions is proportional to the concentration of molecular nitric acid according to equation (27):

$$HNO_3 + H^+ \rightleftharpoons NO_2^+ + H_2O. \tag{27}$$

Since the concentration of nitronium ion is very small the rate of the nitration is determined by equation (28):

$$\text{Rate} = k\,[\text{ArH}]\,[HNO_3]. \tag{28}$$

Relative rate coefficients from (28) are listed in Table 12. The most interesting feature of the results according to Ridd [79] is the limiting reaction rate of

TABLE 12. Relative rates of nitration at 25°C by nitric acid in various media

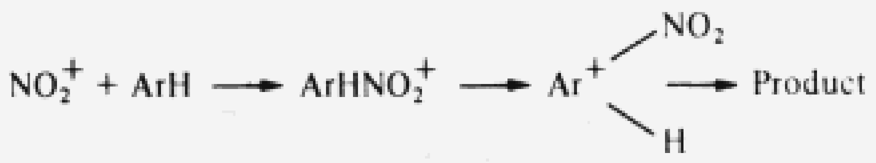
Substrate	Sulphuric acid 68.3%	Perchloric acid 61.03%	Sulfolan 7.5% aq	Acetic acid 8–19% aq
1.	2.	3.	4.	5.
Benzene	1*	1*	1*	1*
Toluene	17	19	20	23
o-Xylene	38		61	
m-Xylene	38		100	136
p-Xylene	38	85	114	
Mesitylene	36	78	350	
Anisole	13†		175	
Phenol	24	31	700	
m-Cresol		59		
Biphenyl	16		15.5	
Naphthalene	28	27	33	*ca.* 66
l-Naphthol		85		
Thiophene		52	*ca.* 150	

* Postulated.

† According to Barnett *et al.* [81].

the compounds being about forty times the reactivity of benzene. This limit is quite inconsistent with the predictions of the additivity principle. From the additivity principle and the partial rate factors for the nitration of toluene the reactivities of *m*-xylene and mesitylene would be expected to exceed that of benzene by factors of 400 and 16,000 respectively [80].

Thus the limiting reaction rate does not arise from the rate of formation of the electrophile NO_2^+ and from a general breakdown in the additivity principle. The authors [80] suggest that the limit arises from the rate-determining formation of an encounter pair ArH NO_2^+ between the nitronium ion and the aromatic substrate according to scheme (29):



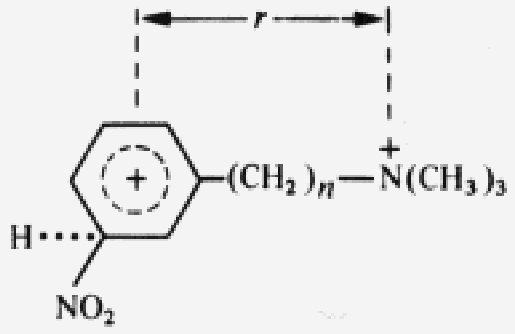
$$NO_2^+ + ArH \longrightarrow ArHNO_2^+ \longrightarrow Ar^+\begin{matrix} NO_2 \\ H \end{matrix} \longrightarrow \text{Product} \qquad (29)$$

A number of Swiss authors described their experiments on mass diffusion and the influence of mixing on nitration: Ott and Rys [82], Pfister, Rys and Zollinger [83].

Schofield and co-workers [94] determined the half life of the nitronium ion on nitration of benzene in the presence of phosphoric acid of the concentration 90.3 to 97.9%. The values were found to be 2 to 33 (increasing with the concentration of H_3PO_4). On the basis of these data they concluded that nitration with NO_2^+ is diffusion controlled at H_3PO_4 over 95%.

INFLUENCE OF A POSITIVELY CHARGED SUBSTITUENT

Ridd [6] examined the influence of positively charged substituent on the yield of ***para*** and ***meta*** product of nitration. He found that $-\overset{+}{N}H_3$ deactivated the position *meta* much more strongly than *para*. Modro and Ridd [95] rationalized the influence of a positively charged substituent on the reacttion of nitration of compounds taking into consideration the distance *r* between two positive charges in the Wheland intermediate:



IV

Thus when $n = 0$ the partial rate factor f_m was 0.9×10^{-7}. When $n = 2$ and 3 the values for f_m were 0.13 and 0.47 and the yield of *meta* derivative was 19 and 5% respectively.

SIDE REACTIONS (Vol. I, pp. 75, 437)

Nitrating medium, that is, nitric acid or mixtures of nitric acid with sulphuric acid or other agents promoting the formation of nitroxonium cation, is obviously a strongly oxidizing medium, hence a number of side reactions – mainly oxidation reactions – take place during nitration. This was described in Vol. I (pp. 75, 437) and more recently reviewed in a number of excellent papers [84–86].

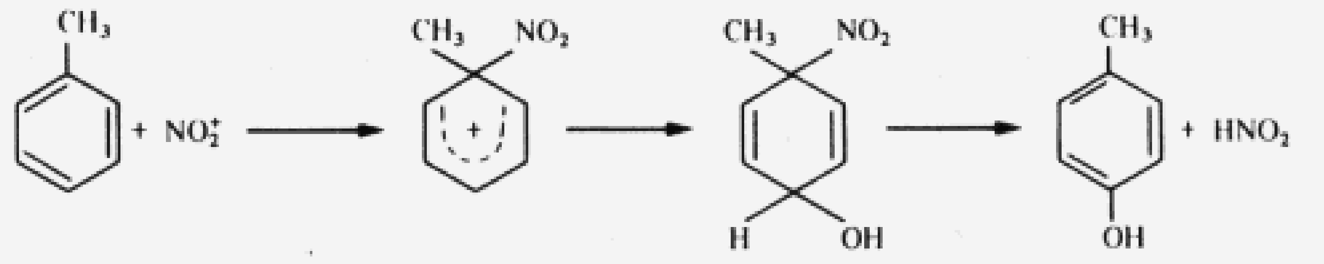
It is generally accepted that nitric dioxide and nitrous acid are catalysts of oxidation reactions. Thus Ross and Kirshen [84] came to the conclusion that the NO_2 evolved in the equilibrium

$$2\,HNO_3 \longrightarrow \tfrac{1}{2}\,O_2 + H_2O + 2\,NO_2. \qquad (30)$$

is the active oxidizer. This was based on their study of the action of nitric acid/sulphuric acid on dinitrotoluenes. The oxygen evolved in (30) is the oxidizing agent.

A striking fact was reported by Longstaff and Singer [87]. They found that formic acid cannot be oxidized by pure nitric acid alone or in mixtures with other mineral acids at 25°C, but oxidation took place in the presence of nitrous acid or NO^+ ion. Halahan and co-workers [88] studied the oxidation of several dinitrotoluenes in the course of their nitration and found that the relative rates of oxidation were in direct inverse relationship to their rates of nitration.

Hanson and co-workers [85] pointed out that nitro compounds with phenolic function are the main by-products of nitration of aromatic hydrocarbons. A number of papers by Dodak and co-workers [89] were dedicated to the formation of phenols in the course of nitration of hydrocarbons. However, the idea of phenols being formed through the action of NO^+ ion does not seem to be feasible on the experimental grounds that the addition of urea to the nitrating mixture does not prevent the formation of phenols and the addition of sodium nitrite does not foster the formation of nitrophenols [85]. Hanson rationalized the mechanism of formation of nitrophenols by an *ipso*-attack of NO_2^+ on hydrocarbon (31):



(31)

Phenols on nitration can yield derivatives of *p*-benzoquinone, for example [90].

Gaseous products which accompany the nitration are CO and CO_2. Toluene on nitration to trinitro derivative forms tetranitromethane (the mechanism of its formation is given in the chapter dedicated to the production of trinitrotoluene). Chlorobenzene and other chlorinated aromatic hydrocarbons yield chloropicrin.

In papers dedicated to side reactions to nitration, no attention has been paid to the formation of ammonia in the course of the reaction. It is formed from hydrogen cyanide produced by drastic decomposition of nitro compounds. This was discussed in detail in Vol. I, pp. 76–77. The mechanism of the formation of HCN from C-nitro compounds also explains the fact that these nitro compounds yield ammonia in Kjeldahl analysis, where the substance is subjected to the action of oleum at high temperature.

A very important oxidation by-product of the nitration of toluene to trinitrotoluene is so called 'white compounds'. It was found in the course of continuous methods of nitration of toluene.

Its structure is dicarboxy-tetranitroazoxybenzene as shown by Joshi and Patwardhan [91]. The formation and proof of the structure will be given in the chapter on formation of trinitrotoluene.

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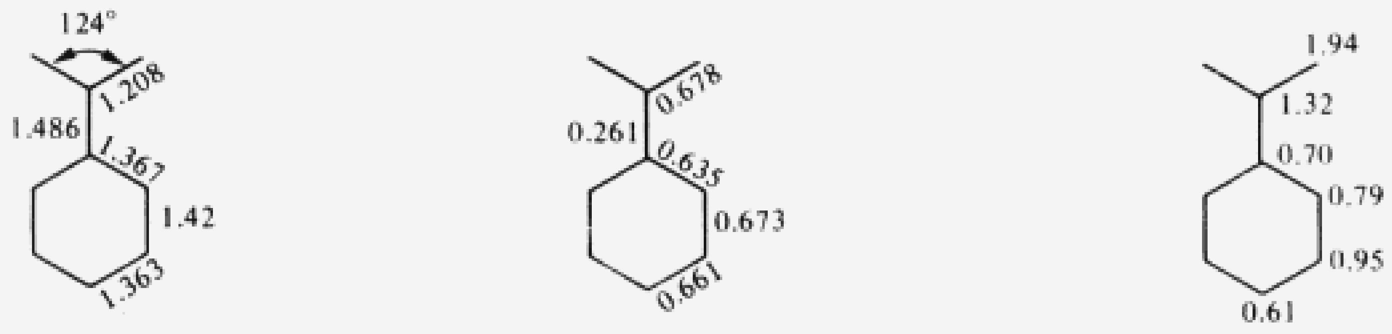
CHAPTER 3

STRUCTURES AND PHYSICO-CHEMICAL PROPERTIES OF NITRO COMPOUNDS

(Vol. I, p. 165).

A few excellent reviews appeared recently on the structure of the nitro group and the spectroscopy of nitro compounds [1–5] including mass spectroscopy of nitro derivatives of arenes and heterocycles reviewed by Khmelnitskii and Terentyev [145] and particularly on the $C-NO_2$ bond [3]. Thus only some problems related to the nitro group will be given here.

The geometry of the nitro group and electron density is depicted in the diagrammatic presentation of the molecule of nitrobenzene [3]:



Bond lengths

Bond orders

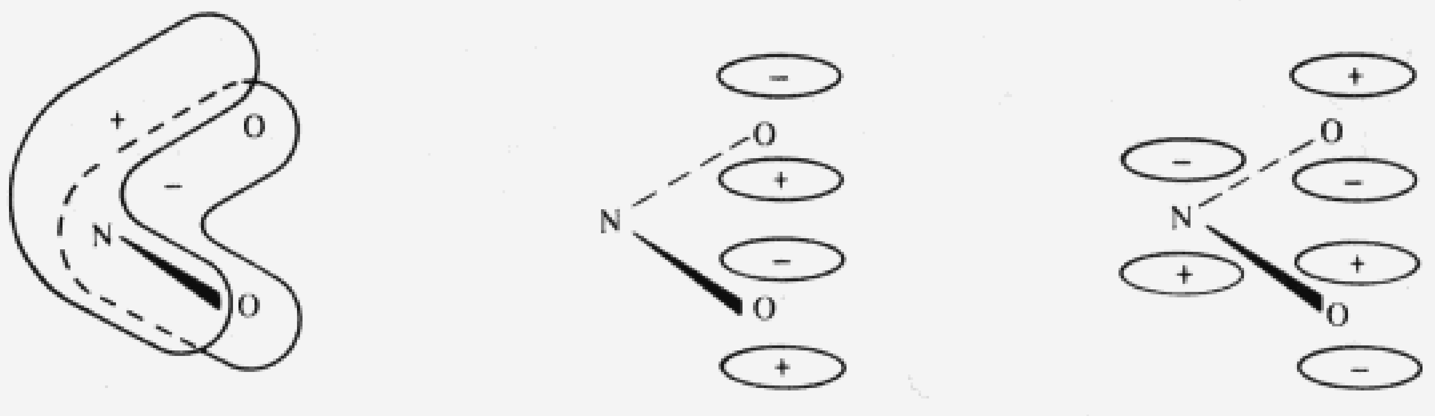
π-Electron density distribution

Nitrobenzene

FIG. 7. Geometry and electron density in nitrobenzene (according to Wagnière [3]).

Four p_x electrons of oxygen and nitrogen are present in the nitro group. They are used for π bonding and belong to the three p_x atomic orbitals *AO* – one from nitrogen and one from each oxygen atom. These *AO* combine three nitro molecular orbitals *MO* one of which is bonding π_1 Fig. 8a, one antibonding π_3^* Fig. 8b and one non-bonding π_2 Fig. 8c.

The diagram also includes the lone-pair orbitals: two and *sp* hybrid orbitals of the two oxygen atoms slightly split in the NO_2 group because of the interaction between the two atoms.



(a) π_1 (b) π_2 (c) π_3*

FIG. 8. The three atomic orbitals of the nitro group: (a) bonding, (b) antibonding, (c) non bonding (according to Jaffe and Orchin [1]).

ELECTRONIC SPECTRA OF THE NITRO GROUP

The nitro group is a chromophore. In the visible and ultraviolet absorption spectra bands π (bonding) $\to \pi^*$ (anti-bonding) and n (non-bonding) $\to \pi^*$ occur most frequently in conjugated molecules including aromatics [1–7].

The energy level – diagram is given in Fig. 9.

The classical example of the spectrum of a nitro compound is that of nitromethane. It consists of two broad bands; a high intensity band at $\lambda_{max} = 210$ nm ($\log \epsilon = 4.2$) and a weak band at $\lambda_{max} = 270$ nm ($\log \epsilon = 1.3$) which probably arise from $\pi_2 \to \pi_3$ and $n_a \to \pi_3^*$ transitions respectively. Theoretically a third band $n \to \pi^*$ from the transition $n_S \to \pi_3^*$ is also present at a very low wave-length in the 'vacuum' ultraviolet and is of low intensity. Ultraviolet-spectra of nitroalkanes including polynitro compounds were described in detail by Slovetskii [6] and reviewed by Novikov *et al.* in their monograph [7].

Attention should be drawn to the fact that polynitro aliphatic compounds such as 1,1-dinitroalkanes and trinitromethane exhibit a cloud in aqueous solutions. This is attributed to the presence of the anion [8].

Nitroalkenes (nitroolefins) are marked by the conjugation of double bonds with those of the nitro group. They show a high intensity absorption band due to $\pi \to \pi^*$ transition within the range 220–250 nm. The $n \to \pi^*$ band is strongly overlapped there by the intense red shifted $\pi \to \pi^*$ absorption band. The spectra of nitroalkenes are reviewed by Perekalin and Sopova [9] and Novikov and associates [7].

The following are data in ethanol [4] which illustrate the effect of lengthening the conjugated system in aliphatic unsaturated compounds Table (13). Kochany and Piotrowska [10] examined the ultraviolet-spectra of a number of nitroalkenes. Their $\pi \to \pi^*$ were observed between 360 and 420 nm. The ultraviolet absorption spectra of nitroethylene, nitropropenes and nitro methane have been taken and interpreted with the Pariser-Parr-Pople self-consistent field – *MO* calculation. The absorption bands $\pi \to \pi^*$ are in good agreement with calculated values [11].

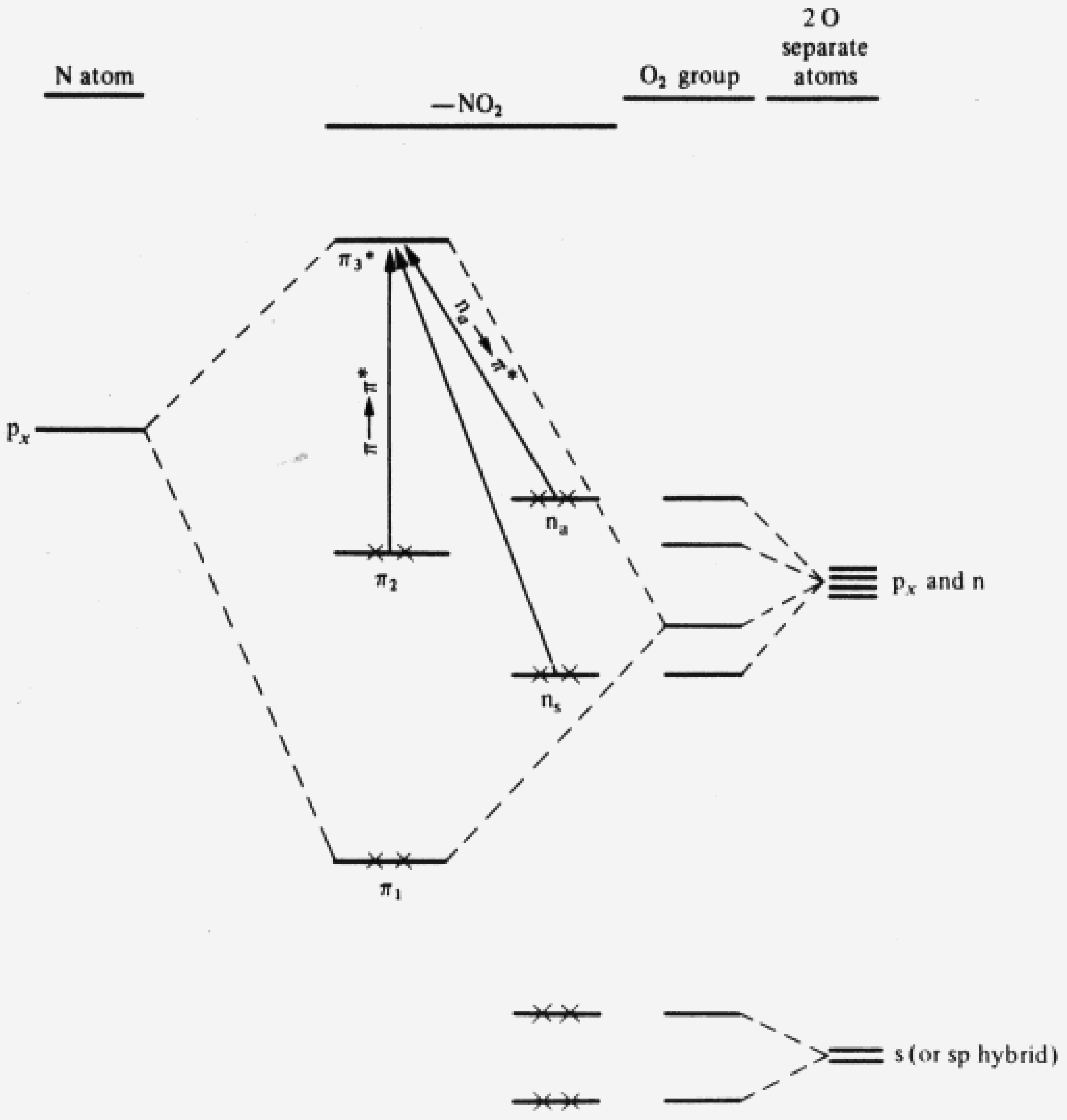


FIG. 9. Energy levels of the nitro group (according to Jaffe and Orchin [1]).

TABLE 13. Effect of lengthening the conjugated system in aliphatic unsaturated compounds

Compound	max nm	max	Transition
Nitromethane	210	5000	$\pi \rightarrow \pi^{\times}$
	270	20	$n \rightarrow \pi^{\times}$
1-Nitropropene-1	229	9400	$\pi \rightarrow \pi^{\times}$
	235	9800	
	ca. 300–330 (shoulder)		$n \rightarrow \pi^{\times}$
1-Nitro-1,3-pentadiene	227	9500	$\pi \rightarrow \pi^{\times}$
	309	16500	

The nitro group in aromatic systems causes strong bathochromic shifts of all the aromatic absorption bands when the nitro group is attached immediately to the aromatic ring. This is the consequence of the fact that the nitro group is strongly electron attracting. Figure 10 shows the spectra of toluene, phenylnitromethane and nitrobenzene.

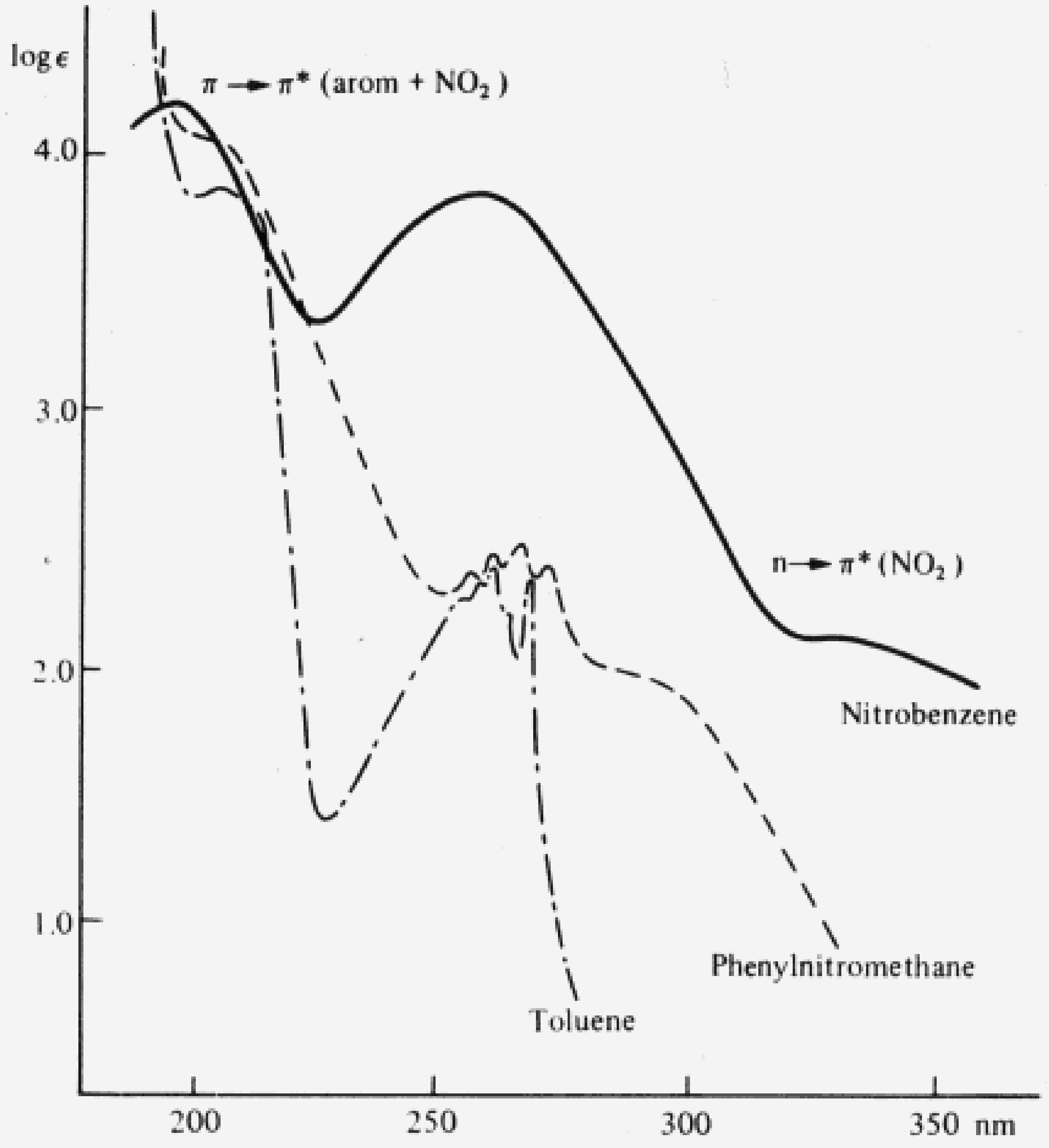


FIG. 10. Electronic spectra of phenylnitromethane and nitrobenzene (according to Buchowski and Skulski [4]).

When the nitro group is not directly attached to an aromatic ring as in phenylnitromethane then the $\pi \rightarrow \pi^*$ bands are only weakly affected by the nitro group and they do not differ appreciably from that of toluene [2].

The band around 260 nm has been assigned by Nagakura and co-workers [12] as being produced in *ca.* 6% by the internal charge–transfer structure.

Extensive study of numerous *para*-substituted β-nitrovinyl- and β-nitropropenylbenzenes were carried out by Skulski and co-workers [13]. Both groups are weaker electron attracting than the nitro group.

The nitro group attached to an aromatic ring takes part, as a rule, in the conjugation of double bonds of the aromatic ring. However, a considerable deviation of λ_{max} of aromatic $\pi \rightarrow \pi^*$ band of *o*-dinitrobenzene as compared with *m*- and *p*-isomers (Table 20, Vol. I, p. 169) is due to the fact that nitro groups in *o*-dinitrobenzene are being twisted off the aromatic plane. This was substantiated by X-ray analysis. Subsequently there is no conjugation of double bonds of that nitro group with the double bonds of the aromatic ring.

Conduit [14] examined ultraviolet and infra-red spectra of several mono-, di- and trinitro derivatives of benzene and toluene and interpreted them in terms of polar and steric effects.

The striking examples are *o*-dinitrobenzene, 2,3-dinitrotoluene and 3,4-dinitrotoluene which show $\pi \rightarrow \pi^*$ peaks at < 210, and 219 nm respectively, whereas all other dinitro compounds examined show peaks between 242 and 283.5 nm. Derivatives of toluene show peaks at a higher wave length probably due to the hyperconjugation of the methyl group.

The trinitro derivatives of benzene and toluene give bands within 227–258 nm. Here, according to Conduit, can exist a mutual reduction of conjugation by the nitro groups. The mean frequencies for the mono-, di- and trinitro compounds are 36,670, 41,760 and 41,970 cm^{-1} respectively i.e. λ_{max} 273, 239 and 238 nm respectively.

The twisting from the plane in some high nitrated derivatives of aniline was examined by Kamlet and co-workers [15].

The figures are given in Table 14.

TABLE 14. Ultraviolet spectra of ring substituted picramides in dioxane

Compound	λ_{max}	nm
Picramide	318	408
2,3,4,6-Tetranitroaniline	320	402
2,3,4,5,6-Pentanitroaniline	316	400
3,3-Diamino- 2,2′,4,4′,6,6′,-hexanitrodiphenyl	326	394

They calculated the angle of twist θ for the nitro groups in 2,3,4,6-tetranitroaniline according to Braude equation [16] and compared it with the X-ray crystallographic data of Dickinson, Stewart and Holden [17] (Table 15).

TABLE 15. Angles of twist θ in 2,3,4,6-tetranitroaniline

Substituent	Angle θ Calculated	Observed
2–NO_2	21°	19°
3–NO_2		64°
4–NO_2	42°	45°
6–NO_2	0°	3°

An example of the steric influence on the ultraviolet-spectrum of the nitro group in non-aromatic systems was given by T. Urbański, Piotrowska and Kędzierski [18]. Absorption bands of the nitro group ($\pi \rightarrow \pi^*$) in 5-nitro-1,3-dioxane were found to be 279 and 283 nm respectively. This was confirmed by Eliel [19].

A few more papers should be mentioned as regards electronic spectra of aromatic nitro compounds: nitrobenzene, dinitrobenzene and trinitrobenzene [20] and the work of Barth [21] who subjected mono-, di- and tri-nitrobenzenes and toluenes to detailed spectrophotometric ultraviolet-visible studies and developed a quantitative analysis of TNT in the presence of cyclonite, octogene and waxes.

Theoretical calculation of $\sigma + \pi$ electronic structure of nitrobenzenes and nitrotoluenes were carried out by LCAO method and gave a good agreement with electronic spectra and dipole moments [22]. Later the CNDO and *ab initio* calculation for nitro-, dinitro- and trinitrobenzenes gave a very good agreement with spectral features and dipole moments [23].

SOLVENT EFFECT

A very prominent effect is of solvent upon the $\pi \rightarrow \pi^*$ aromatic band in aromatic nitro compounds. When given spectra of organic compounds, thought should be given to the solvent used. This is particularly important in the ultraviolet region. Schubert and Robins [24] give some figures for nitrobenzene in some common solvents – Table 16.

TABLE 16. Ultraviolet absorption of $\pi \rightarrow \pi^x$ aromatic bands of nitrobenzene

Solvent	λ_{max}, nm
Water	267.5
95% Ethapol	259.7
t-Butanol	257.7
t-Butyl chloride	257.1
iso-Pentane	250.1
Acetonitryl	261.0
Nitrobenzene in gas phase	239.0

Solvatochromic shifts in the ultraviolet-visible absorption spectra of *p*-nitrophenol and *p*-nitroaniline have been taken as measures of relative solvent affinities [25].

It should be borne in mind that the acidity and basicity of the examined compounds and the use of some solvents can influence the ionic dissociation (the equilibrium acid–base) in a more appreciable way and produce the change of λ_{max} and the intensity, in electronic spectra.

INFRA-RED AND RAMAN SPECTROSCOPY

Numerous published papers have dealt with infra-red and Raman spectroscopy of nitro compounds. A general description is given in the monograph by Bellamy [26] and more recent reviews by Rao [27] and for non-aromatic nitro compounds by Novikov and co-authors [7].

The following are fundamental frequencies for nitromethane, the simplest nitro compound: Table 17.

TABLE 17. Fundamental frequencies for infra-red and Raman spectra of nitromethane according to Popov and Shlyapochnikov [28]

Vibrational class	Vibrational motion	Frequencies cm^{-1}	Intensity
Asymmetric	NO_2 asym stretching	$\nu_{as} = 1582$	vs
Symmetric	NO_2 sym stretching	$\nu_s = 1384$	s
	C–N stretching	$\nu = 921$	w
Deformation	ONO	$\delta = 647$	m
Non-planar	NO_2 bending	$\rho = 599$	w
Deformation	C–NO non-planar	$\delta = 476$	vw

Popov and Slyapochnikov [28] were able to calculate force constants in the molecule of nitromethane and Novikov [7] extended the calculation to a number of nitro compounds.

Slovetskii and co-workers according to [7] examined the frequencies of principal NO_2 bands for primary, secondary and tertiary nitro groups (Table 18).

TABLE 18. Mean ν values of frequencies of mononitro alkanes

Compounds	ν_{as}	ν_s
RCH_2NO_2	1554 ± 6	1382 ± 6
$RR'CHNO_2$	1550.5 ± 2.5	1360 ± 3.5
$RR'R''CNO_2$	1538.5 ± 4.5	1348.5 ± 4.5

Bellamy [26] collected information on the range of two main bands of aliphatic and aromatic nitro compounds:

asymmetric 1650–1500 cm^{-1},
symmetric 1350–1250 cm^{-1}.

Higher nitrated alkanes, for example, di- and trinitromethane show a splitting of the bands of symmetric vibrations. Thus Levin and Legin according to [7] reported bands for dinitromethane:

asymmetric: 1580 cm^{-1},
symmetric: 1386 and 1350 cm^{-1}.

The frequency of deformation vibrations δ(ONO) cm^{-1} is strongly influenced by the number of nitro groups [7]:

CH_3NO_2	δ = *ca.* 650 cm^{-1}
$CH_2 NO_2{}_2$	*ca.* 402 cm^{-1}
$CH NO_2{}_3$	*ca.* 360 cm^{-1}
$C NO_2{}_4$	340 cm^{-1}

Buczkowski and T. Urbański [29] found the bands in 2,2-dinitropropane in both infra-red and Raman spectra: asymmetric NO_2:1588 cm^{-1}, symmetric NO_2:1367, 1342 and 1258 cm^{-1}.

Salts of nitro alkanes show a considerable deviation from the non-ionized nitroalkanes. Novikov and co-workers [7] give the frequencies of mononitro anion as follows:

ν(C–N)	1610–1440 cm^{-1}
$\nu_{as}(NO_2)$	1285–1140 cm^{-1}
$\nu_S(NO_2)$	< 1000 cm^{-1}

Figure 11 depicts the change of frequencies when 'true' nitro compounds are transformed into their salts, according to Novikov and co-workers [7].

Conduit [14] established the influence of steric effects upon the symmetric vibrations. All dinitro derivatives of benzene and toluene which contain one nitro group strongly hindered and non-planar with the benzene ring show a splitting of the symmetric vibrations band, Table 19.

TABLE 19. Infra-red bands of sym-NO_2 in sterically hindered nitro compounds

o-dinitrobenzene shows	1368 and 1350 cm^{-1}
2,3-dinitrotoluene shows	1364 and 1346 cm^{-1}
3,4-dinitrotoluene shows	1360 and 1346 cm^{-1}
2,6-dinitrotoluene shows	1363 and 1348 cm^{-1}
3,5-dinitrotoluene shows	1356 and 1341 cm^{-1}

Unsymmetrically substituted trinitrotoluenes show a splitting of both bands, for example, 2,3,4-trinitrotoluene show asymmetric 1572, 1558 and symmetric vibration 1360, 1347 cm^{-1}. Similar bands are given by 2,3,5-, 2,3,6- and 3,4,5-trinitrotoluenes.

The asymmetric band widths reveal a regularity. The band width of an isolated nitro group is 8–11 cm^{-1} but in the presence of some hindering groups such as CH_3, C_2H_5 broadens to 19 cm^{-1}.

Varsányi, Holly and Fenichel [30] confirmed the finding of Conduit [14]

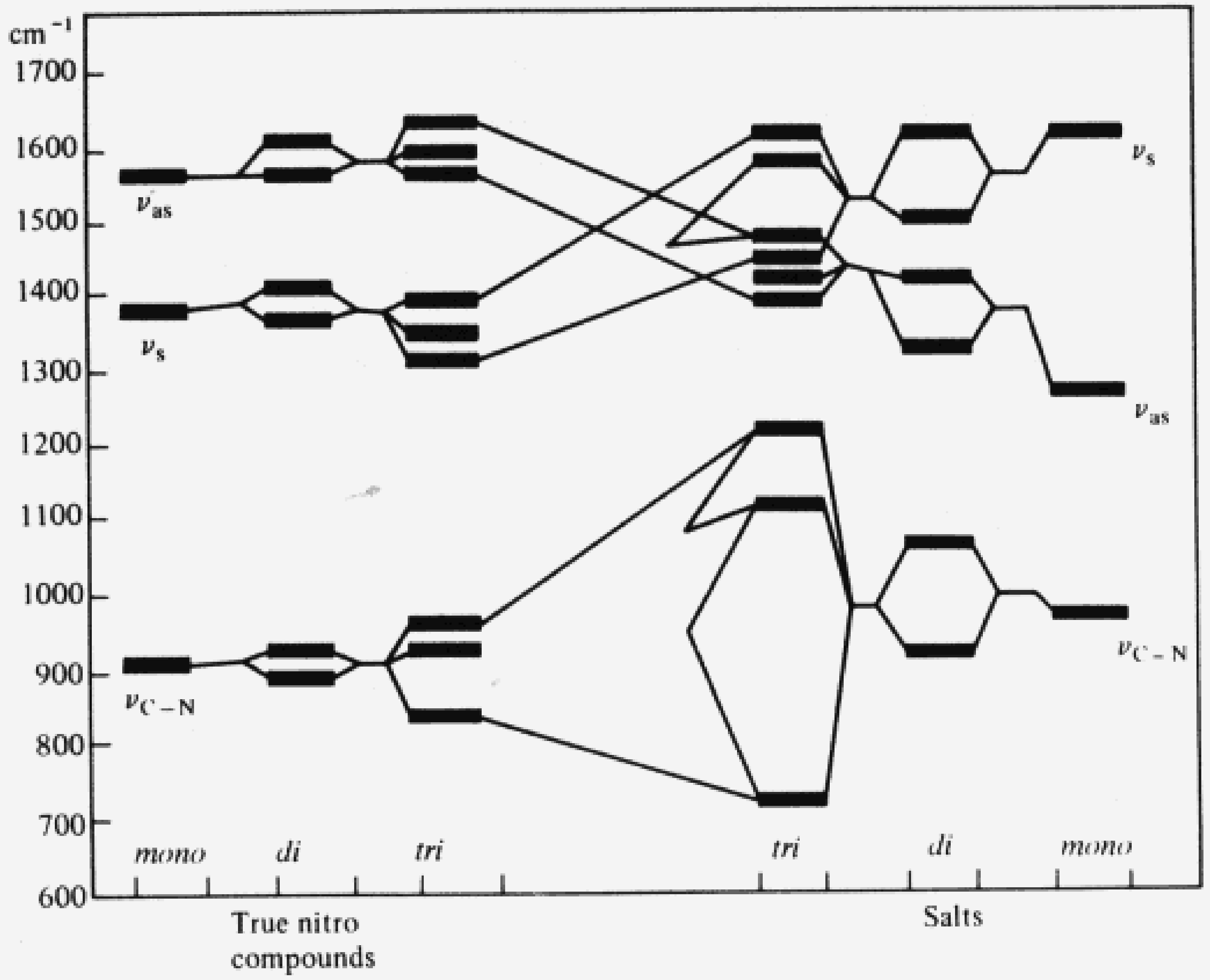


FIG. 11. Change of frequencies of aliphatic nitro compounds and their salts (according to Novikov *et al.* [7]).

and added one more band of C—N stretching vibrations in nitrobenzene, nitrotoluene and nitroanisole as being 859–851 cm^{-1}.

Steric influence was also referred to NO_2 deformation and C—N stretching vibrations in aromatic nitro compounds by Nakamura and co-workers [31]. They examined aromatic nitro compounds containing halogen substituents in various positions. They found (as anticipated) that *ortho* substitution lowered NO_2 bending and deformation modes owing to steric hindrance. This can be seen from Table 20.

TABLE 20. NO_2 bending and deformation vibration in substituted nitrobenzenes

	NO_2 bending cm^{-1}	NO_2 deformation cm^{-1}
m-chloronitrobenzene	537	733
p-chloronitrobenzene	533	740
o-chloronitrobenzene	459	686
m-bromonitrobenzene	535	728
p-bromonitrobenzene	522	732
o-bromonitrobenzene	413	685

The C—N stretching frequencies are not much influenced by substituents and in some cases the substitution increases the frequency. Thus the C—N frequency in pentabromonitrobenzene 895 cm^{-1} is much higher than in nitrobenzene 852 cm^{-1}. This is in agreement with Trotter's conclusion [32] that the C—N bonds in nitrobenzene derivatives have no resonance interaction.

T. Urbański and Dąbrowska [33a] examined infra-red spectra of mono-, di-, and trinitrophenols and particularly [33b] the action of solvents on hydrogen bonding between *o*-nitro and the phenolic group. They found that polar solvents can break a hydrogen bond. This is discussed in the paragraphs on hydrogen bonds and in the description of dinitro and trinitro phenols.

The already mentioned work of Kędzierski, Piotrowska and T. Urbański [18] on spectra of 5-nitro-1,3-oxazine revealed also the influence upon the infra-red frequency of the nitro group of its stereochemistry.

Thus the axial and equatorial NO_2 groups showed the frequencies 1556–1548 cm^{-1} and 1536–1533 cm^{-1} respectively.

A very interesting attempt was made by Boisard *et al.* [34] to use the rapid Raman spectrometry of 10 ns to study the structure of explosives immediately preceding the decomposition produced by a shock. They obtained spectra of cyclonite after the shock and the beginning of decomposition. A displacement was observed by 11 cm^{-1} of the frequency of the bond N—NO_2. This is probably due to lengthening of the bond N—N. It is expected to obtain more information in the future.

NUCLEAR MAGNETIC RESONANCE OF NITRO COMPOUNDS

(Vol. I, p. 179)

The application of nuclear magnetic resonance spectroscopy involves proton and nitrogen chemical shifts: ^1H-NMR and ^{14}N–NMR respectively.

Proton Magnetic Resonance

A number of aliphatic nitro compounds were examined by T. Urbański, Witanowski and co-workers [35]. The nitro group, being strongly electron attracting, decreases local electron density around alkyl protons in nitroalkanes, thus shifting their resonance signals to lower magnetic fields. The effect depends on the number of nitro groups, as can be seen in the series:

	CH_4	CH_3NO_2	$CH_2(NO_2)_2$	$CH(NO_2)_3$
δ ppm	0.23	4.28	6.10	7.52

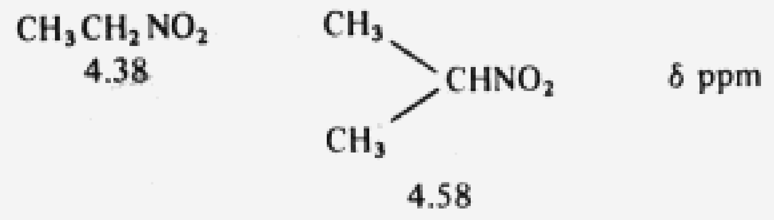
The negative inductive effect of the NO_2 group operates significantly as far as the third carbon atom in the chain. This can be seen from δ ppm data for 1-nitropropane to 1-nitropentane:

$$\begin{array}{ccccccc} CH_3 & - & CH_2 & - & CH_2 & - & NO_2 \\ 1.05 & & 2.04 & & 4.30 & & \end{array}$$

$$\begin{array}{ccccccccc} CH_3 & - & CH_2 & - & CH_2 & - & CH_2 & - & NO_2 \\ 1.00 & & 1.46 & & 2.03 & & 4.33 & & \end{array}$$

$$\begin{array}{ccccccccccc} CH_3 & - & CH_2 & - & CH_2 & - & CH_2 & - & CH_2 & - & NO_2 \\ 0.96 & & 1.33 & & 1.33 & & 2.03 & & 4.30 & & \end{array}$$

Also a difference was observed between primary and secondary nitroalkanes:



Proton spectra have also been used for the examination of nitro alkenes such as the isomerization of nitropropenes [36]:

$$\underset{75\%}{CH_2=CH-CH_2NO_2} \xrightleftharpoons{RONa} \underset{25\%}{CH_3-CH=CH-CH_3} \qquad (1)$$

A number of aromatic nitro compounds, derivatives of benzene, toluene, xylenes, mesitylene and durene have been investigated by proton resonance spectra [37–41]. The nitro group was found to shift the aromatic proton resonance signals to low fields from that of benzene in the order *ortho* > *para* > *meta*.

T. Urbański, Witanowski and associates [42] found convincing proof of the hydrogen bond between the phenolic group and the *o*-nitro group through ^1H–NMR examination of dilute solutions of nitrophenols, 2,4-dinitrophenol and picric acid. Thus *o*-nitrophenol gives $\delta = 10.67$ ppm whereas *m*- and *p*-nitrophenols 4.87 and 5.14 ppm respectively.

More information on H–NMR of nitro compounds is given by Rao in his review paper [2].

Nitrogen Magnetic Resonance

Recently less attention has been dedicated to the study of proton NMR of nitro compounds and attention has been shifted to nitrogen – ^{14}N–NMR.

The first systematic study of ^{14}N–NMR of nitroalkanes has been done by Witanowski, T. Urbański and Stefaniak [43]. It led to a simple spectral differentiation between nitromethane, primary, secondary and tertiary nitroalkanes.

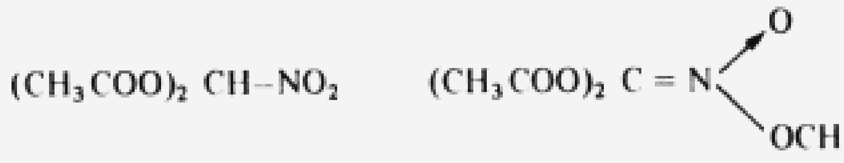
Nitromethane was taken as a primary standard for referencing nitrogen chemical shifts.

A summary of the existing data is given in Table 21 [44–46].

TABLE 21. ^{14}N–NMR of typical nitro compounds

Compounds	Nitrogen screening constants ppm
Nitromethane	0.0
$C(NO_2)_4$	+46.59
Nitrobenzene	+ 9.56
Hexanitrobenzene in CH_2Cl_2	+38.5
Nitroalkanes:	
tertiary R_3C-NO_2	*ca.* −30
secondary R_2CH-NO_2	*ca.* −20
primary $R\,CH_2-NO_2$	*ca.* − 8
gem – Dinitroalkanes $RCH(NO_2)_2$	*ca.* +20
gem – Trinitroalkanes $R\,C(NO_2)_3$	*ca.* +30
Aromatic nitro groups	+ 5 to +30
N-Nitro group R_2N-NO_2	+20 to +40 NO_2
O-Nitro group $R-O-NO_2$	+35 to +60

Electron attracting substituents in the nearest vicinity to the nitro group tend to increase the screening constant for the latter. Nitrogen chemical shifts differentiate clearly nitroalkanes, nitroaromatics, *N*-nitro and *O*-nitro groups. They are also helpful in distinguishing between the true nitro structure and that of an aci-nitro compound:



+ 16 ppm nitro compound

+ 70 ppm aci-nitro derivative

Additivity rules were found for the nitrogen chemical shifts in nitroalkanes [49].

The experiments on ^{14}N–NMR were extended to correlations of the ^{14}N chemical shifts with the infra-red frequencies of the nitro group [49b, 50] and with the Taft constants [48, 49a].

NMR spectra of nitrophenols offered a great help in examination of intramolecular hydrogen bond in β-nitroalcohols [68a] and *o*-nitrophenols [42]. The problem is discussed in the paragraph on hydrogen bond (p. 81).

A number of papers deal with the ^{14}N–NMR spectra of anions derived from mono- and polynitroalkanes. The change of structure from that of a true anion of aci-nitroalkane to that of a true nitrocarbanion was suggested in the series of anions of mono-, di-, and trinitroalkanes on the basis of the ^{14}N spectra [50]. Some data on the ^{14}N, ^{15}N, ^{13}C and ^{17}O resonance shifts were reported for nitroalkane anions [51–53] and ^{17}O for nitroalkanes [54].

The ^{14}N resonance spectra of aromatic nitro compounds [55] show inductive effects of substituents on the nitro group.

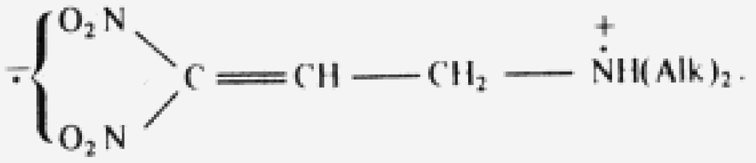
The nitrogen resonance spectra have been reported for the nitronium ion (NO_2^+) [56].

For more information and details the monographs [44–46] should be consulted.

Electron Spin Resonance

As is generally known, electron spin resonance reveals the presence of unpaired electrons. This is of course characteristic of free radicals and the most well known stable free radical is α, α′-diphenyl-β-picrylhydrazyl(DPPH) (I, 213). In the ESR spectrum it gives a narrow signal close to free spin value $g = 2.0036$ and is used for calibrating the magnetic field [2].

Unpaired electrons are also present in free radicals, radico-ions and in charge–transfer complexes. Among the latter a very prominent group is formed by polynitro compounds as acceptors and aromatic hydrocarbons mainly with condensed rings. The nature of these complexes is discussed further on p. 83. Now it should be mentioned that all CT complexes give a prominent ESR signal. More recently T. Urbański and co-workers [57] found that nitro compounds, both aliphatic and aromatic, give ESR signals if they contain a donor such as the amino group. Typical examples are nitroanilines, *m*-nitroaniline. Among aliphatic compounds 1,1-dinitropropenyl-3-dialkylamines show a strong ESR signal very likely due to the structure


$$\overset{\cdot}{-}\left\{\begin{matrix}O_2N\\ O_2N\end{matrix}\right\rangle C{=}CH-CH_2-\overset{+}{\dot{N}}H(Alk)_2 .$$

These compounds can be regarded as 'internal' CT complexes, or 'autocomplexes'. A number of such complexes with nitro groups were described by Freimanis *et al.* [141].

Micro-wave Spectroscopy

Micro-wave spectroscopy has been very little used for the examination of nitro compounds. Only a few data exist on the rotational constants of NO_2 group about the symmetry axis for nitromethane [2, 7] and some derivatives of nitromethane [7].

Magnetic and Electric Birefringance

Magnetic birefringance (Cotton–Mounton effect) and electric birefringance (Kerr effect) of nitrobenzene, *p*-dinitrobenzene and 1,3,5-trinitrobenzene was recently examined by Battaglia and Ritchie [58] at 25°C and 633 nm.

The following were figures for Δχ molecular magnetic anisotropy:

benzene	– 64
nitrobenzene	– 96
p-dinitrobenzene	– 151
1,3,5-trinitrobenzene	– 147

Optical Rotatory Dispersion

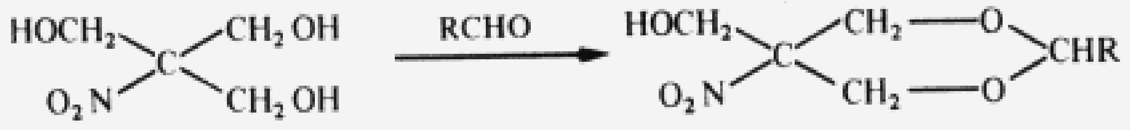
Optical rotatory dispersion and circular dichroism of compounds with a nitro group as a chromophore was described by Djerassi and co-workers [59].

HYDROGEN BOND WITH THE NITRO GROUP (Vol. I, p. 170).

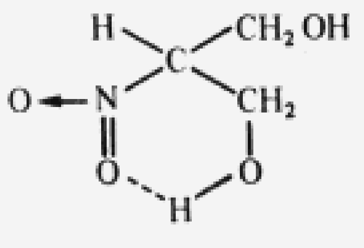
Malinowski and T. Urbański [60] advanced a suggestion that a hydrogen bond can exist between the nitro and the hydroxy group in β-nitro alcohols. This was based on the experimental fact that 2-nitropropane-1,3-diol (I) formed cyclic acetals-1,3-dioxane derivatives (II) and ketals with great difficulty, while on the contrary the triol 2-hydroxymethyl-2-nitro-propane-1,3-diol (III) forms the corresponding cyclic acetal (IV) and ketal with great ease.

These facts were rationalized in terms of the hydrogen bonds between the nitro and the hydroxy groups: Ia and IIIa

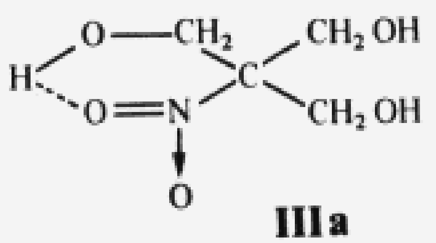
I **II** **(2a)**



III **IV** **(2b)**



Ia



IIIa

The presence of the intramolecular hydrogen bond between NO_2 and OH groups or NO_2 and NH groups was later confirmed by the author [61] on the basis of ultraviolet spectra of *ca.* 50 β-nitroalcohols, diols and β-aminomethyl-β-nitroalcohols and the comparison of their spectra with those of nitroalkanes.

The conclusion of T. Urbański was questioned by Ungnade and Kissinger [62] who admitted only a very weak hydrogen bond between β-nitroalcohol and chloroform used as a solvent. Schleyer and co-workers [63] have criticized the conclusions of Ungnade and Kissinger thus supporting the view of T. Urbański. Also Krueger and Mettee [64] confirmed the existence of the discussed hydrogen bonding. Two earlier papers [65, 66] referred to infra-red spectra of β-aminoalcohols and the authors rationalized the results in terms of the hydrogen bond between NO_2 and OH groups.

Final proof of the existence of the hydrogen bonding between NO_2 and OH groups in β-nitroalcohols was given by further experiments of T. Urbański and co-workers. The following methods were used in their experiments: measurement and calculation of dipole moments [67], ultraviolet, infra-red (including overtone region), NMR spectroscopy [68a, b].

A number of nitrophenols, nitroanilines, nitronaphthols etc. have been examined through ultraviolet spectroscopy, the point of acid–base equilibria, solute–solvent effect and internal hydrogen bonding and partly reviewed [2, 69, 70] Lutskii and Gorokhova [71] have calculated and interpreted the electronic spectra of nitrophenols by a LCAO SCF MO method in Pariser–Parr–Pople approximation. On scrutinizing the experimental electronic spectra (both ultraviolet and visible) of nitrophenols in different solvents (cyclohexane, absolute and 20% aqueous methanol) Skulski [72] has come to the conclusion that *o*-nitrophenol is strongly chelated in cyclohexane solution, but not appreciably in methanolic and probably not at all in aqueous methanol. Also by measuring dipole moments in dioxane and benzene he obtained [73] valuable information on the stability of the intramolecular hydrogen bond to the action of dioxane and other active solvents.

The effect was examined [74] of surfactants on the visible spectra of nitrophenols in 3% aqueous ethanol and interactions between the nitrophenols and micelles. The electron absorption spectra of dinitroanilines have been discussed [75] in terms of energy and intensity of lowest energy absorptions, the intramolecular hydrogen bond extension of the π electron conjugated system etc.

T. Urbański and Dąbrowska [33b] examined infra-red spectra of several mono-, di- and trinitrophenols and established the influence of the solvent on the hydrogen bond between the *o*-nitro and phenolic groups. It was found that polar solvents can break the intramolecular hydrogen bond.

Reeves and co-workers [76] correlated the change in the chemical shift of NMR spectra caused by formation of an intramolecular hydrogen bond in *o*-substituted phenols including *o*-nitrophenol, 2,4-dinitrophenol, 1-nitro-2-naphthol, 2,4-dinitro-1-naphthol etc.

Final evidence of intramolecular hydrogen bonding in nitrophenols and hydrogen bonding in nitrophenols was given by T. Urbański, Witanowski and co-workers [77] by examining their NMR spectra. The values of δ calculated for infinite dilutions for OH groups and the infra-red frequencies are shown in Table 22.

TABLE 22. Chemical shifts δ_{OH} ppm and infra-red frequencies in cm^{-1} for nitrophenols

Compound	δ_{OH} ppm	IR bands cm^{-1}
o-Nitrophenol	10.67	3250
2,4-Dinitrophenol	11.12	3210
2,5-Dinitrophenol	10.76	3270
2,6-Dinitrophenol	11.41	3170
Picric acid	9.16	3100
m-Nitrophenol	4.87	3615
p-Nitrophenol	5.14	3615

The infra-red data [30a] refers to solutions in carbon tetrachloride. They show a considerable difference between *ortho* nitro phenols and *m*- and *para*-nitro derivatives.

A number of authors [78–81] examined the intramolecular hydrogen bonds between NO_2 and NH_2 in *o*-nitroaniline.

CHARGE–TRANSFER COMPLEXES (CT-COMPLEXES) OR ELECTRON–DONOR–ACCEPTOR COMPLEXES (EDA-COMPLEXES) (Vol. I, p. 220).

As pointed out in Vol. 1, trinitrobenzene and its derivatives possess the ability to form addition compounds, especially with aromatic hydrocarbons composed of condensed rings, such as naphthalene, anthracene, phenanthrene, acenaphthene etc. Addition compounds of picric acid have been known since 1858 [82] and those of sym-trinitrobenzene since 1882 [83]. Complexes of sym-trinitro-benzene with aromatic amines were also described in 1882 [84].

Currently problems connected with CT or EDA complexes form one of the topics of physical–organic chemistry. A few excellent monographs and review articles have appeared [85–90]. After the remarkable work of Briegleb, Weiss, Brackman and other authors (Vol. I, p. 220) the most important treatment of the nature of bonds keeping donor and acceptor together, was given by Mulliken [91] on the basis of quantum mechanical assumption of the electron transfer from the donor to the acceptor.

Here are the main points deduced by Mulliken. The electronic ground state wave functions of the complex ψ_N are a combination of a 'no-bond' wave function ψ_0 and one or more 'dative bond' functions ψ_1, ψ_2 etc.:

$$\psi_N = a\psi_0 + b\psi_1 + c\psi_2 + \ldots,$$

where a, b and c are coefficients with $a > b > c$.

The no-bond function includes the electronic energy of the component molecules, plus terms representing the effect of dipole interactions, dispersion forces, hydrogen bonding and other intermolecular forces. The dative bond functions represent states where an electron has been transferred from the donor molecule to the acceptor, introducing electrostatic interactions and forming a weak covalent link between the resulting radical ions:

$$\begin{tikzcd} AD \arrow[r, leftrightarrow] \arrow[d, "h\nu"] & A^- + D^+ \\ A^- + D^+ \arrow[r, rightleftharpoons] & A^- \leftrightarrow D^+ \end{tikzcd}$$

EDA Complex

Excited states with a dative structure as the main contributor, have the same form with the coefficients varied to give predominance to the dative bond contribution.

The Mulliken treatment provided the theoretical basis for interpretation of spectroscopic and formation constant data and initiated research on semiconductivity and magnetic properties of molecular complexes.

According to McGlynn [85] and Briegleb [87] the complex addition compounds should be called 'EDA-complexes' for Electron–Donor–Acceptor–Complexes and the term 'Charge–Transfer' should be reserved for the absorption band characterizing the complex. The symbol $h\nu_{CT}$ is given to the energy of the 'charge–transfer band' characterizing the complex. Thus the term 'Charge–Transfer', according to Briegleb, is reserved in this particular instance.

According to Dewar and Lepley [92] the following are CT-bands of complexes of sym-trinitrobenzene and hydrocarbons (Table 23). Also they calculated the energy E_m of the highest occupied *MO*.

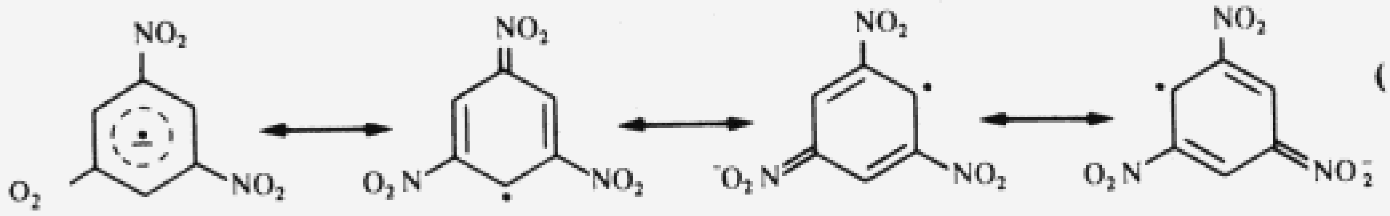
TABLE 23. The CT-bands of complexes of sym-trinitrobenzene and hydrocarbons

Hydrocarbon	CT-band ν nm	E_m
Benzene	284	1.000
Naphthalene	365	0.618
Acenaphthylene	353	0.637
Anthracene	460	0.414
Naphthacene	520	0.294
Phenanthrene	370	0.605

The figures brought to coordinates – E_m against ν – form a straight line.

A very important feature of EDA-complexes is the fact that in the magnetic field they show the existence of an unpaired electron, i.e. signals in the electron spin resonance apparatus.

Briegleb and Czekalla [86] depicted the formation of radical-ions of trinitrobenzene in the following way (3):



(3)

The electron affinity of trinitrobenzene which characterizes the ability of the compound to form charge–transfer complexes is not very high and is estimated to be equal to 0.6 eV, whereas stronger electron acceptors such as tetracyanethylene and chloranil show values of 1.6 and 1.35 eV respectively [86].

The Mulliken treatment provided a simple classification of molecular complexes according to the type of orbitals involved in charge–transfer [93]. The complexes of nitro compounds with hydrocarbons belong to π–π complexes i.e. π-donors and π-acceptors.

For maximum charge–transfer interaction the relative orientations of the two molecules must provide maximum overlap of the filled donor orbital and the vacant acceptor orbital. This is known as Mulliken's 'Overlap and Orientation principle' [94].

X-ray examination of π–π molecular complexes shows that the crystals of the complexes are formed from stacks of alternate donor and acceptor molecules – in agreement with theoretical analysis of Mulliken.

This was described by a number of authors (Vol. I) for example, Powell and Huse, Rapson, Saunder and Stewart and Wallwork [95] subjected a few complexes of *s*-trinitrobenzene to X-ray analysis. Wallwork concluded that the structure can be summarized and plane-to-plane packing of the components. The relative dispositions of the components are such as to allow the maximum degree of overlap between their molecular π-orbitals. Figure 12 gives a diagrammatic presentation of the complexes of sym-trinitrobenzene with naphthalene, and Fig. 13 – with anthracene [96].

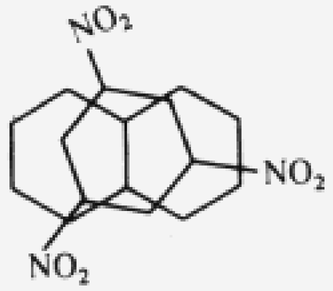


FIG. 12. CT – complex of sym-trinitrobenzene with naphthalene (according to Brown, Wallwork and Wilson [96]).

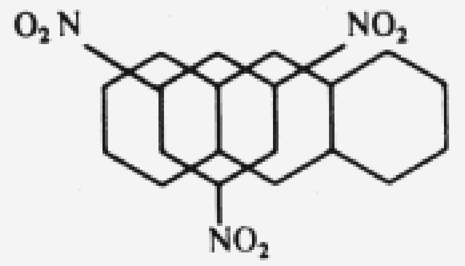


FIG. 13. CT – complex of sym-trinitrobenzene with naphthalene (according to Brown, Wallwork and Wilson [96]).

Particular cases of EDA complexes are those of nitrophenols and bases, for example, dinitrophenols with aniline described by Zeegers-Huyskens [96a], mono-, di-, and trinitrophenol with hexamethylenetetramine of Vagaonescu and Ionescu [96b]. The complexes show the presence of hydrogen bonds in addition to the existence of $\pi-\pi$ complexes. High nitrated aromatic compounds have been used for the identification of multi-ring aromatic hydrocarbons and various amines. Thus Willstätter and M. Fischer [97] used styphnic acid, an acceptor to detect porphyrins, and later a few papers were added on similar detection of chlorophyll and other porphyrin-like molecules with 1,3,5-trinitrobenzene and 2,4,7-trinitrofluorenone [98–100]. Some alkaloids and drugs can be detected and subjected to quantitative analysis by measuring the intensity of the charge–transfer band produced in the spectrum of complexes with 1,3,5-trinitrobenzene or picric acid [101, 102].

Also highly nitrated compounds can be detected and identified by means of donors, such as hydrocarbons. Their identification was suggested by the method of thin-layer chromatography [103]. A method of rapid detection, of explosives such as TNT, TNB, Picryl chloride, *m*-DNB, Tetryl in the form of charge–transfer complexes with aromatic amines, such as aniline, dimethylaniline, toluidines, anisidines, naphthylamines, benzidine etc. was developed by Dwivedy *et al.* [104]. The authors used for identification thin-layer chromatography establishing R_f values for model complexes.

An original approach to the stereostructure of complexes on the basis of infra-red spectra was given by Severin [105]. He examined the complexes of sym-trinitrobenzene with phloroglucinol or nitrophloroglucinol and of picric acid with phloroglucinol and came to the conclusion that the approach of the acceptor molecule can be sterically hindered if the donor molecule is non-planar. Hence complex formation is difficult as the non-planarity increases the distance between the components. For example, *trans*-stilbene forms a picrate, but the *cis*-isomer does not. The planar molecule of 2-phenylnaphthalene also forms a picrate, while its non-planar isomer, 1-phenylnaphthalene, fails to do so.

A number of papers have appeared which describe absorption spectra of charge–transfer complexes in solutions without however isolating the actual complexes.

Thus Foster and Thomson [106] examined complexes of *p*-phenylenediamine and its *N*-methyl derivatives, and bis(dimethylamine) derivatives, of diphenyl and stilbene with 2,4-dinitrotoluene, 2,4,6-trinitrotoluene, 1,3- and 1,4-dinitrobenzene and 1,3,5-trinitrobenzene. Similarly Wacławek and Hurwic [107] described complexes formed in solutions by 1,3,5-trinitrobenzene with pyridine, picolines, aminopyridines and cyanopyridines. They also used dielectric titration, refractive index and density measurements to establish the formation of the complexes. Aliphatic nitro compounds can also be electron acceptors. Thus Lewańska and Lipczyńska [108] established the existence of a complex of ter-nitrobutane with dimethylaniline in molar proportion 1:1 by measuring electronic spectrum of solutions with different proportions of the donor and acceptor, according to the method of constant dilutions of Job [109].

Hammond and Burkardt [142] described the electron accepting properties of tetranitromethane. They came to the conclusion that tetranitromethane interacts only weakly with aromatic hydrocarbons and does not form isolable complexes.

Hetnarski [110] in a number of papers has described a new donor – ferrocene. It gives EDA complexes with sym-trinitrobenzene, picric acid, picryl chloride while using Job's method [109] to establish the ratio between the acceptor and donor.

More recently T. Urbański, Hetnarski and Południkiewicz [111] established that nitrate esters form EDA complexes with a strong donor – *N,N'*-tetramethyl-*p*-phenylenediamine. Particularly interesting are nitrate esters with five or six ONO_2 groups, such as D-arabitol pentanitrate, D-mannitol and D-sorbitol hexanitrates. A particular stereochemistry of such complexes was suggested with nitrate esters coiled in pseudo-rings. Complexes of erythritol tetranitrate with biologically important pyrimidine and purine bases were examined by T. Urbański, Wacławek and Pobłocka [112]. The ratio donor:acceptor was established by examining NMR spectra.

T. Urbański, Krasiejko and Południkiewicz [113] suggested using *N,N'*-tetramethyl-*p*-phenylenediamine to detect nitrate esters: a magenta colour makes the detection easy.

Like most EDA complexes, those of sym-trinitrobenzene, for example, with *N,N*-dimethylaniline show a semiconducting property [114].

X-Ray Structure

A considerable number of X-ray examinations of nitro compounds have been done over the last two decades. They will be given in the description of particular compounds. However, the following are reviews which should be mentioned: X-ray analysis of aliphatic nitro compounds, nitrate esters and nitramines were described by Novikov and co-workers [7], nitramines by G. F. Wright [115], polynitroaromatic addition compounds by Hall and Poranski [116]. The X-ray crystal structure of EDA complexes – by Prout and J. D. Wright [88] and Foster [90].

THERMOCHEMISTRY

Thermochemical data of explosives will be given in the description of particular compounds. General problems of thermochemistry of nitro compounds was given in the monograph by Lebedev, Miroshnichenko and Knobel [117]. In recent years a considerable number of contributions have been given by Pepekin and co-workers [118] on such problems as the enthalpy of formation of nitro and nitramino compounds and nitrate esters and enthalpy of detonation. Also Pepekin and co-workers [119] contributed considerably to the solution of problems of the energy of dissociation of the bond $C-N_3$.

A very important review article on thermal analysis of explosives was given by Collins and Haws [140]. The results of thermal analysis will be described in properties of particular compounds.

MASS SPECTROGRAPHY

A number of papers have appeared on the fragmentation of nitro compounds by mass spectrography. They were reviewed by Beynon [120] and recently by Khmel'nitskii and Terentiev [121] therefore only main outlines will be given here. Three main molecular ions have been found: $M-O^+$, $M-NO^+$ and $M-NO_2^+$. The first one was present in a small yield 1–2%. There are two schools of thought, as far as the mechanism of rearrangement of the molecular ion prior to its dissociation. According to some authors [122] the molecular nitro-ion is first rearranged into a nitrite. McLafferty and Bursey [123] found a marked distinction between compounds having *meta* and *para* positions of the nitro group relative to other substituents.

Beynon, Saunders and Williams [122], Fields, Meyerson and co-workers [124] compared mass-spectra of isomeric dinitrobenzenes (Table 24) and came to the conclusion that *meta* and *para* isomers give similar fragments, whereas *ortho* differ considerably.

The fragmentation of negatively charged molecular ions of mono- and dinitrobenzenes does not differ from that of the positive ions [125, 126].

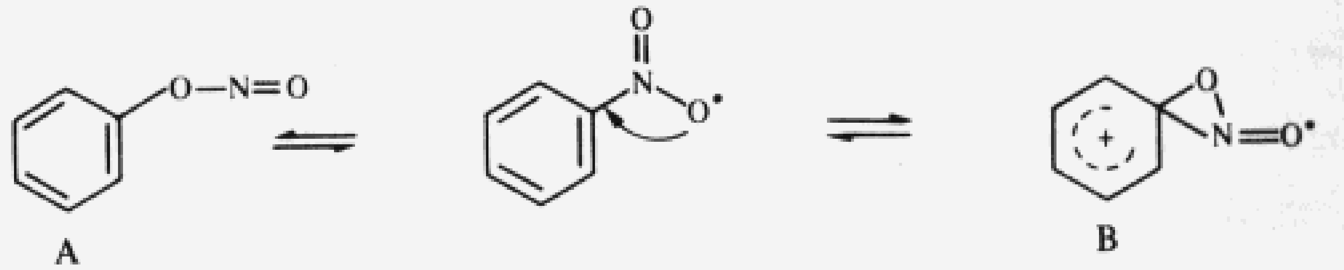
Meyerson *et al*. [127] examined the fragmentation of sym-trinitrobenzene. A much more complicated picture appeared from the spectrum with one particular feature: the most prominent is the elimination of NO_2 as the first step of the fragmentation.

Experiments with isomeric nitrotoluenes show that the fragmentation of *meta*- and *para*-isomers is similar to that of nitrobenzene [122].

Both isomers are characterized by the high presence, *ca*. 70%, of the molecular ion, while nitrobenzene shows 49% and *o*-nitrotoluene only 25%. The spectrum of *o*-nitrotoluene shows a high peak with a mass of 120 which is not present in *meta*- and *para*-isomers. According to Beynon *et al*. [122] it corresponds to the ion $M-OH^+$ with the structure according to scheme (5)

TABLE 24. Intensity of the peaks of mass-spectra of isomeric dinitrobenzenes in percentages

Ions	Isomers of DNB *ortho*	*meta*	*para*
M^+	6.98	11.00	10.30
$M-O^+$	0.24	0.63	0.57
$M-NO^+$	0.07	0.21	0.34
$M-NO_2^+$	0.41	4.76	4.12
$M-NO_2^+$	0.03	0.04	0.09
$M(NO)NO_2^+$	1.66	5.82	3.64
$M(NO_2)_2^+$	3.84	11.20	9.18
$M-NO_2+HNO_2^+$	2.03	10.80	11.30
NO^+	26.70	17.20	21.30



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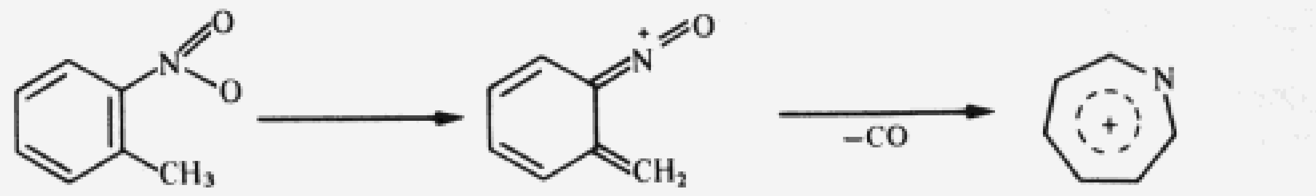


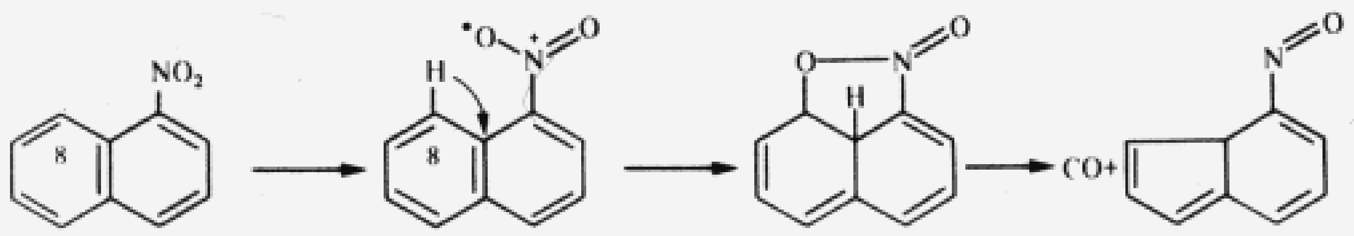
(5)

The ion 20 is losing CO to be transformed probably into the azatropilium ion 92. The mass spectra of *m*- and *p*-nitrotoluenes yielded only $M-NO^+$ and $M-NO_2^+$ ions. Nitroxylenes and polynitrotoluenes yielded ions $M-OH^+$ [122].

Mass spectrum of TNT yielded ion $[(M+H)-OH_2]^+$ [128].

The peak $(M-OH)^+$ is present in the mass spectra of all three nitroanilines [122, 129].

Benoit and Holmes [130] examined a number of *o*-nitro compounds, such as *o*-nitroanisol, *o*-nitrobenzoic acid, *o*-nitrobenzamide etc. to study the *ortho*-effect. They came to the conclusion that two *ortho*-effects exist. One is marked by the migration of hydrogen from one substituent to another. The second effect consists in migration of an atom or a group of atoms from the substituent of a vacant place in *ortho* position. Particular attention is now being paid to elucidating different features of the *ortho* effect. Among interesting facts a similar effect was recorded in *peri*-position in 1-nitronaphthalene [131, 132]. The following mechanism was rationalized by labelling position 8 of the naphthalene ring with ^{13}C [133]:



(6)

Nitroalkanes: nitromethane, nitroethane and nitropropanes were examined by Collin [134].

ELECTROCHEMICAL PROPERTIES

Galvanic Cells

Nitro compounds and metals as reducing agents can form galvanic cells [134]. Particularly interesting are results with *m*-dinitrobenzene [135]. The system *m*-dinitrobenzene and magnesium gave a rather high yield of 160 wh/kg through the reaction:

$$R(NO_2)_2 + 4H^+ + 4e \longrightarrow R(NHOH)_2 + H_2O \qquad (7)$$

in a neutral medium.

Photoconductivity. It has been found that the conductivity of nitrobenzene increases when irradiated with ultraviolet light [136]. This will be discussed in the paragraph on the photochemistry of nitro compounds.

Lasers. Chelates of europium with some aromatic nitro compounds with phenolic and aldehydic function can be used to produce laser beams [137].

BIOLOGICAL ACTIVITY OF NITRO COMPOUNDS

Nitro compounds possess strong biological activity. Moncrieff [138] has given a first monograph of such properties as sweet and bitter or pungent taste, musk odour. A review by Venulet and Van Etten [139] described the biochemistry and pharmacology of nitro compounds and included a description of antibiotics containing the nitro group such as naturally occurring nitro compounds, toxic substances with their practical use as insecticides, molluscicides, fungicides and herbicides. A separate chapter is dedicated to the toxicity of commercially important nitro compounds.

Reactive aromatic nitro compounds were successfully used as antitumour agents. Such is chlorodinitrobenzene [143] and some 2,4-dinitrophenyl derivatives, such as 5-aziridino-2,4-dinitrobenzamide [144].

The toxicity of nitro compounds was discussed in Vol. I in the description of particular compounds. This method will be followed in the present volume: any novel information on the toxicity of compounds, were available, will be given in the description of the compounds.

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CHAPTER 4

REACTIVITY OF AROMATIC NITRO COMPOUNDS

(Vol. I, p. 192)

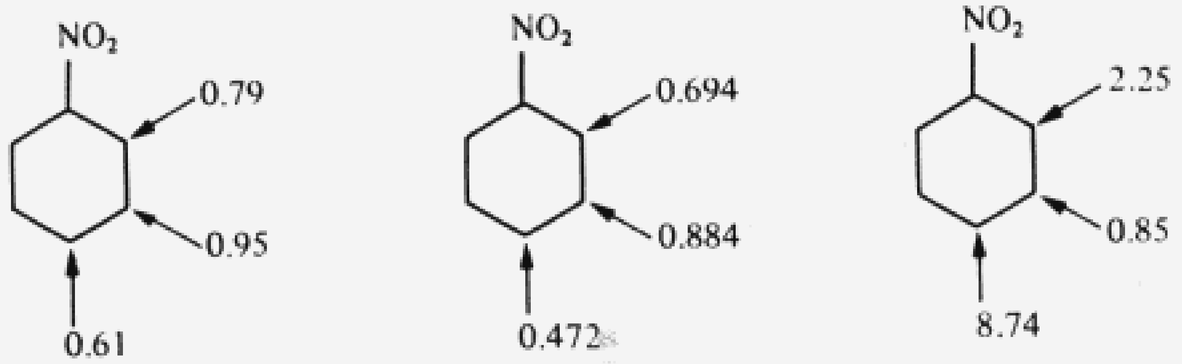
A great number of reactions of nitro compounds were described in the well known monograph edited by H. Feuer which forms a part of the monographs edited by S. Patai [1]. Reference will therefore be made to these and some other books and only the most important and more recent papers will be given here.

SUBSTITUTION (HETEROLYTIC AND HOMOLYTIC)

It is well known that heterolytic substitutions occur through 'electrophilic' and 'nucleophilic' attacks produced by cation E^+ ('electrophile') and anion Nu^- ('nucleophile') respectively. Homolytic substitutions involve the action of uncharged free radicals.

In electrophilic and nucleophilic substitution of aromatic nitro compounds different directing effects are dictated by electron distribution. The simple case of nitrobenzene π-electron distribution is given in diagram Fig. 14a [2], and the free valence of aromatic cations of nitrobenzene $C_6H_5NO_2^+$ is given in Fig. 14b [3].

Both diagrams show that electrophilic substitution should occur mainly in *meta* position, whereas the nucleophilic one should yield mainly *ortho* and *para* substituted products.



a b c

FIG. 14. Nitrobenzene: (a) π-electron density (see also Fig. 7); (b) free valencies; (c) localization energy.

Another approach consists of the calculation of relative rates for substitution from the atom localization energies of Wheland. It gives a more qualitative insight. However in the instance of homolytic reactions at 80°C the relative reaction rates are better approaching the experimental results (Fig. 14c).

ELECTROPHILIC SUBSTITUTION

A few monographs have been dedicated to the description of electrophilic substitution of nitro compounds in general [2, 5–7] and a review has been published on the subject [8]. The mechanism of nitration was discussed in Chapter II. Nitration with NO_2^+ containing agents belongs to the mechanism SE 2 as already mentioned in Chapter II.

Diagrams – Fig. 14a–c – shows that substitution can occur not only in *meta*, but also in *ortho* and *para* positions. According to the diagrams it should be expected that the proportion of *ortho* isomer should be superior to that of the *p*-dinitrobenzene. Indeed this is in agreement with the experiment: the proportion of *o*-dinitrobenzene is larger and at high temperature of nitration much larger than that of *p*-dinitrobenzene (Vol. I, p. 243, Tables 38 and 39).

Also in the homologues of benzene the influence of alkyl groups should not be neglected, their directing influence being *ortho* and *para*.

NUCLEOPHILIC ADDITION AND SUBSTITUTION (Vol. I, p. 197)

One of the characteristic features of aromatic nitro compounds, particularly those with two or more nitro groups is their ability to react with bases and in many instances the reaction is accompanied by an intense colour. The colour had caught the attention of chemists by the late nineteenth century and initiated a considerable amount of research on the nature of the formed substances. Thus considerable literature appeared on reactions known as Janovsky or Jackson–Meisenheimer or Meisenheimer reactions which are discussed later. They are nucleophilic reactions and are not only of theoretical but also of practical importance. Thus the Janovsky reaction became an important analytical method, and reactions of di- and trinitrobenzene and their homologues with bases, are of great importance in the problem of the safety of manufacture and of the stability of these nitro compounds.

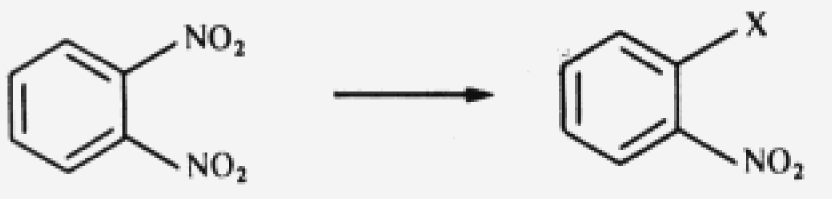
The reactions of nitro compounds with bases are nucleophilic reactions and recently have received much attention. Numerous monographs include chapters on nucleophilic substitution of nitro compounds and review articles have been published. Such are the excellent reviews by de Boer and Dirkx [9], Hall and Poranski [10]. References in [9] are brought up to 1966, and it seems appropriate to complete the list of review articles by mentioning the later review papers: Challis [11], Buncel and co-workers [12], Miller [13], Pietra [14], Buck [15], Crampton [16], Strauss [17], Bernasconi [18], Sekiguchi and Yuki [19], Makosza [20], Kornblum [144], Bolton [174], Blumenfeld and co-workers [178].

Two excellent monographs appeared recently on analytical problems of explosives. Gawargious [179] gave a description related to the nitro group. Yinon and Zitrin [189] tackled a wide range of analysis of various explosives.

However the analytical problems are outside the scope of the present book.

NUCLEOPHILIC DISPLACEMENT OF NITRO GROUP

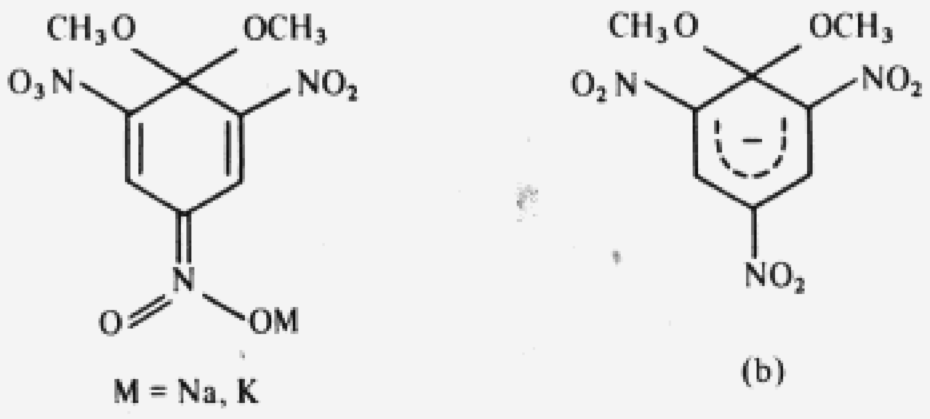
Nucleophilic displacement of aromatic nitro group was recently reviewed by Beck [234]. An attention was drawn to his own work and that of Cadogan and co-workers [225, 226], e.g.:



$X = PO/OC_2H_5/_2$,
$PO/CH_3/OC_2H_5$,
$PO(C_6H_5)_2$

JACKSON–MEISENHEIMER REACTION (OR MEISENHEIMER REACTION) AND σ-COMPLEXES

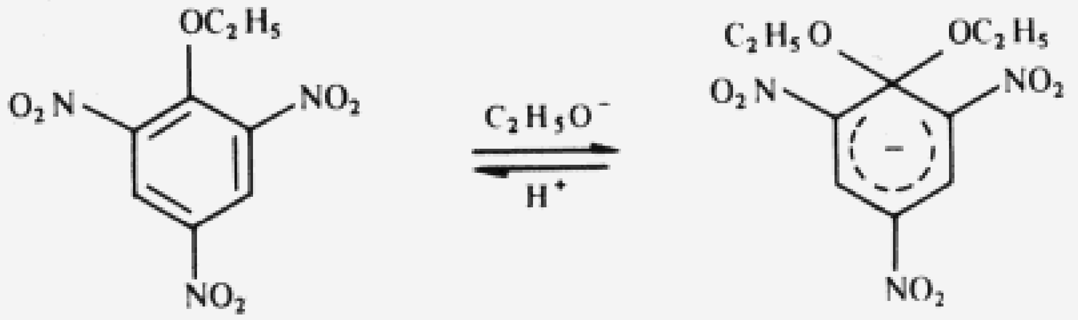
As early as 1895 Lobry de Bruin [22] described a red solid which he isolated from the reaction of 1,3,5-trinitrobenzene with potassium hydroxide in methanol. V. Meyer [23] suggested this to be a complex compound. Hantzsch and Kissel [24] rationalized that the complex might be a potassium salt of aci-form of one nitro group. Jackson and Gazzolo [25] suggested in 1900 two structural formulae for the sodium salt obtained by acting with sodium methoxide on 2,4,6-trinitroanisol – Fig. 15a. Meisenheimer [26] (probably unaware of Jackson's paper) suggested the same formula for potassium salt. Jackson and Earle [27] supplied analytical proof of the structure.



(a) (b)

FIG. 15. Jackson–Meisenheimer σ complexes (a) former, (b) current method of writing.

Jackson–Meisenheimer compounds are now recognized as σ-complexes. Currently their mode of writing is given in Fig. 15b, and the formation presented in diagram (1):



(1)

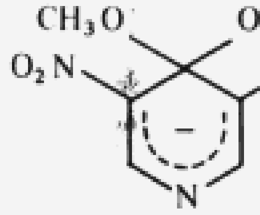
This can be classified as a SNAr mechanism.

Attention should be drawn to the fact that the reaction is reversible and under the action of an acid, the starting nitro compound is formed.

Naphthalene analogues of Jackson–Meisenheimer complexes were described [28, 42] and 9-anthracene derivative has already been discussed by Meisenheimer [26].

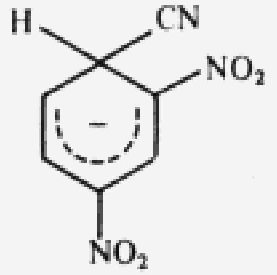
A few heterocyclic Jackson–Meisenheimer complexes were recorded, viz.: I [29]; II [30]. Vickery [31a] rationalized the structure of the complex (III) obtained in 1883 by Lobry de Bruin [31b] while acting with potassium cyanide on *m*-dinitrobenzene.

Similar σ-complexes (IV) can be obtained by acting with CH_3O^- on picramide and its derivatives [32–34, 37].

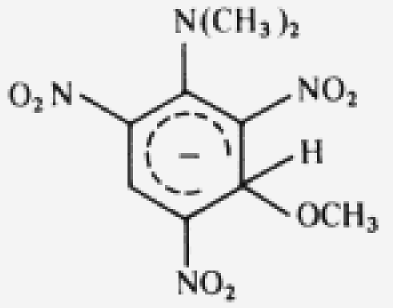


I

II



III



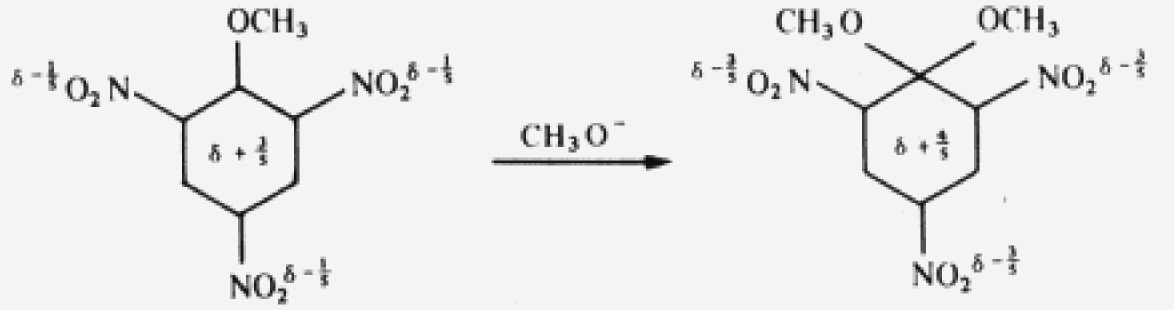
IV

Gold and Rochester [32] and Pollitt and Saunders [35] examined electronic spectra, Dyall [36] infra-red spectra of σ-complexes. NMR spectra were studied in the pioneering work of Crampton and Gold [37], the works were reviewed by Hall and Poranski [10] and Crampton [38]. More recent works were done by Norris [39] and Epiotis [40]. Kinetic studies of σ-complexes were made by a number of authors [41, 42] and thermodynamic control by Fendler and co-workers [43]. Bernasconi [18] reviewed the work on kinetic behaviour of σ-complexes.

In their recent work Crampton and Gibson [33] used a modern technique of stopped flow and T-jump spectrometry in their study of the reaction of *N*-alkyl picramide and CH_3O^-.

All of these works confirmed in principle the structure of Jackson–Meisenheimer complexes. It was also supported by X-ray analysis by Simonetta and co-workers [44] and Ueda and co-workers [45] with one correction: the length of the bonds between carbon atoms 2–3 (and 5–6) is relatively short (1.35 Å), close to the length of the olefinic bond. Subsequently the original formula – Fig. 15a – with quinoid structure should be preferred. Crampton and Gold [37b] arrived at a similar conclusion.

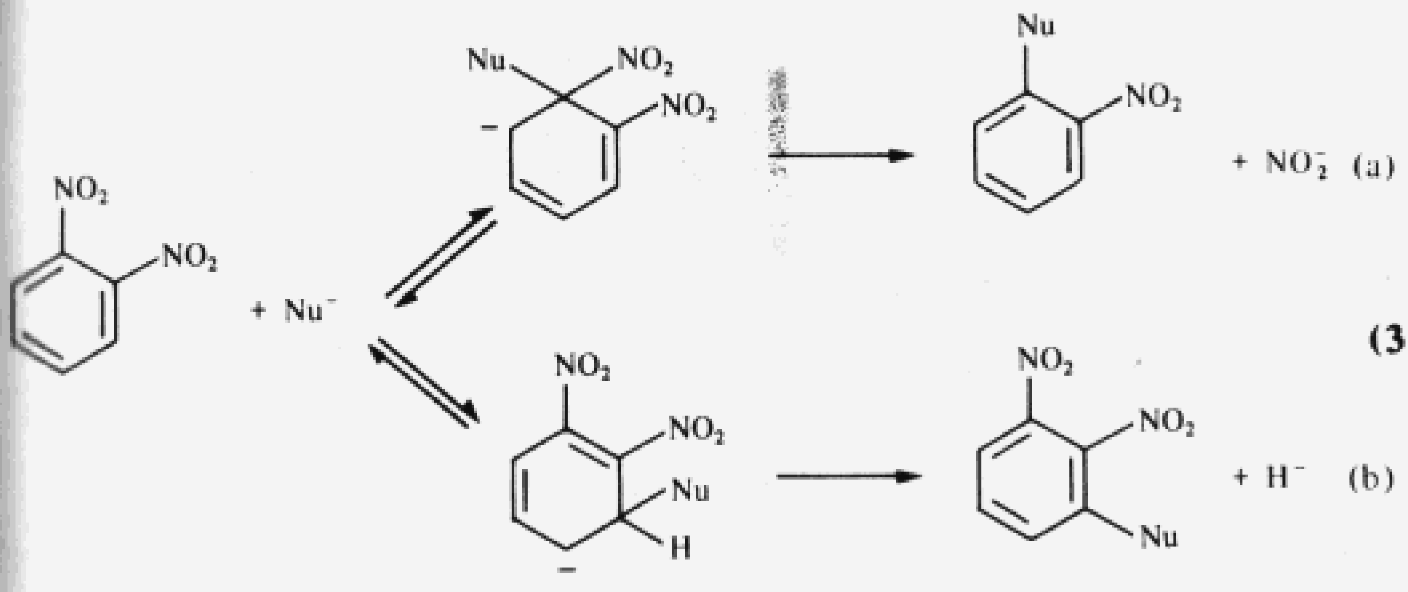
However, Heilbronner, Zollinger and co-workers [46] came to the conclusion that the existing formula of Jackson–Meisenheimer complexes is insufficiently exact in the light of the present theories of molecular orbital calculation. By using HMO method a shifting of π-electrons by the nitro groups should be considered. Thus the reaction of trinitroanisol with the methoxy anion can be depicted by diagram (2):



(2)

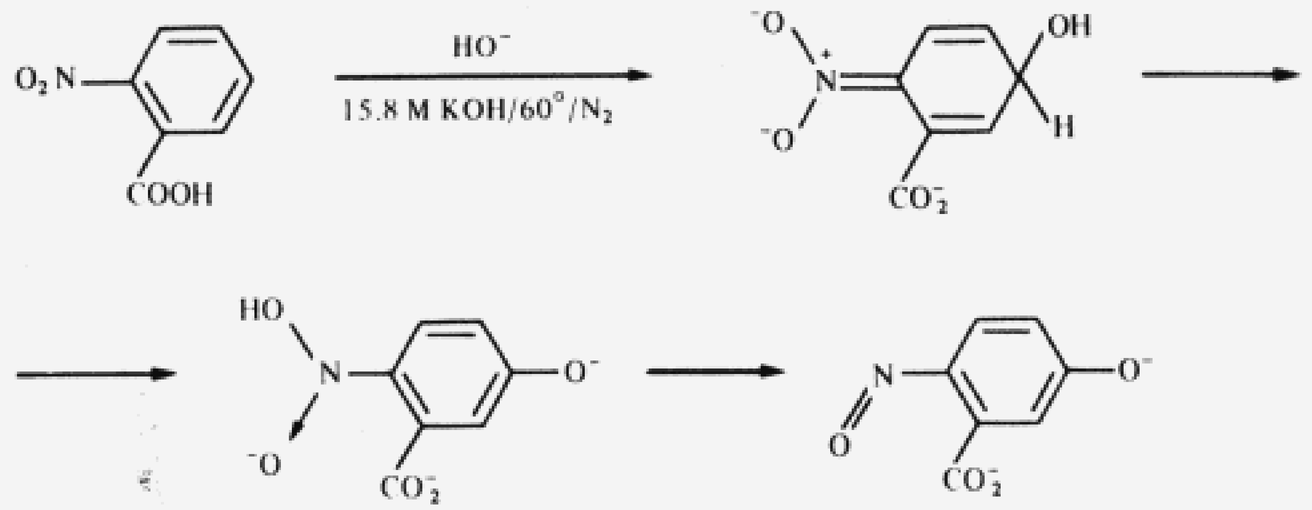
An interesting and novel approach to the Addition–Rearrangement–Elimination mechanism of tautomeric migration was recently reviewed by Minkin, Olekhnovich and Zhdanov [217]. The review also contained *N,N'* transfer of 2,4-dinitro- and 2,4,6-trinitrophenyl groups in a series of benzamidine derivatives [218, 219] and a description of previously unknown dipolar Meisenheimer spiro complexes. The authors point out the importance of this work to the design of new tautomeric systems with short living intermediate species.

Jackson–Meisenheimer type complexes can become intermediates which are further transformed into products of nucleophilic attack. Bowie [47] has produced diagrams as follows:



(3)

An interesting reaction of converting nitrobenzene into *p*-nitrosophenol [48] was now rationalized in terms of the formation of Jackson–Meisenheimer intermediate, according to scheme (4):

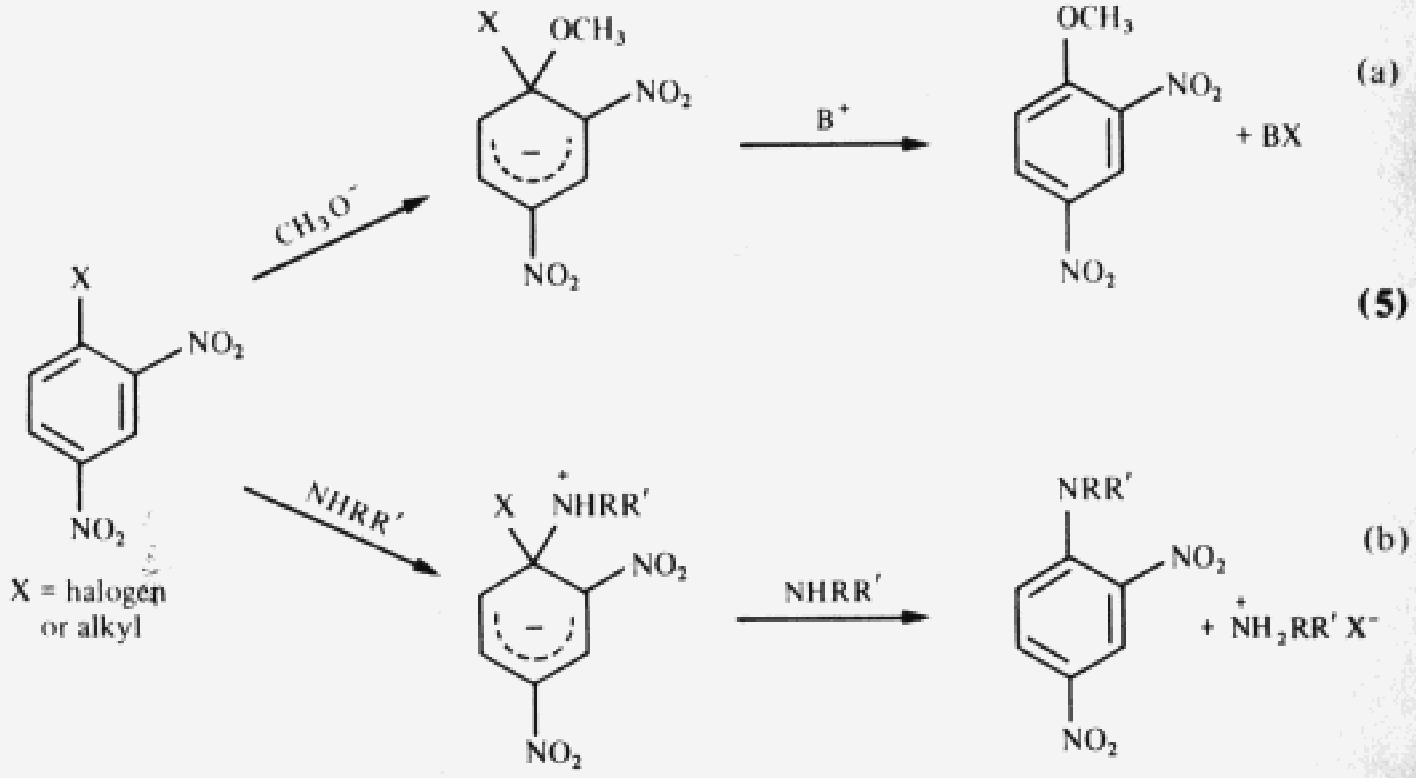


(4)

Practical Significance and Application of Jackson–Meisenheimer Reaction

The Jackson–Meisenheimer reaction is of considerable theoretical and practical significance for analytical and preparatory work in the laboratory and in industry. The latter refers to replacing halogen or alkoxy groups in nitroaromatics by acting with bases and it received full attention in Vol. I (pp. 197, 453, 461, 467, 484, 545, 547, 549, 559, 563, 571) and Vol. III (pp. 47, 61).

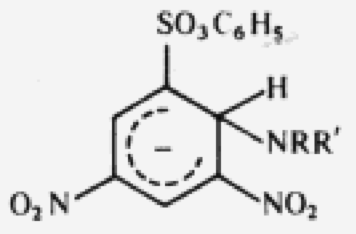
The reaction should be rationalized in terms of the formation of intermediate σ-complexes [21, 42]:



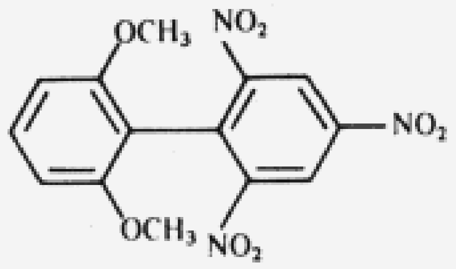
A free-energy contour diagram of reaction (5a) is given in a review paper [18].

Fluoro-2,4-dinitrobenzene is extensively used in the determination of *N*-terminal groups in peptides. A number of other nitro compounds reacting with nucleophiles are in use in biochemical work. A very wide description of the structure, kinetic properties and equilibrium of Jackson–Meisenheimer complexes was recently given by Terrier [223]. For review see [50].

J. Urbański [51] developed a nucleophilic colour reaction of dinitroarenesulphonic esters with primary and secondary amines and quaternary ammonium hydroxides. The reaction was originally used to determine small quantities of epoxy groups in polymers. The coloured products possess the structure of σ-complexes, for example V:



V



VI

Jackson–Meisenheimer complexes can serve in obtaining nitro derivatives of diphenyl. An original approach to this type of reaction was given by Wennerström [52]. He reacted a derivative of phenylsilver with 1,3,5-trinitrobenzene in the presence of pyridine. The oxidation of the σ-complex yielded compound VI.

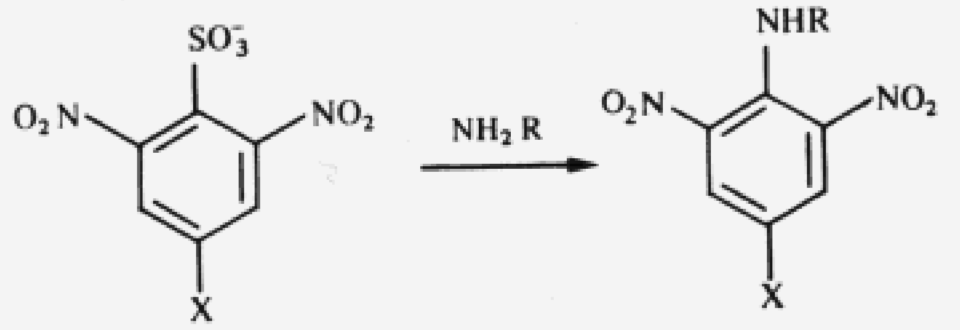
REACTION POTENTIAL MAP (RPM)

The calculation of the Reaction Potential Maps (RPM) [215] is a new kind of molecular reactivity index which is very helpful in elucidating the site selectivity observed in some chemical reactions. This was a development of the original calculation of electrostatic potential maps (EPM) by Bonaccorsi and co-workers [216].

The RPM method was proposed by Klopman *et al.* [215] to elucidate the reaction of ambient nucleophilic agents such as S CN$^-$ with hard and soft electrophiles: picryl fluoride and iodide respectively. The products contain the groups C–NCS and C–S CN respectively.

MYCELLAR NUCLEOPHILIC REACTIONS

Bunton and co-workers [53] made a significant contribution to reaction (6, X = halogen) by introducing cationic surfactants (detergents) which effectively catalysed the reaction of dinitrohalobenzenes with nucleophiles in aqueous solution by forming cationic mycelles. Cetyltrimethylammonium bromide and chloride (CTABr and CTACl) were used. Thus Bunton and co-workers [54] reported that the reaction of 2,4-dinitrofluorobenzene with $C_6H_5O^-$ and $C_6H_5S^-$ was catalysed by CTABr by factors 230 and 1100 respectively. Also the reaction of arene sulphonates with amines can be catalysed by cationic mycelles [55] (6):



(6)

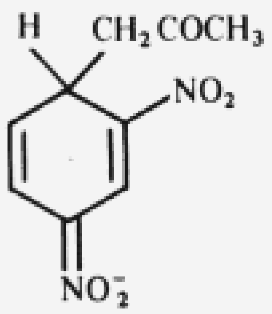
X = NO_2, CF_3

It should be pointed out that the reaction is inhibited or unaffected by anionic surfactants.

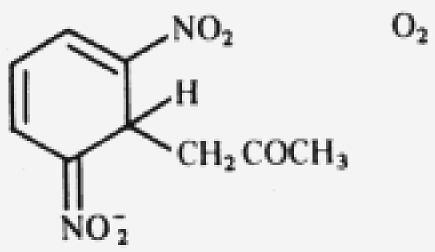
JANOVSKY REACTION (Vol. I, p. 207)

The Janovsky reaction became an important analytical test which could be used to detect both reagents: di- or trinitro-compounds or ketones and aldehydes. The modification of the reaction consisting in the use of *m*-dinitrobenzene as a test for 17-ketosteroids is sometimes called the Zimmerman reaction [15, 56].

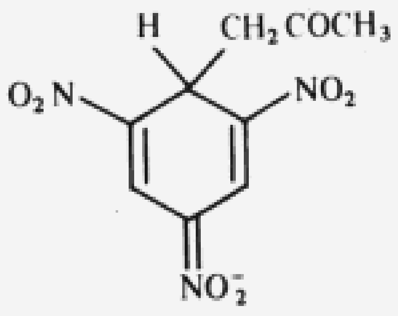
The Janovsky reaction was reviewed by Hall and Poranski [10], Buck [15], Strauss [17] and more recently by Gitis and Kaminskii [57]. The structure given in Vol. I, p. 209 is now regarded as incorrect. Instead formulae VIIa, VIIb and for 1,3,5-trinitrobenzene VIII (see also Vol. I, pp. 210–211) are now accepted. They were suggested by Hantzsch and Picton [58] as early as 1909 and more proof was given in their favour by Gitis and Kaminskii [59], Foster and Fyfe [60], Severin and Schmitz [61] and Kimura [62].



VII a



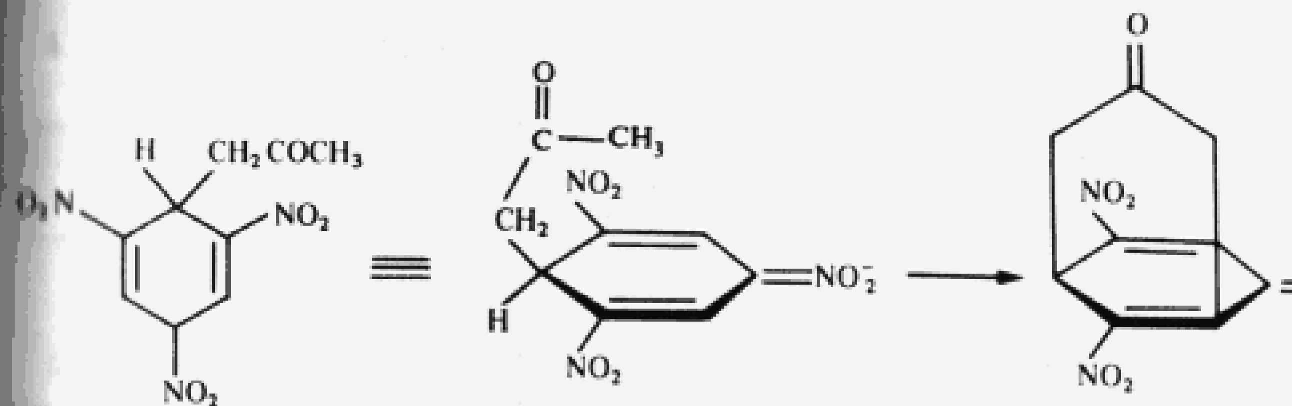
VII b



VIII

Similar to the reaction by Jackson–Meisenheimer the formation of compounds VII–VIII is reversible and acids reproduce the substrates.

These compounds however form the first step of the Janovsky reaction. They can further react to yield bicyclic products (IX) according to Strauss and Schran [17, 63], Kohashi, Ohkura and Momosa [64] (7)



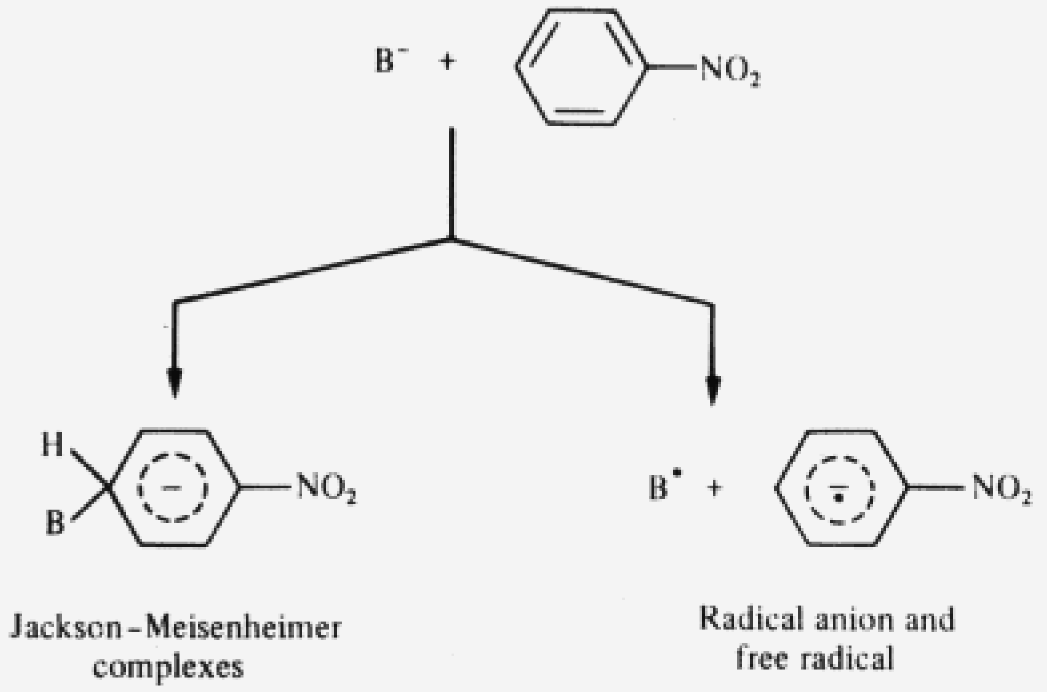
(7)

IX

The mechanism of formation VII and IX was rationalized by Sosonkin and co-workers [65] using ultraviolet, infra-red and ESR techniques.

ACTION OF BASES IN NUCLEOPHILIC REACTIONS OF NITRO COMPOUNDS

Nitro compounds can react with carbanion through the nucleophilic mechanism. Carbanions (as well as radical anions and free radicals) can be formed by the action of strong bases on nitrocompounds. Russell and co-workers [66] presented it in scheme (8):



(8)

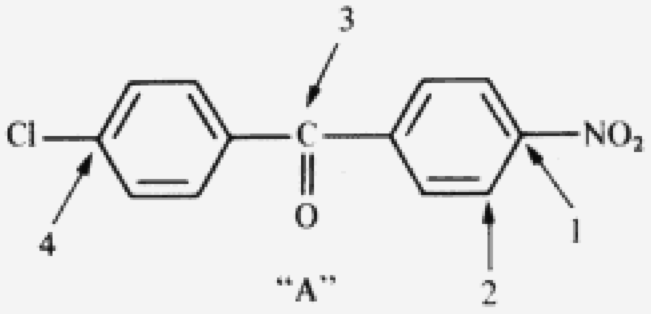
Mąkosza and Jawdosiuk [67] have found that nitrobenzene can react exothermally with nitriles in the presence of such bases as NaOH, $NaNH_2$ and CH_3ONa and in various solvents. Substitution in *para* position can occur. The yield was greatly influenced by the solvent. The highest (15%) was in liquid ammonia and THF at −60 to −30°C.

Mąkosza [20, 68] developed a new two phase nucleophilic reaction which consists in the use of quaternary salt of a cation (Q^+) – most frequently tri-

ethylbenzylammonium (TEBA) – chloride suggested originally by Jarousse [126]. The cations of TEBA are present in the aqueous phase containing a concentrated solution of NaOH (usually 50%), whereas organic phase, inmiscible in water, contains the nitro compounds and a nitrite, for example 2-phenylpropionitrite. The reaction is now known as 'Jarousse–Mąkosza' or 'Mąkosza' reaction.

Thus *p*-chloronitrobenzene does not react with 2-phenylpropionitryl in 50% aqueous NaOH, but the addition of a catalytic quantity of TEBA chloride immediately produces an exothermic reaction with the yield *ca*. 80% of the substitution product.

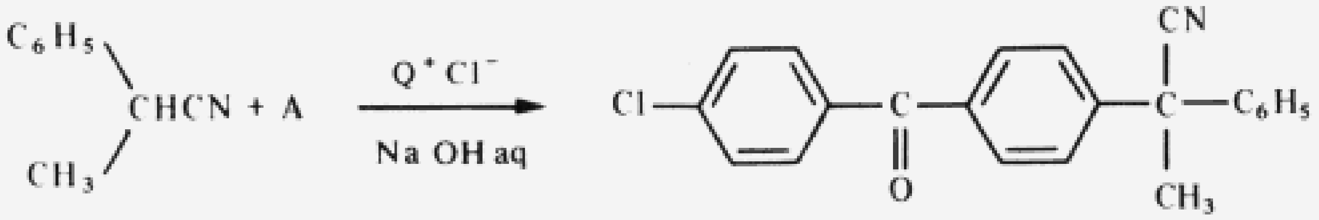
A model depicting a variety of reactions is 4-chloro-4-nitrobenzophenon (X). It contains four possible positions of attack:



X

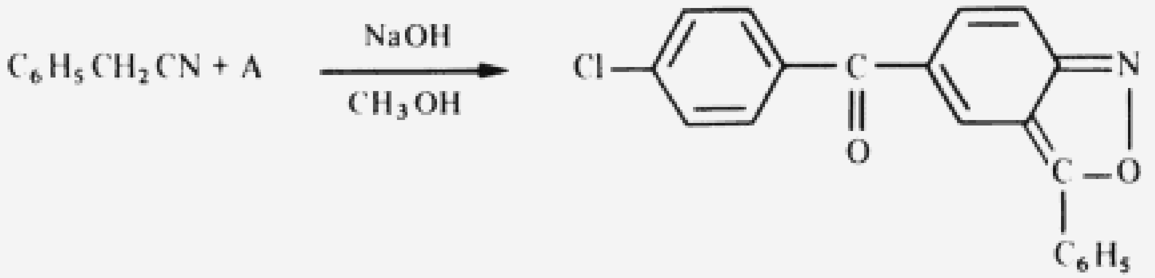
All these positions can be attacked by a suitable nucleophile, as can be seen in schemes (9–12) [69–71].

1. Substitution of the nitro group



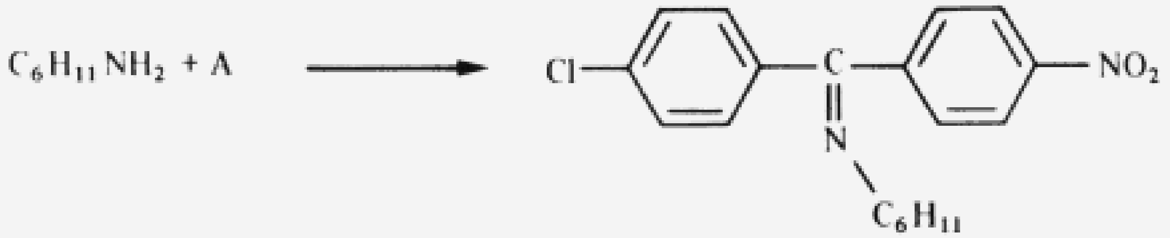
(9)

2. Substitution in position 2



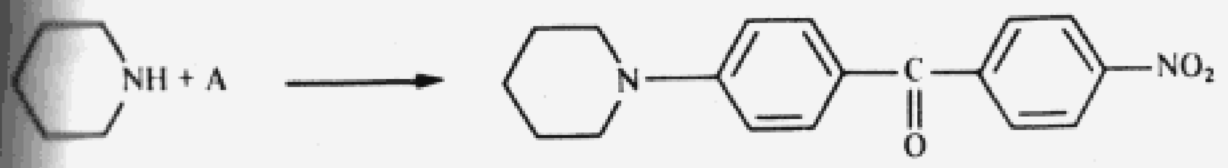
(10)

3. Attack of the carbonyl group



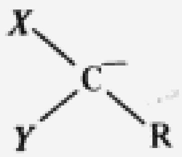
(11)

4. Substitution of chlorine



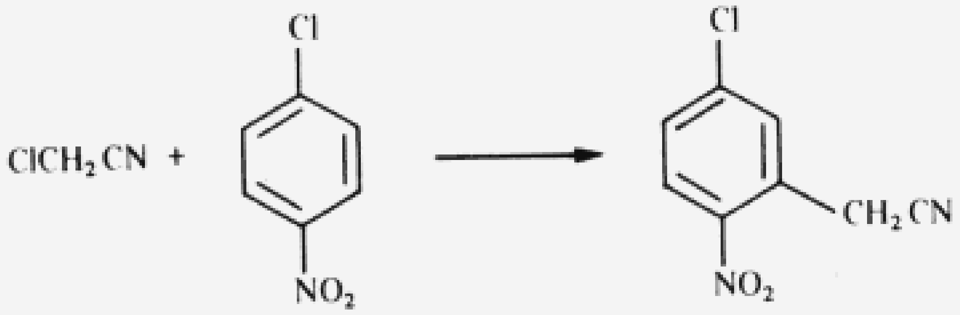
(12)

Another kind of substitution of nitro compounds was 'vicarious' substitution [72, 73], which takes place when the attack is carried out by a nucleophile



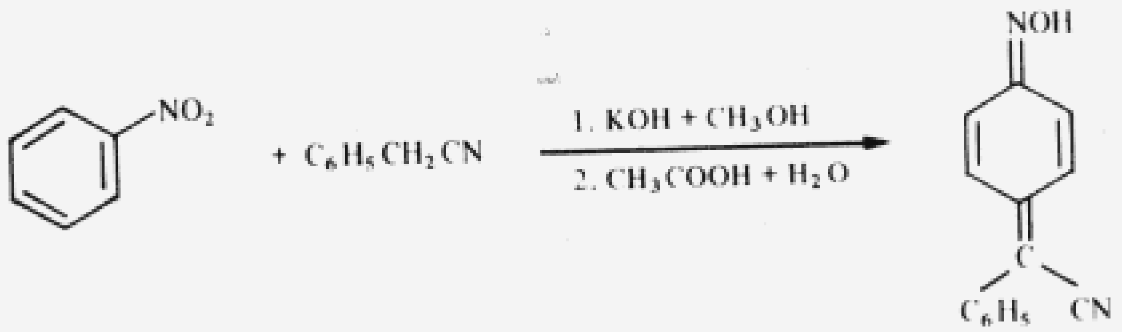
where X is a leaving group in a form of anion
Y is a group stabilizing carbanion

An example of such a substitution is reaction (13):



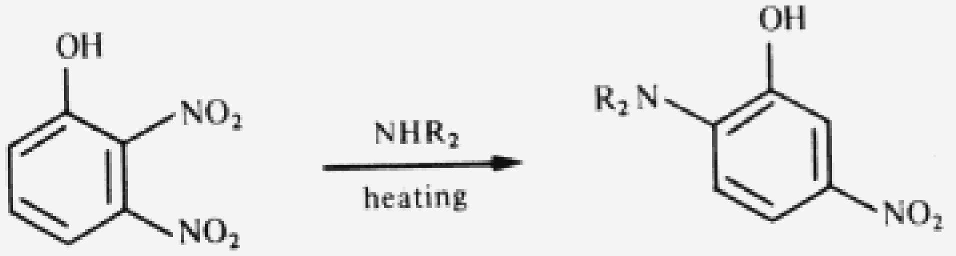
(13)

An example of nucleophilic substitution combined with a partial reduction of the nitro group was given by Davis and co-workers [74–76]. They examined the action of phenylacetonitryl anion on nitrobenzene and found that it formed a substitution compound with a p-quinoid ring according to scheme (14):



(14)

Cine-nucleophilic substitution is an interesting example of nucleophilic substitution with the loss of a nitro group. This was reviewed [77] and a few new examples were given: by Barnett, Dickens and West [78] and by Markwell [79]. The latter work gives an example of such substitution (15):



(15)

A nucleophilic introduction of an amino group into p-nitrobenzenephenone through the action of potassium amide in liquid ammonia was recently reported [80]. The substitution occurred in the *ortho* position to the nitro group with a yield of 17%.

Important for industry is the reaction of the substitution of a nitro group by a sulphonic group as was described in Vol. 1 (pp. 201, 207). The mechanism of the reaction is now given in the chapter dedicated to the manufacture of TNT and other higher nitrated aromatics.

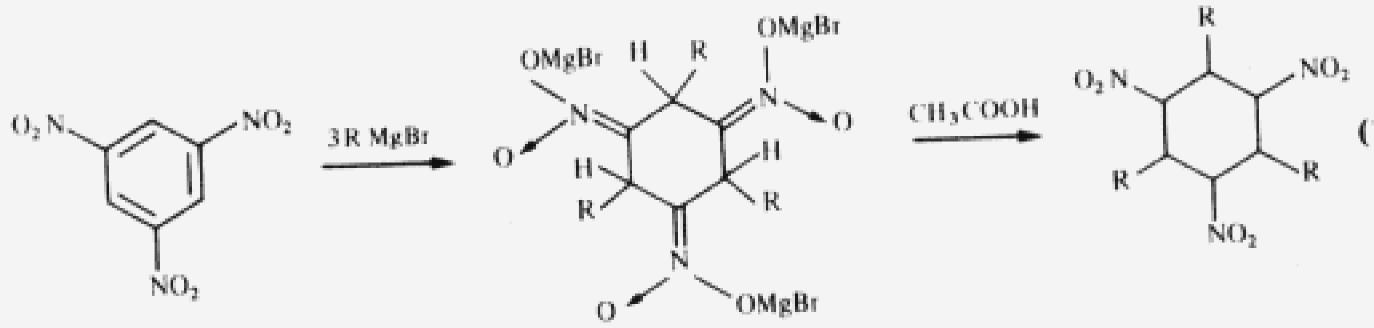
Salts of TNT (and strictly speaking salts of the products of decomposition of TNT through the action of strong bases) were described in Vol. I, pp. 303–304. They possess interesting pyrotechnic properties such as ease of burning. They seem to be the base of delay compositions described in a patent by du Pont de Nemours [220].

ACTION OF GRIGNARD REAGENT ON NITRO COMPOUNDS

(Vol. I, p. 186)

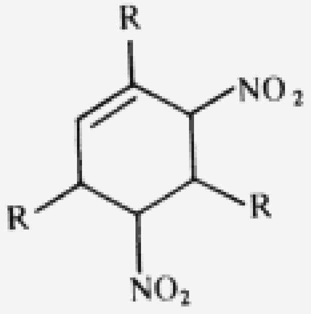
In addition to a few rather confusing papers on the action of Grignard reagent on nitro compounds (see 15), two papers should be mentioned: on the reduction of the nitro group to an amino group [81] and advice on how to carry out the reaction at low temperature (e.g. −70°C) otherwise undefined resinous products can be formed [82].

As it was stated, Severin (Vol. I, p. 187) obtained, 1,3,5-trialkyl-2,4,6-trinitrocyclohexane from 1,3,5-trinitrobenzene and Grignard reagent followed by acidification with acetic acid of the originally formed σ-complex, Severin and R. Schmitz [83] described fully the reaction as below (16):



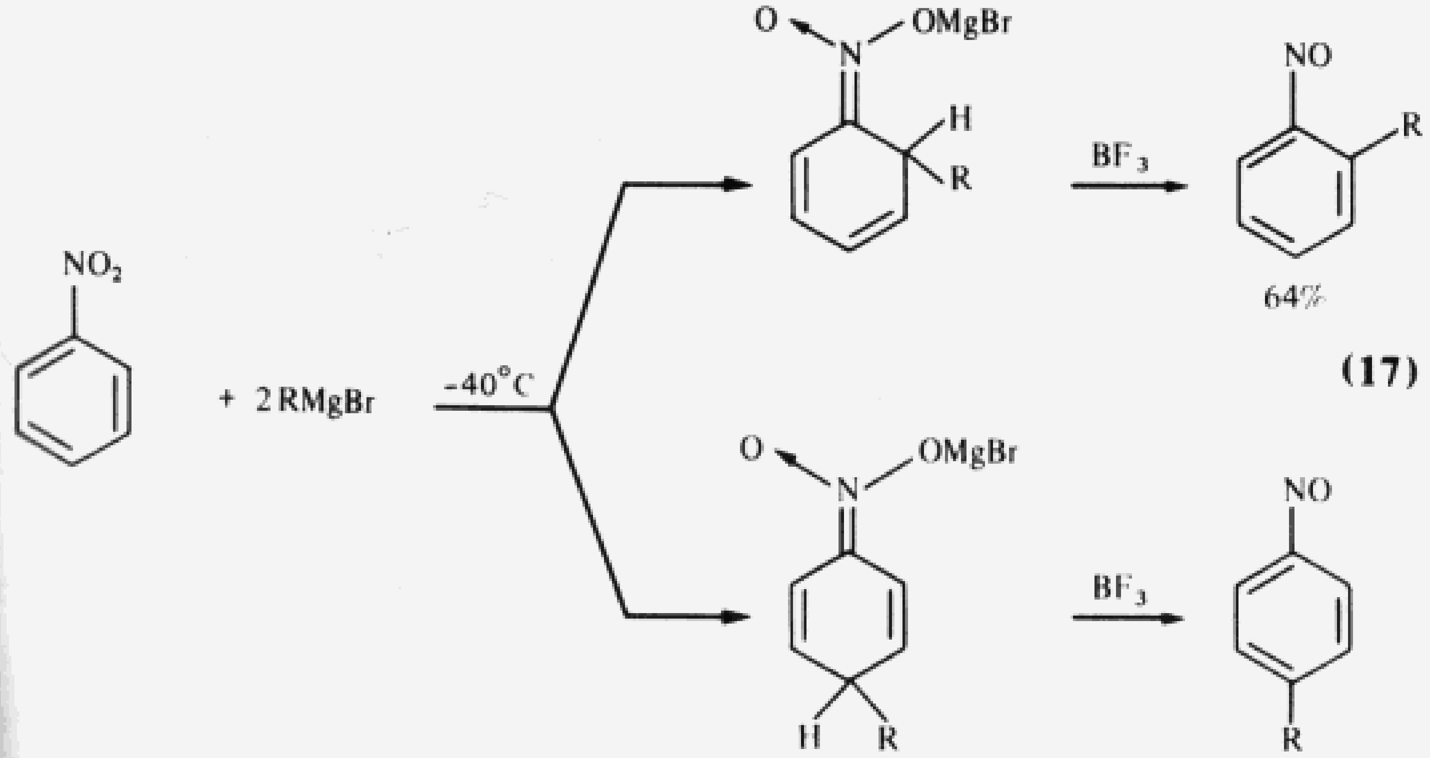
(16)

Similarly m-dinitrobenzene yielded a cyclohexene derivative (XI) [84]



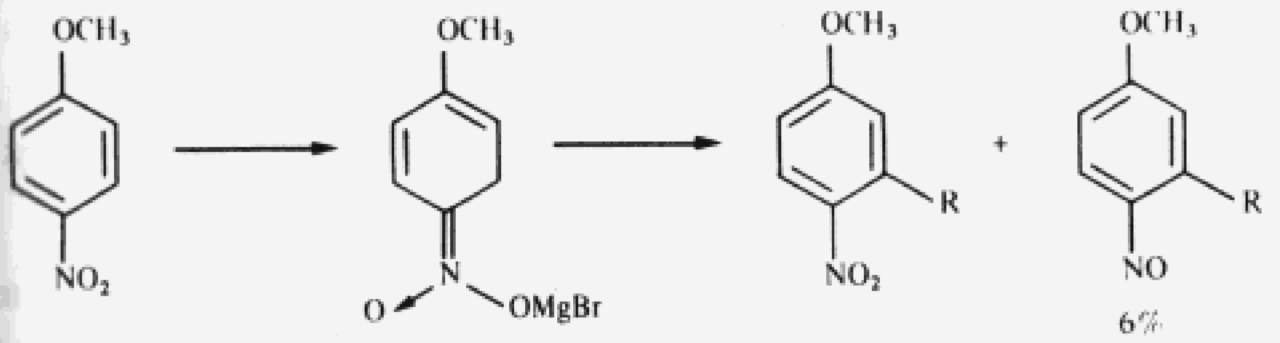
XI

Recently Bartoli and co-workers [85–87] have published a number of papers dedicated to the systematic study of the reaction of aromatic nitro compounds with Grignard reagent. They confirmed the nucleophilic character of the alkylation of the ring. They also found that under their experimental conditions the nitro group was reduced to the nitroso group (17):



(17)

However *p*-nitroanisol gave an 'anomalous' reaction (in the findings of Bartoli *et al.*). The main product was 3-alkyl-4-nitroanisol and only a small quantity of nitroso compound was found (18):



(18)

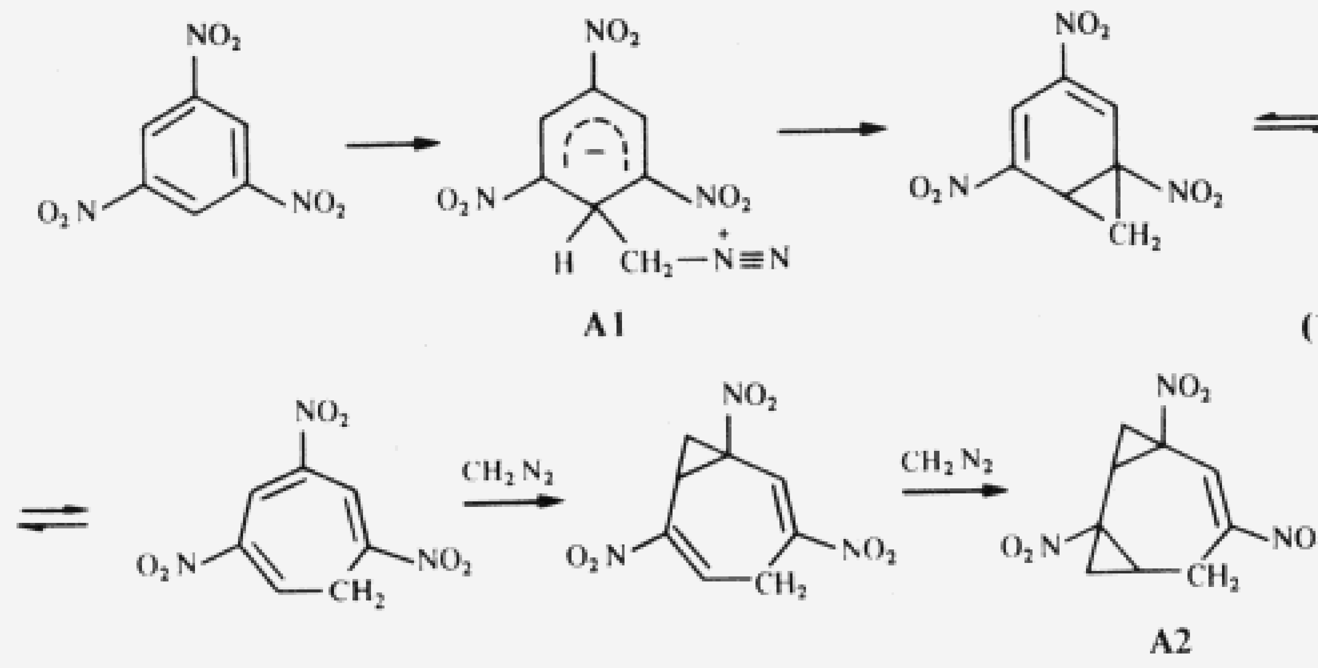
Bartoli and co-workers pointed out that their results did not contradict those of Severin and the differences were due to the different substrates and different experimental conditions.

Interesting cases of reactions of metal salts of secondary amines with nitrobenzene have also been recorded. Thus Montmollin [142] reacted potassium salt of carbazol with nitrobenzene. The nucleophilic substitution of nitrobenzene occurred in *para* position to the nitro groups. A similar reaction with diphenylamine [143] has also been described.

REACTION OF AROMATIC NITRO COMPOUNDS WITH DIAZOMETHANE (Vol. I, p. 195)

The reaction of 1,3,5-trinitrobenzene with diazomethane was carried out as early as 1898–1900 [88, 89], but only recently de Boer rationalized it as a nucleophilic addition leading to seven member ring condensed with two cyclopropane rings when the molar ratio of trinitrobenzene to diazomethane was 1:3. The first step of the reaction was a type of Jackson–Meisenheimer complex (A_1) and the final product was trismethylene-trinitrobenzene (A_2) [90–92a] (19). The reaction is temperature dependent: at −80°C compound (A_3) was formed.

With an excess of diazomethane (molar ratio 1:4) the last double bond can enter the reaction forming a stable pyrazoline ring not a cyclopropane (20)



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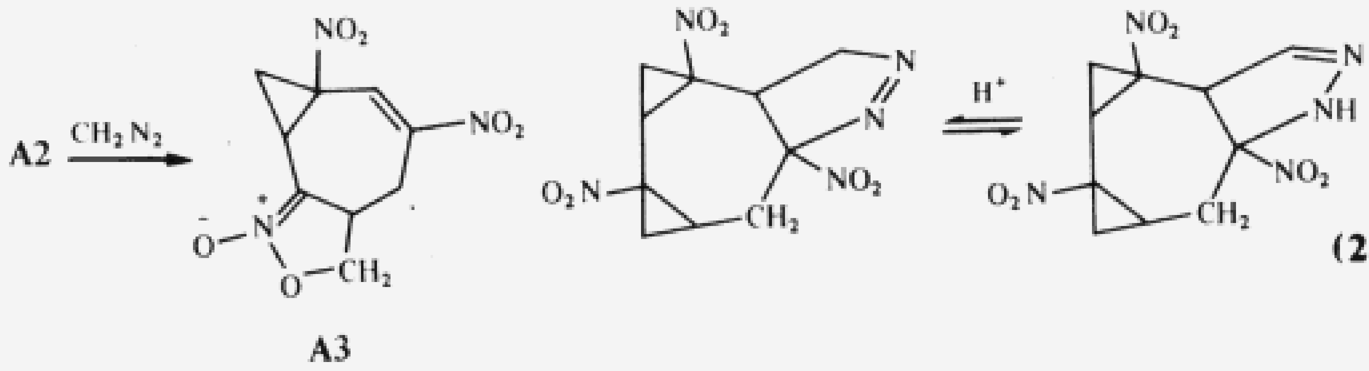
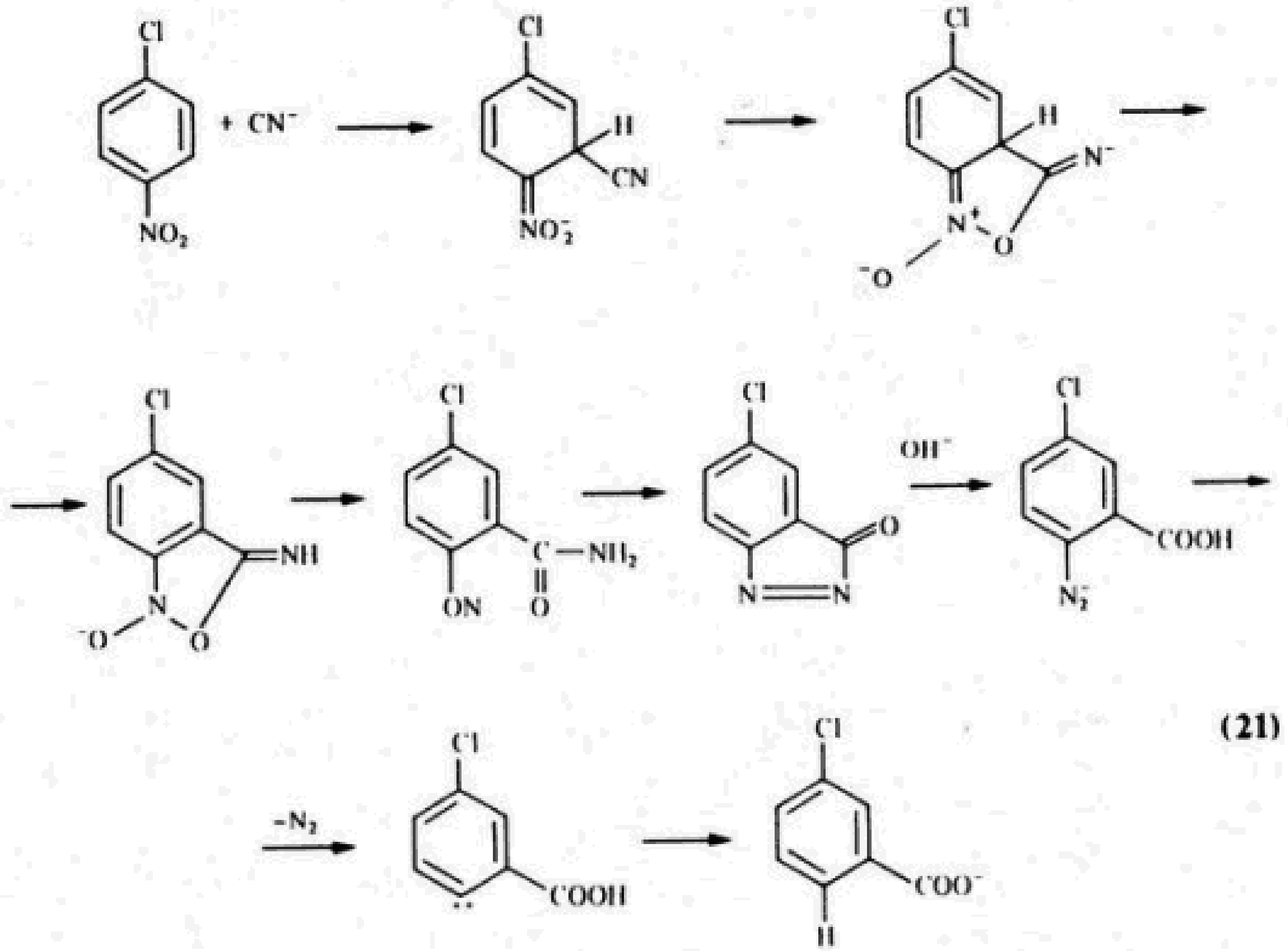


(20)

A similar reaction was given by picric acid which in the first instance was methylated to trinitroanizol [93].

MECHANISM OF RICHTER REACTION (Vol. I, p. 205)

In Richter reaction *m*-bromobenzoic acid may be obtained by reacting potassium cyanide with *p*-nitrobromobenzene. The original mechanism of th reaction given by Bunnett (Vol. I, p. 205) was further developed and can be presented in the form of scheme (21) [94, 95].



(21)

NUCLEOPHILIC SUBSTITUTIONS IN GAS PHASE

Nucleophilic substitutions can be carried out in gas-phase. Such reactions are much faster than in solution. They were recently reviewed by Bowie [47]. Some of these reactions are produced by radical anions.

REACTIONS OF RADICAL IONS

The reactions of radical ions form an important part of organic chemistry and a monograph [96] and review articles [97–101] have appeared.

A radical ion is a molecule which in addition to one or more unpaired electrons has a positive and negative charge in radical cation and anion respectively. A formal presentation is shown in diagrams (22) according to [100]:

$$\begin{array}{ll} \text{M} + \text{e} \longrightarrow \text{M}^{\overset{-}{\cdot}} \text{ radical anion} & \text{(a)} \\ \text{M} - \text{e} \longrightarrow \text{M}^{\overset{+}{\cdot}} \text{ radical cation} & \text{(b)} \end{array} \qquad (22)$$

Radical anions of nitro compounds

The radical anions of nitrobenzene and substituted nitrobenzenes may be formed by electrolytic or metal reduction [100].

The treatment of *o*- and *p*-nitrotoluenes with a basic agent (e.g. potassium *t*
butoxide) in the absence of air can give rise to oxidation of nitrobenzyl radica
anions which further react to yield dinitrodibenzyl [102]. The reaction can pro
ceed through a radical chain mechanism [103] (23):

$$p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_3 \overset{\text{B}^-}{\rightleftharpoons} p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2^- \qquad \text{(a)}$$

$$p\text{-NO}_2\text{C}_6\text{H}_4^- + p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_3 \longrightarrow [p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_3]^{\overset{-}{\cdot}} + p\text{-NO}_2\text{C}_6\text{H}_4\dot{\text{C}}\text{H}_2 \qquad \text{(b)} \quad (23$$

$$p\text{-NO}_2\text{C}_6\text{H}_4\dot{\text{C}}\text{H}_2 + p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2^- \longrightarrow [p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{C}_6\text{H}_4\text{NO}_2\text{-}p]^{\overset{-}{\cdot}} \qquad \text{(c)}$$

Russell and co-workers [104] also examined the action of potassium
butoxide on *p*-nitrotoluene, 2,4-dinitrotoluene, 2,4,6-trinitrotoluene, *m*-dinitr
benzene and 1,2,5-trinitrobenzene. The higher the nitrated hydrocarbons th
slower the oxidation.

Hass and Bender [105] described a reaction of *p*-nitrobenzyl chloride wit
salts of nitroalcanes, for example of 2-nitropropane. The mechanism of the r
action was rationalized by Kornblum and co-workers [106] and Russell ar
Danen [107] as a sequence of chain reactions:

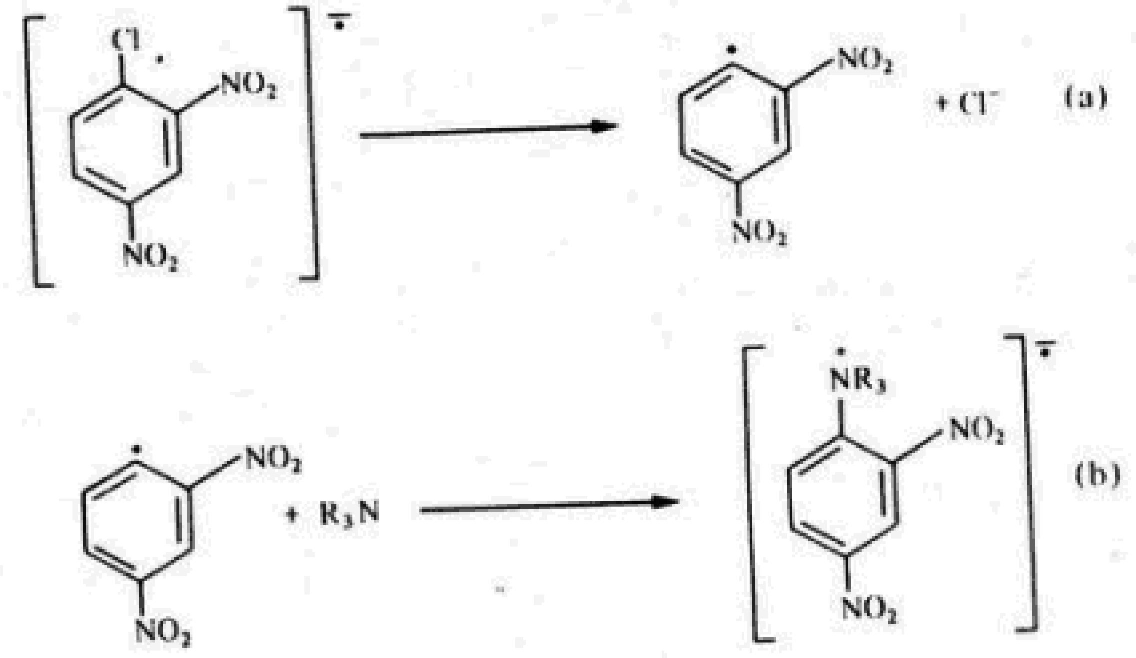
$$p\text{-NO}_2\text{C}_6\text{H}_4\text{Cl} + (\text{CH}_3)_2\text{C}=\text{NO}_2^- \longrightarrow (\text{CH}_3)_2\dot{\text{C}}\text{NO}_2 + [p\text{-NO}_2\text{C}_6\text{H}_4\text{Cl}]^{\overset{-}{\cdot}} \qquad \text{(a)}$$

$$[p\text{-NO}_2\text{C}_6\text{H}_4\text{Cl}]^{\overset{-}{\cdot}} \longrightarrow p\text{-NO}_2\text{C}_6\text{H}_4\dot{\text{C}}\text{H}_2 + \text{Cl}^- \qquad \text{(b)}$$

$$p\text{-NO}_2\text{C}_6\text{H}_4\dot{\text{C}}\text{H}_2 + (\text{CH}_3)_2\text{C}=\text{NO}_2^- \longrightarrow [p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{C}(\text{CH}_3)_2\text{NO}_2]^{\overset{-}{\cdot}} \qquad \text{(c)} \quad (2$$

$$\begin{array}{l} [p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{C}(\text{CH}_3)_2\text{NO}_2]^{\overset{-}{\cdot}} + p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{Cl} \longrightarrow \\ \longrightarrow p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{C}(\text{CH}_3)_2\text{NO}_2 + [p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{Cl}]^{\overset{-}{\cdot}}. \end{array} \qquad \text{(d)}$$

Another example of chain reactions with radical anions was described
Shein and co-workers [108]: that is the reaction (25) between 2,4-dinitrochlo
benzene and trialkylamines:



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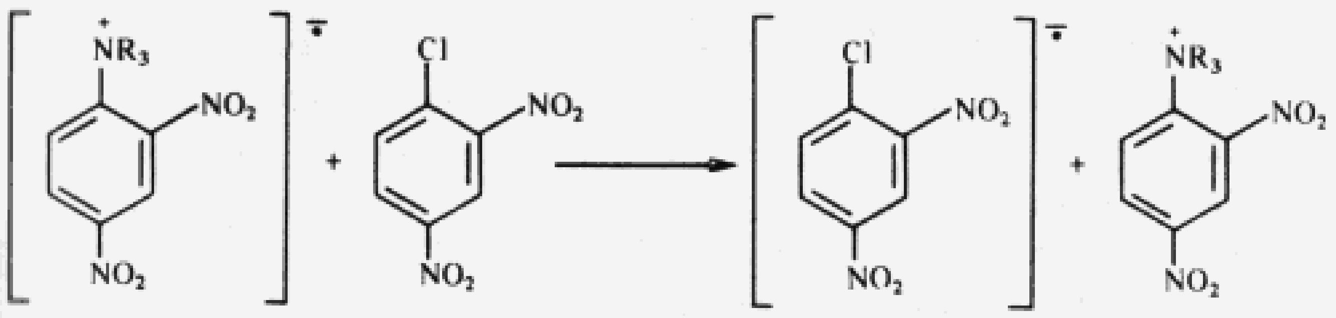


(c)

(25)

An interesting example of a radical anion reaction is the action of oxygen negative ion formed in chemical ionization in a mass spectrometer [109]:

$$p\text{-}NO_2C_6H_4Cl + O_2^{-} \longrightarrow p\text{-}NO_2C_6H_4O^{-} + ClO. \qquad (26)$$

Nitroaromatics can act as catalysts of some oxidation reactions, such as the oxidation of benzoin [110] and polynitroaromatics in the oxidation of 'hindered' phenols [111]. Russell and co-workers [112a, b] rationalized it in terms of radical ion reactions where the radical ion Ar $NO_2^{\overset{\cdot}{-}}$ activates oxygen (27):

$$Ar\,NO_2^{\overset{\cdot}{-}} + O_2 \longrightarrow Ar\,NO_2 + O_2^{\overset{\cdot}{-}}. \qquad (27)$$

FREE RADICAL REACTIONS (Vol. I, p. 212)

A few monographs have been dedicated to free radical reactions including substitutions. The most important are those by Williams [113] and Sosnovsky [114] and a review article has appeared concerning the homolytic substitution of nitro compounds [115].

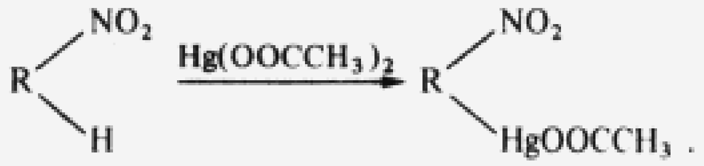
The nitro group activates aromatic rings towards a homolytic substitution. As previously pointed out the nitro group directs a substitution into *ortho* and *para* positions through the greater availability of an unpaired electron at the *ortho* and *para* positions and a greater stability of *ortho* and *para* quinoid which can be regarded as intermediates of some homolytic substitutions.

Some of the main reactions of aromatic nitro compounds with free radicals are given here [116]. Nitrobenzene reacts with hydroxyl produced by hydrogen peroxide ferrous salt reaction (28)

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + HO^{-} + HO^{\cdot}. \qquad (28)$$

The reaction furnished *o*-, *m*- and *p*-nitrophenols with yields of 25–30%, 20–25% and 50–55% respectively.

Another typical free radical reaction is that of mercuration of nitrobenzene with mercuric acetate in a non-polar solvent [117] (29):



$$R\begin{smallmatrix}NO_2\\ H\end{smallmatrix} \xrightarrow{Hg(OOCCH_3)_2} R\begin{smallmatrix}NO_2\\ HgOOCCH_3\end{smallmatrix}. \qquad (29)$$

Ortho and *para* isomers are formed in proportion in 57%, and *meta* in 43%. A relatively large proportion of *meta* isomer is probably due to the lack of a clear demarcation line between the electrophilic and the radical substitution.

A partial radical substitution may be responsible for the nitration of nitrobenzene to dinitrobenzenes by nitric acid in the presence of mercuric oxide reported by Ogata and Tsuchida [118]. They found 26% of *o*- and only 24% *m*-dinitrobenzenes.

Hey and co-workers [119–124] studied the arylation of nitrobenzene through the action of various sources of aryl radicals *p*-R $C_6H_4^{\cdot}$ generated from such sources as diazotates (*p*-$RC_6H_4N_2ONa$), nitrosoacylarylamines (*p*-R $C_6H_4\underset{\underset{NO}{|}}{N}\,COCH_3$) and acyl peroxides (*p*-R $C_6H_4CO_2)_2$. The average substitution in the *meta* position for R = Br and CH_3 was only 12.1 and 8.6% respectively and was independent of the source of aryl radical.

The phenylation of nitrobenzene gave the figures shown in Table 25.

TABLE 25. Substitution of nitrobenzene with phenyl radical (average figures)

Source of phenyl radical	Nitrophenyls % *ortho*	*meta*	*para*
Sodium benzenediazotate	54	9	37
Benzoil peroxide	59.5	8.5	32

However, when the free radical is *p*-nitrophenyl, the proportion of *meta* isomer increases. This is explained by the fact that the radical *p*-$NO_2C_6H_4^{\cdot}$ is somewhat electrophilic in character.

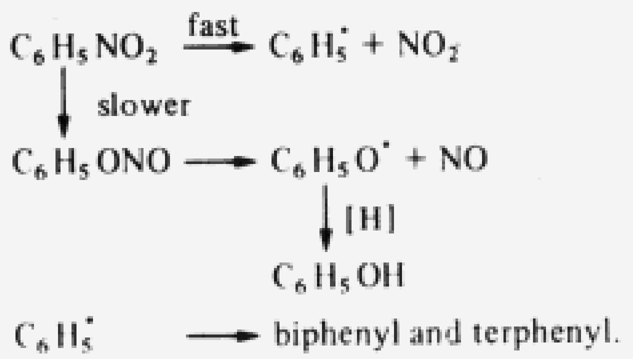
Hey and Grieve [125] found in 1934 that the nitro group activates the aromatic ring towards homolytic substitution. For example, the competitive phenylation of toluene and nitrobenzene by phenyl radicals showed that the yield of nitrodiphenyls was about four times greater than the yield of methyldiphenyls.

Hey and co-workers [119, 121, 124] gave a quantitative analysis of the rate of homolytic attack on nitrobenzene as compared with that on chlorobenzene. The phenylation of nitrobenzene gave proportions of *ortho, meta* and *para* products: 58, 10 and 32% respectively, whereas the phenylation of chlorobenzene yielded 62, 24 and 14% respectively. However when the entering group is more electrophilic than benzene (e.g. *o*- and *p*-nitrophenyl radicals) the proportion of *meta* substituents increased.

Fields and Meyerson [127] have described in numerous papers the formation of free radicals from aromatic nitro compounds at temperatures of 400–600°C. Their work has been summarized in a review paper [128]. They found that the C – N bond in nitroaromatics breaks above 400°C generating phenyl and similar aromatic radicals. The decomposition at 600°C seems to be closely paralleled to its decomposition under electron impact in a mass spectrometer. Nitrobenzene at 600°C, gave within 20 s. a 30% yield of phenol, biphenyl, dibenzofurane, benzene, hydroxybiphenyl, nitrobiphenyl and in some instances of naphthalene.

In the presence of benzene, toluene, pyridine and tiophene, considerable proportions of biphenyl and terphenyl and their homologues and analogues were formed.

The mechanism of the reactions is rationalized by the authors, as follows (30):



(30)

Naphthalene can be formed, according to the authors, through the intermediate formation of benzyne.

A few more free radical reactions of nitro compounds should be mentioned. Some of these reactions are photo-induced and are described in the chapter on photochemistry of nitro compounds.

In 1866 Kekulé [129] described the reaction of nitrobenzene with bromine at 250°C which under pressure yielded tetra- and hexabromobenzene [130], thus the replacement of the nitro group by bromine occurred. Later it was found [131] that chlorobenzene was the main product when acting with chlorine on nitrobenzene at 375°C in 46 s contact time with only a small proportion of chloronitrobenzenes. The substitution of nitro groups in *m*-dinitrobenzene by chlorine in gas phase at 200–300°C appears to be a commercial method of manufacturing *m*-dichlorobenzene [132]. Ponomarenko [133] studied this reaction and found the yield to be 92%. He also stated that aromatic nitro compounds are transformed into chloro derivatives by acting on nitro compounds with carbon tetrachloride at 220–310°C under pressure.

A similar, but probably nucleophilic substitution was studied by Lobry de Bruin and van Leent [134]. By acting with hydrochloride at 250°C they replaced nitro groups in dinitrobenzenes and *s*-trinitrobenzene to obtain dichlorobenzenes and *s*-trichlorobenzene respectively.

Gerstman and Bickel [111] observed that polynitroaromatics can act as catalysts in the oxidation of hindered phenols.

The mechanism of the catalytic action of aromatic nitro compounds was not clear until Russell and co-workers [136] rationalized it in terms of free radical reactions. Their particular study was dedicated to the oxidation of fluorene by molecular oxygen in ter-butoxide in the presence of potassium ter-butoxide. The reaction is catalysed by aromatic nitro compounds, such as nitrobenzene and particularly *m*- and *p*-dinitrobenzene and *p*-bromo- and *p*-chloronitrobenzene.

A rather unusual free radical reaction should be mentioned here: aryl free radical produced by heat or copper powder can displace and substitute a nitro group [172, 173].

ACTION OF AROMATIC NITRO COMPOUNDS ON POLYMERIZATION

(Vol. I, p. 214)

Aromatic nitro compounds inhibit radical polymerization. However, they do not seem to inhibit ionic polymerization [137]. On the contrary Rumanian authors reported [190] that nitrobenzene as well as nitromethane and nitroethane increase the rate of cationic polymerization of *N*-vinylcarbinol.

With regard to radical polymerization some controversial results have also been obtained. Thus Mondvai and co-workers [138] have shown that *o*-dinitrobenzene was a stronger retardant of radical polymerization of methyl methacrylate than other isomers. On the contrary Hammond and Bartlett [139] found that *o*-dinitrobenzene was a weaker retardant than other isomers of polymerization of allyl acetate.

T. Urbański and Buźniak [140, 141] undertook the task of a systematic study of the action of mono-, di- and trinitro derivatives of benzene and toluene (a few dozen compounds) on the polymerization of unsaturated polyester resin 'Polymal 109'. The polymerization was initiated with benzoil peroxide at 12°C. It was found that nitro compounds with an *ortho* substituent are particularly active as inhibitors of polymerization.

The strongest inhibitor was found to be *o*-nitrotoluene.

Steric factors, such as those produced by two methyl groups in *ortho* position reduces the inhibitory activity of the nitro compounds.

Tüdös and co-workers [175] described inhibition of polymerization of styrene by *sym*-trinitrobenzene.

All these studies may have a certain significance in the technology of solid propellants for rockets.

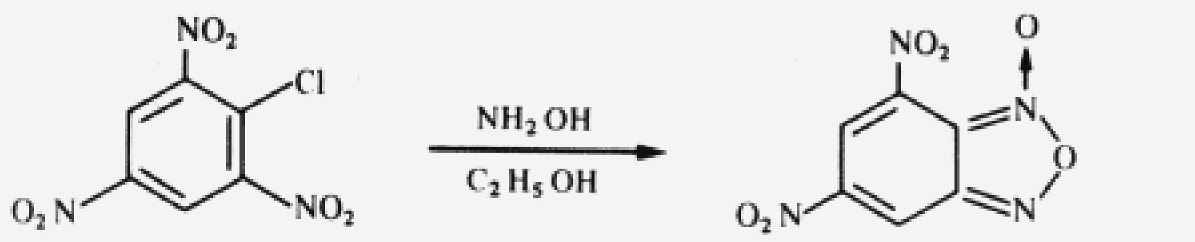
REDUCTION OF AROMATIC NITRO COMPOUNDS. FORMATION OF NITROSO COMPOUNDS

The reduction of the nitro group to amino and hydroxyamino groups is well known and described in textbooks dedicated to intermediates and dyestuffs.

Less known is the reduction of nitro to nitroso group. It was reviewed by Boyer in a chapter 'Reduction and Deoxygenation of Nitro Compounds' [147]. The following are methods giving good yields of nitroso derivatives:

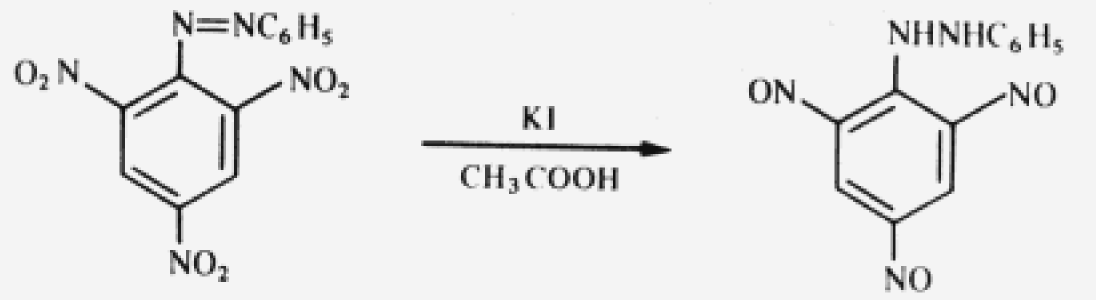
electrolytic reduction [148],
catalytic reduction in the presence of iron powder in CO_2 at 220°C [149],
deoxygenation of nitro group by free radicals [150].

Reduction of a nitro group can lead to a ring closure to form furoxane derivatives [151]



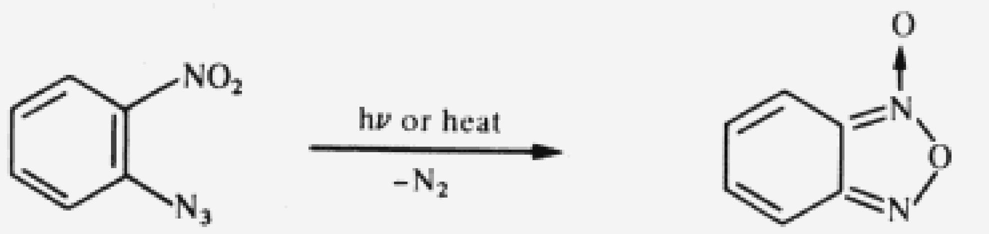
(31)

Another interesting reaction was reported by Willgerodt [152] on the action of potassium iodide in acetic acid on *N*-1,3,5-trinitrosophenyl-*N*-phenylhydrazine (from picrylazobenzene) (32):



(32)

The classical photochemical reaction of Ciamician and Silber [153] of *o*-nitrobenzaldehyde transformed into *o*-nitrosobenzoic acid is described in the chapter on photochemistry of nitro compounds. *o*-Nitrophenyl azide can readily yield benzofuroxane [154].



(33)

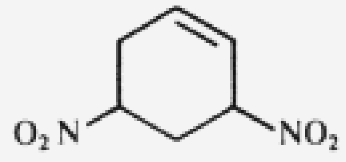
It is highly probable that a nitroso intermediate is formed in the Richter reaction (p. 109).

Reduction of Aromatic Ring

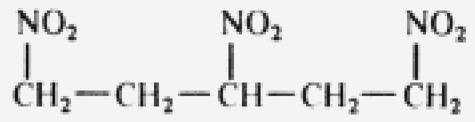
A remarkable reaction was discovered by Severin and co-workers [155, 156] (Vol. I, p. 252). He succeeded in reducing the aromatic ring of nitro compounds

without reducing the nitro groups. The reducing agent was sodium borohydride. *s*-Trinitrobenzene was dissolved in tetrahydrofurane and $NaBH_4$ in aqueous methanol was added at 0°C. 1,3,5-Trinitrocyclohexane resulted in a yield of 40% [155]. 1,8-Dinitronaphthalene was reduced by the same method to 1,4-dihydro-1,8-dinitronaphthalene (78% yield).

m-Dinitrobenzene was partially reduced [156] to 3,5-dinitrocyclohexene (XI) and picric acid to 1,3,5-trinitropentane (XII) through the ring opening.



XI



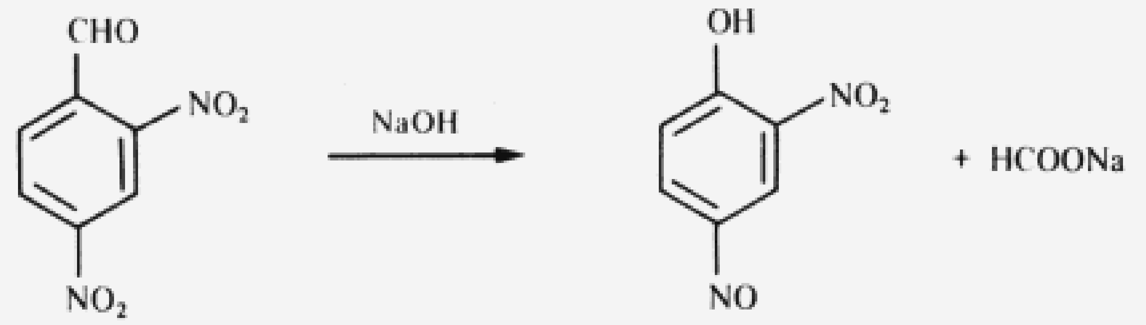
$$\overset{\mathrm{NO_2}}{\mathrm{CH_2}}-\mathrm{CH_2}-\overset{\mathrm{NO_2}}{\mathrm{CH}}-\mathrm{CH_2}-\overset{\mathrm{NO_2}}{\mathrm{CH_2}}$$

XII

The reaction has been studied by a number of authors [157, 158], who came to the conclusion that the hydride reacts initially on the electron-deficient carbon atom at position 3 and forms a kind of Jackson–Meisenheimer adduct, the latter is eventually subject to reduction.

Okamoto and Attarwala [159] brought an improvement to the reaction of Severin, by adding a cationic surfactant (as a phase transfer catalyst) to the reaction medium. They examined the reduction of unsymmetrically substituted -2,4,5- and 2,3,4-trinitrotoluenes by sodium borohydride in methylene dichloride at 23–24°C in the atmosphere of nitrogen in the presence of ethylhexadecyldimethylammonium bromide.

An interesting instance of oxido-reduction of a nitro compound was given by Forbes and Gregory [180]. 2,4-Dinitrobenzaldehyde when warmed with a concentrated solution of sodium hydroxide yielded 2-nitro-4-nitroso instead of the expected acid and alcohol according to the Cannizzaro reaction.



(34)

The reaction is similar to that of Ciamician and Silber – a classical photochemical reaction (Chapter V).

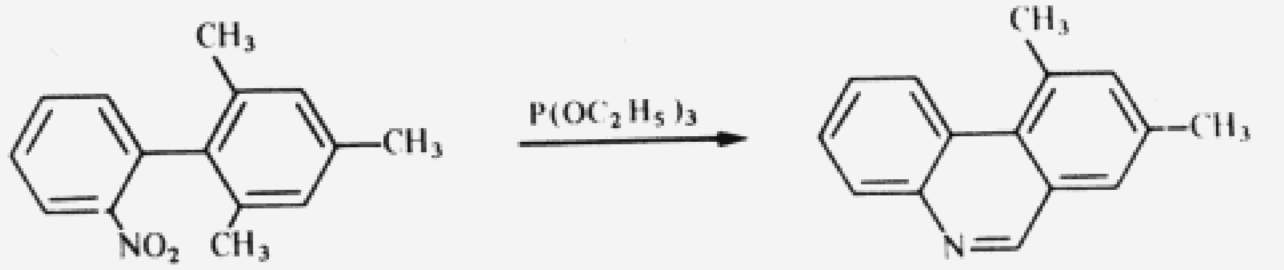
A partial reduction of the aromatic ring of trinitrobenzene was recently described by Ohno, Yamamoto and Oka [160]. By acting with 1,4-dihydronicotinic acid derivatives, 1,3,5-trinitrobenzene was reduced to dihydrotrinitrobenzene at room temperature in dry acetonitryl in the atmosphere of argon and away from light.

Sodium amide can reduce the nitro group of aromatic nitro compounds to give a small yield of diazo compounds [161, 162].

Kemula and co-workers [163] developed the polarographic reduction of the nitro group as an analytical method.

The case of the reduction of nitro compounds leads to their use as oxidizing agents. The use of nitrobenzene in the Skraup reaction is well known. *o*-Dinitrobenzene was reported to be a good agent for oxidizing ascorbic acid to diketone [164].

A nitro group can yield *N*-heterocycles (see Vol. I, p. 195) through the action of various reducing agents such as metal oxalates [165, 166], triethyl phosphite [167–169] or iron pentacarbonyl [170] (35):



(35)

The reaction of nitro aromatic compounds with carbon monoxide was recently reviewed by Manov-Yuvenskii and Nefedov [221]. Particularly interesting is the formation of isocyanates apparently produced in the same way in Japan [222].

DIAZOTIZATION OF AMINO NITRO COMPOUNDS

The NO_2 group reduces the basicity of amino group and makes the diazotization more difficult. Diazotization of dinitro aniline and particularly trinitroaniline requires more drastic conditions, such as the use of more concentrated acid medium and higher temperature. This can be found in textbooks on diazotization and on dyestuffs chemistry.

On the other hand the nitro group renders the diazo group more electrophilic and more reactive in the process of coupling to form azo compounds. Thus 2,4,6-trinitrobenzodiazonium ion couples with mesitylene which is less reactive than anisole and does not react with other diazonium ions [171].

Reactions of the replacement by hydrogen of the tertiary nitro group in aliphatic and alicyclic compounds were recently described by Kornblum and co-workers [145]. They occur at room temperature when the nitro compounds are treated with the sodium salt of methyl mercaptan.

Łytko-Krasuska, Piotrowska and T. Urbański [146] described the replacement by hydrogen of tertiary nitro group in 5-nitro-1,3-dioxane by acting with ethylene glycol in KOH at 120–140°C with yields of up to 60%.

An interesting case of the substitution of nitro group by adamantyl radical was reported by Italian authors [188]. Free adamantyl radical was produced from carboxylic acid according to [187].

1,3-CYCLOADDITION OF NITRO COMPOUNDS

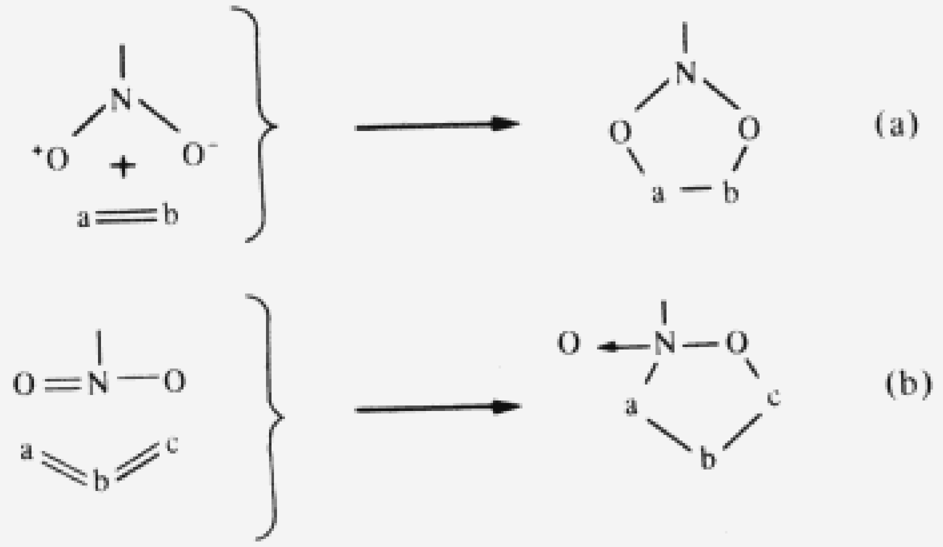
Nitro compounds can be subjected to the so-called 1,3-cycloaddition which is manifested by adding a system with double bonds to 1,3-dipole.

1,3-Dipole can be represented in two limiting forms: a sextet and an octet:

$$^{+}O — N — O^{-} \qquad O = N^{+} — O^{-}$$

sextet octet

Cycloaddition can be represented by schemes (36): (a) and (b)

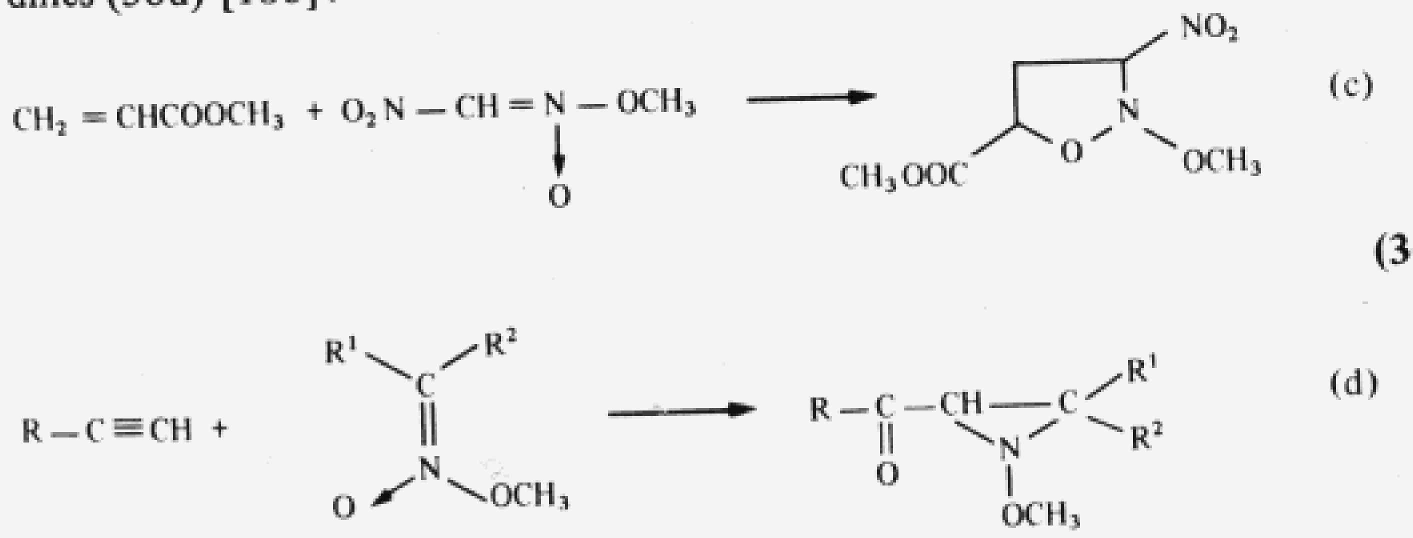


(36)

An excellent review of 1,3-cycloaddition was given by Huisgen [135].

A considerable number of experiments with 1,3-cycloaddition were reported by Tartakovskii, Novikov and co-workers [181–185]. They reacted nitronic acid esters (esters of aciform of primary or secondary nitro alkanes) with dipolephiles such as styrene, vinyl chloride, acrylic esters and methyl–vinyl ketone (36c). The reaction occurs at room temperature (or lower) with an excess of unsatured compound, the yield is 60–90%.

The reaction of nitronic acid esters with acetylene derivatives yielded aziridines (36d) [186].



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Some 1,3-cycloadditions occur under irradiation with ultraviolet light. They are described in Chapter V (reactions by Büchi and Ayer and by Charlton and de Mayo).

THERMAL STABILITY OF AROMATIC NITRO COMPOUNDS

It is generally accepted that aromatic nitro compounds are thermally stable and are only sensitive to the action of bases which produce deep changes in their structure. Nevertheless the action of high temperature on TNT had already been examined in 1911–12 by Verola (Vol. I, p. 306). He found that an evolution of gases started when TNT was kept at 160°C, and the m.p. of TNT was reduced from 80.75° to 79.9°C after keeping the substance for 177 hours at 145–150°C. Thus Pasman, Groothuizen and Vermeulen [191] made a statement that 'fused TNT is unstable at elevated temperatures ($> 150°C$)'.

The high thermal stability of nitro compounds is manifested by the high activation energy E of their thermal decomposition. The following are figures referring to mono-, di- and trinitro compounds:

Nitrobenzene $E = 53.4$ kcal/mol, log B = 12.65 at 395–445°C
m-Dinitrobenzene 52.6 kcal/mol, log B = 12.7 at 345–410°C
1,3,5-Trinitrobenzene 51.9 kcal/mol, log B = 13.6 at 270–355°C

as given by Maksimov [192].

Andreev [193] gave figures for:

$$\left.\begin{array}{l}\text{Picric acid,}\quad E = 38.6\ \text{kcal/mol, log B} = 11.6\\ \text{Styphnic acid, } E = 34.6\ \text{kcal/mol, log B} = 11.2\end{array}\right\}\ \text{at } 183\text{–}270^\circ\text{C.}$$

Roginskii and Magid [194] found $E = 27.0$ kcal/mol and log B = 11.4 for the decomposition of TNT.

Similar figures were obtained by Robertson [195], Pasman *et al.* [191] for the temperatures in the interval of 126–196°C, and for higher temperatures (380–440°C) T. Urbański [196] found 14.0 kcal/mol.

Pasman *et al.* [191] carried out experiments on thermal decomposition of TNT using the adiabatic storage test method. They found that the total heat evolved during 120 hours of keeping at 175°C was 74 kcal/kg.

A few accidents which have recently occurred demonstrate that prolonged heating, much below their ignition temperature, (the deflagration point) can produce an explosion even if this is referred to lower nitrated compounds. Such an accident was recorded (probably for the first time) in 1972 when an explosion took place at 218°C in the U.S.A. in a 100 m long pipe filled with dinitrotoluene [197]. Previous experiments determined ignition temperature as being 270°C, although some sources give an even higher temperature of 300°C [198]. The problem revived in 1976 in the United Kingdom when 1300 kg of 3,5-dinitro-*o*-toluenediamine kept in a closed drier at 118–130°C exploded after 27 hours of heating [199]. In order to create a method which could be used to establish the stability of aromatic and possibly other nitro compounds, Camera and Biasutti [199] developed an ingenious method of 'Isothermal Pressure Meter' which is a perfection of the method used by Small and co-workers. The method consists in keeping a sample 65 g in a steel pressure vessel in a thermostat (accuracy ± 0.2°C). The induction period is considered to be terminated when the pressure in the vessel increased by 0.2 kG/cm^2. The experiment was continued until the disc closing the vessel was ruptured.

For DNT (a mixture of 2,4- and 2,6-dinitrotoluene) the induction period was found to be:

175000 hours at 100°C
1040 hours at 150°C
18 hours at 200°C

The calculated energy of activation was 32.2 kcal/mol.

The addition of 2,4,6-trinitrotoluene to DNT reduced the induction time at 235°C, viz.:

pure DNT	1.70 hours
TNT:	1.70 hours
addition of 5000 ppm TNT	1.53 hours
25,000 ppm TNT	1.09–1.14 hours
50,000 ppm TNT	0.88–1.00 hours
100,000 ppm TNT	0.20

Similar influence was shown by addition of 2,4-dinitro-*o*- and 2,6-dinitro-*p*-cresols.

Attention is also drawn to the paper by Dacons, Adolph and Kamlet [200] who described a spontaneous self-ignition of TNT after being kept for 14–16 hours at 210°C.

A review of kinetic data from low-temperature thermolysis of polynitro compounds was recently given by Zeman [201].

Free Radicals

In the course of thermal decomposition of aromatic nitro compounds free radicals are formed. The ESR signals were detected by Janzen [202], Japanese workers [203] and Soviet workers [204]. The latter authors obtained strong signals from picric acid after an induction period of 30–5 min at 190–210°C respectively.

Janzen reported the formation of free radicals in 2,4-dinitrotoluene, 2,4,6-trinitrotoluene and picric acid at 260°, 240° and 130°C respectively. 2,4-Dinitro- and 2,4,6-trinitroaniline give the signal at room temperature. This can be rationalized by the author of the present book in terms of the intramolecular charge–transfer as described by T. Urbański *et al.* [205], that is when the molecule contains both electron donor and electron acceptor groups.

FUROXANES (Vol. I, p. 603)

Aromatic nitro compounds which in *ortho* position have azido group can readily be transformed into benzofuroxanes (31, 33). An excellent review on furoxanes was written by Kaufman and Picard [206]. Recent works on the structure of benzotrifuroxane were also published: on X-ray analysis [207, 208], vibrational and Raman spectra [209, 210], nitrogen NMR [211], carbon 13 NMR [212]. Explosive properties were also discussed [213].

Korsunskii and Apina [214] examined the kinetics of the transformation of 1,3,5-triazido-2,4,6-trinitrobenzene into benzotrisfuroxane at 70–115°C. The reaction is of the first order with activation energy 26 kcal/mol.

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CHAPTER 5

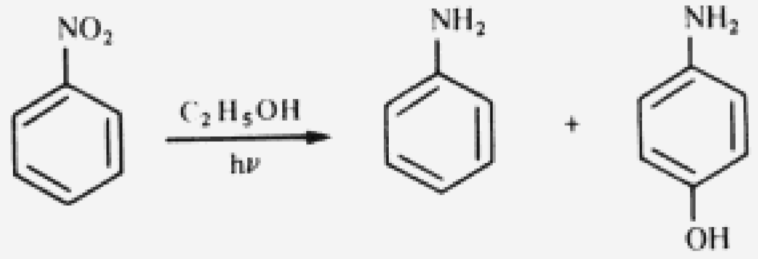
PHOTOCHEMISTRY OF NITRO COMPOUNDS

(Vol. I, p. 225)

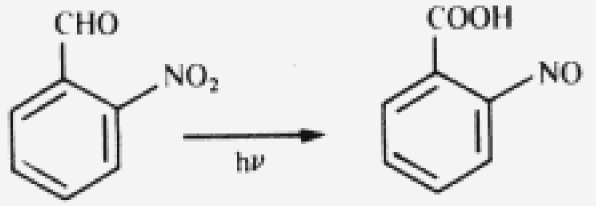
Photochemistry has received much appreciation in the last two decades manifested by several fine monographs and review articles. Most of them have a general character [1–5]. Excellent reviews dedicated to photochemistry of the nitro and nitroso groups were given by Morrison [6], Carless [35] and Kaye [47].

It is assumed that photochemical reactions originate from the lowest energy singlet and triplet excited states. They are due to absorption bands which have been described in Chapter III on the spectroscopy of nitro compounds: the $\pi \longrightarrow \pi^*$ transition (*ca.* 210 nm) of high intensity and $n \longrightarrow \pi^*$ (*ca.* 270 nm) of a relatively low intensity; some nitro compounds show the second transition $n \longrightarrow \pi^*$ (*ca.* 350 nm). It is accepted that the lowest lying singlet and triplet states for nitro compounds are n, π^*.

The photochemistry of nitro compounds began with the pioneering work of Ciamician and Silber [7, 8] who described two photochemical reactions (1, 2):



(1)



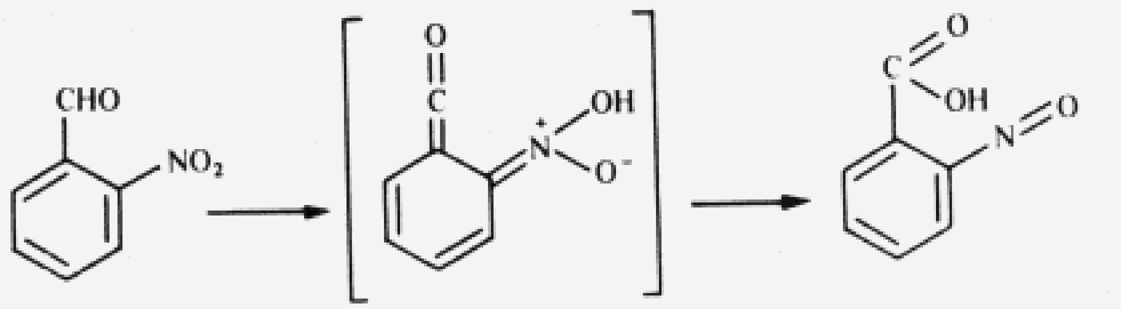
(2)

In reaction (1) ethanol is oxidized [9, 10] to acetaldehyde, nitrobenzene is reduced partly to phenylhydroxylamine (which rearranges into *p*-aminophenol) and partly to aniline.

Reaction (2) in alcoholic medium was examined by Bamberger and Elger

[11], who found that it passed through the formation of acetals.

Recently George and Scaiano [12] examined the reaction of Ciamician and Silber and came to the conclusion that photolysis of *o*-nitrobenzaldehyde proceeded by a triplet state with a life-time of 0.6 ns. Laser flash photolysis showed the formation of a transient intermediate according to (3):

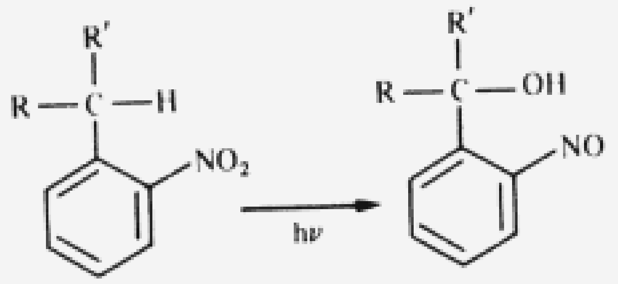


(3)

Similar photochemical reactions were recorded for 2,4-dinitrobenzaldehyde [13] and nitroterephthaldehyde [14].

o-Nitrobenzyl ester yielded *o*-nitroso benzaldehyde [48a] by the same mechanism.

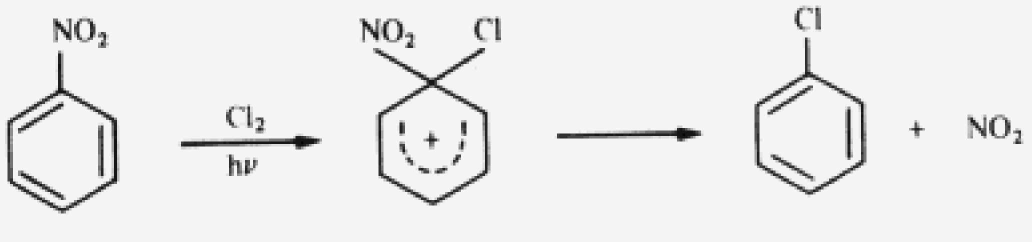
A rule of Sachs and Hilpert [15] should be mentioned: "all aromatics which have a hydrogen *ortho* to a nitro group are light sensitive". They expressed it by a scheme (4)



(4)

Photolysis of nitramine derivatives of steroids has also been recently described [16].

Some photoinduced reactions of nitro compounds involving a formation of free radicals or radical ions were reviewed by Traynham [17]. He classified such reactions as occurring through the "*ipso*" attack, that is, the entering group is (in the first instance) attached to the same carbon as the group to be removed, as in the classical case of replacing the nitro group of nitrobenzene by chlorine under the action of light:



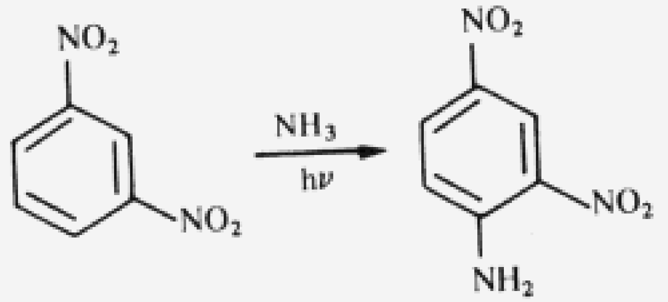
(5)

(see also [18] and [19]).

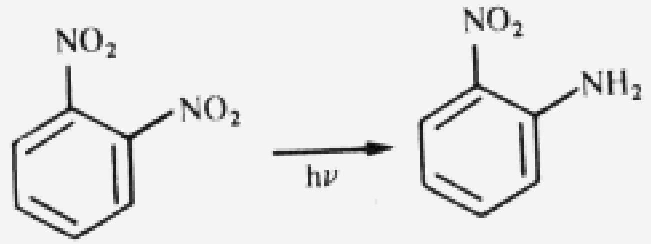
Some reactions described in [6] merit particular attention, for example:

Havinga, de Jongh and Dorst [20] reported the photoinduced hydrolysis of *m*-nitro phosphoric ester to *m*-nitrophenol. *m*-Nitroanisol was also hydrolysed to *m*-nitrophenol [21] and by the action of potassium cyanide yielded *m*-cyanonitrobenzene [22]. Gold and Rochester [23] reported the formation of 3,5-dinitrophenoxide ion from *s*-trinitrobenzene and hydroxylic ion. Van Vliet [24] obtained a number of nitro derivatives of aniline by acting with liquid ammonia on some aromatic nitro compounds under irradiation with ultraviolet-light, viz. (6), (7) and (8):

(6)



(7)



(8)

Photoinduced condensation of *m*-dinitrobenzene and *sym*-trinitrobenzene to nitro derivatives to azoxybenzene was reported by Stenberg and Holter [36]. The most important factor is the solvent. The reaction does not proceed in benzene but gives a good yield in tetrahydrofurane. In ethanol a smaller yield was obtained and ethanol was partly oxidized to acetaldehyde, as found in other reactions [9, 10].

A few papers by Reid and co-workers [37] and de Boer and co-workers [60, 61] were dedicated to the photochemistry of aliphatic nitro compounds. The photochemistry of 17-nitrosteroids was also described [38].

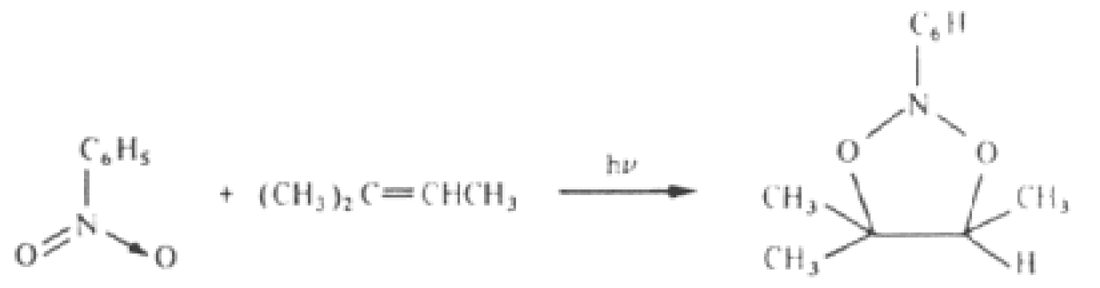
An interesting instance of remote oxidation with photoexcited nitrobenzene derivatives was given in [39].

An excellent review was given by Frolov, Kuznetsov and Eltsov [52] on the photoreduction of aromatic nitro compounds through intermolecular action. Alcohols and hydrochloric acid supply the hydrogen needed for reduction: alcohols are converted into aldehydes, as in reaction (1) and hydrochloric acid becomes a strong chlorinating agent, for example [53].

Gold and Rochester [54] and Johnson and Rees [55] described a transformation of 1,3,5-trinitrobenzene into 3,5-dinitrophenol under photochemical action of OH^- [compare with reaction (11) in Vol. I, p. 251].

Wan and Yates [56] reported the photochemical oxidation of *m*-nitrobenzyl alcohol in aqueous solution to *m*-nitrobenzaldehyde and azoxy compounds.

An interesting photochemical reaction of 1,3-cycloaddition (see Chapter IV) was reported by Büchi and Ayer [58] (9)



(9)

A similar reaction to the addition of nitrobenzene to cyclohexane was reported by Charlton and de Mayo [59].

A heterolytic substitution of 1-methoxy-3,5-dinitrobenzene through the action of ultraviolet light was described by Havinga and co-workers [57]. 3,5-Dinitrophenol resulted, i.e. demethylation occurred.

ALIPHATIC AND ALICYCLIC NITRO COMPOUNDS

A primary photochemical reaction of nitro alkanes is a cleavage of the C—N bond [47, 48]:

$$CH_3NO_2 \xrightarrow{h\nu} CH_3^{\cdot} + NO_2 \qquad (10)$$

followed by recombination to yield methyl nitrite

$$CH_3^{\cdot} + NO_2 \longrightarrow CH_3ONO \qquad (11)$$

For a full discussion of the reactions see [6] Vol. I, p. 583 and Chapter VIII.

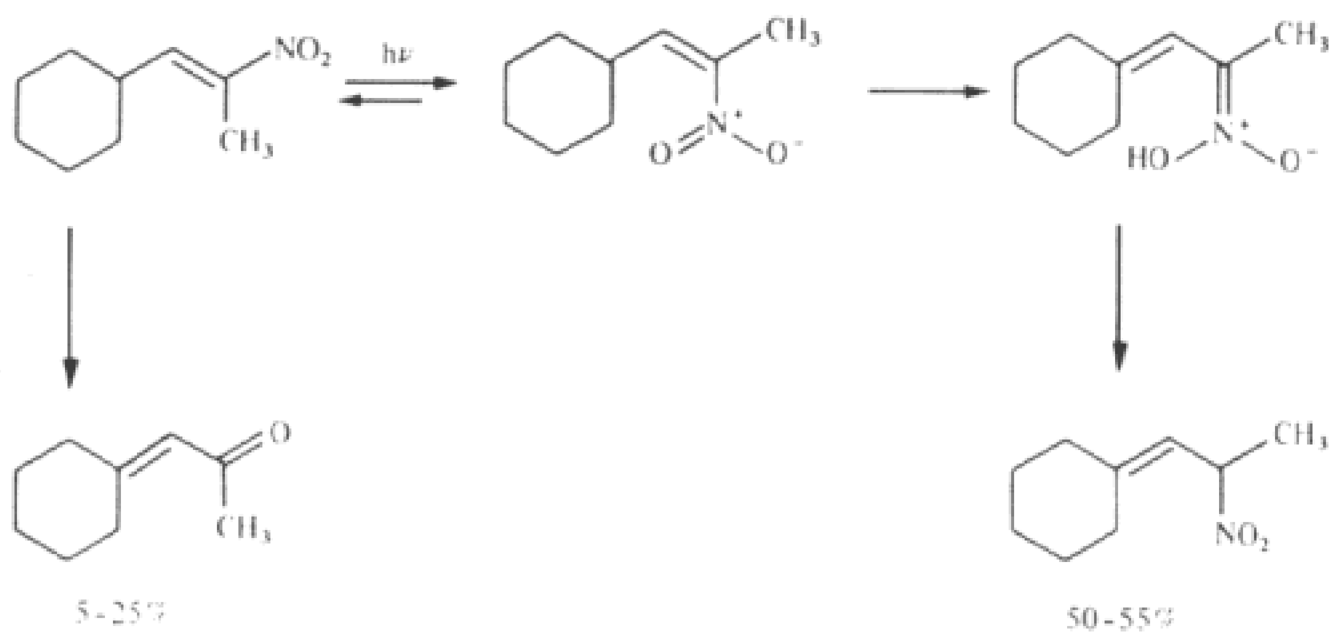
Photochemistry of nitromethane and its substituted derivatives (XCH_2NO_2, X = CH_3, NH_2, F, and F_2CHNO_2, F_3CNO_2) was examined by Slovetskii and co-workers [49]. They came to the conclusion that the transition from the ground state to the triplet state leads to an increase of the density of the positive charge at the central carbon atom and decrease at the nitrogen. They also suggested probable conformation of monosubstituted derivatives of nitromethane. Slovetskii *et al.* [50] also examined the photolysis of tetranitromethane:

$$C(NO_2)_4 \xrightarrow{h\nu} C(NO_2)_3^- + NO_2^+. \qquad (12)$$

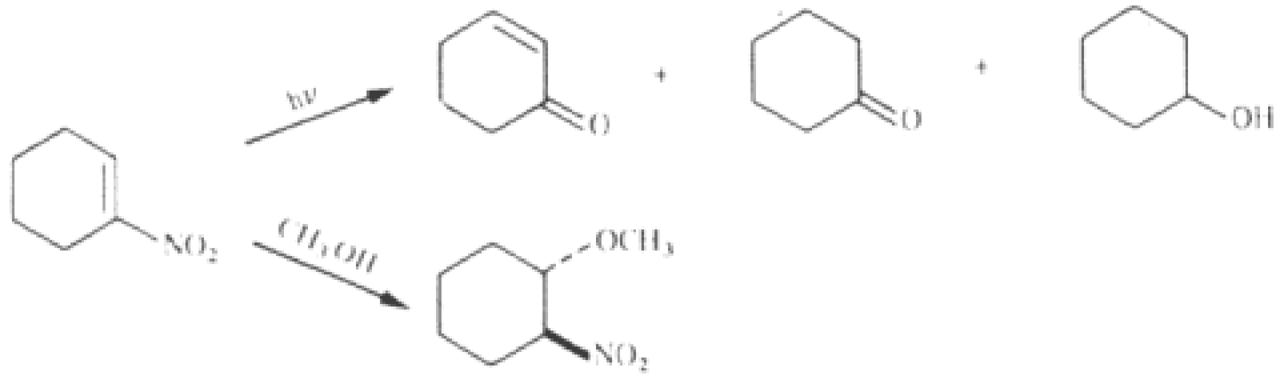
The reaction is influenced by solvents and begins by a triplet state.

An important reaction is the photochemical 1,2-cycloaddition of nitroalkenes [6].

S. T. Reid and co-workers [51] examined the photochemistry of some nitro alkenes. They are depicted by formulae (13) and (14):



(13)



(14)

Photoconductivity of Nitro Compounds

The phenomenon of photoconductivity, that of nitro compounds was recently reviewed by Jarosiewicz [25].

Photoconductivity of liquid nitrobenzene was described by Brière and Gaspard [26]. They rationalized it as the result of photoionization of the compound. The increase in conductivity occurred in the course of irradiation by the light of the wave-length corresponding to the absorption by nitrobenzene. The process is reversible when irradiation is of short duration, but after prolonged irradiation it can attain a constant value.

Some authors have drawn attention to the fact that photoconductivity can be due to impurities in nitrobenzene [27]. On the other hand it is known that radico-ions can be formed in pure nitrobenzene under the action of an electric current [28].

Szychliński [29] described the same phenomenon and found the influence of the solvent, for example the photoconductivity, is prominent in ethyl ether or

1,4-dioxane but less noticeable in benzene. This author explains it in terms of the formation of CT (EDA) complexes. An important finding was made by Japanese authors [30, 31] that 1,3,5-trinitrobenzene shows a strong photoconductivity. Among other aromatic nitro compounds 2,4,7-trinitro-9-fluorenone possesses similar properties [32].

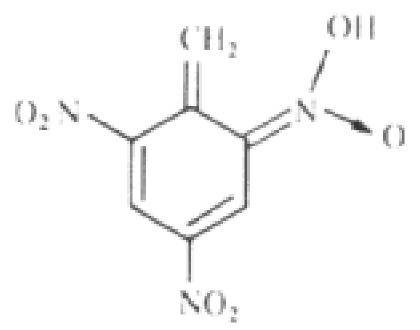
Also nitroalkanes have demonstrated photoconductivity [33, 34].

An interesting proof has recently been given of photochemical splitting of free radical NO_2 from nitroalkane: Marciniak and Paszyc [62] irradiated nitromethane dissolved in cyclohexane and received nitrosocyclohexane dimer:

$$CH_3NO_2 \xrightarrow[(254\ \text{nm})]{h\nu} CH_3^{\bullet} + \bullet NO_2 \xrightarrow{\text{cyclohexane}} \begin{array}{l}\text{trans-nitrosocyclohexane}\\ \text{dimer}\end{array}$$

PHOTOLYSIS

Flash photolysis of aromatic nitro compounds was carried out by a number of authors: Wettermark [40], Suryanarayanan, Capellos, Porter and co-workers [41–43]. Among various findings the latter authors came to the conclusion that 2,4,6-trinitrotoluene under flash photolysis is transformed into aci-quinoid isomer (I) with an absorption maximum at 460 nm.



I

Important contributions to the mechanism of photolysis of aliphatic nitro compounds were made by Bolsman, de Boer and co-workers. In the first paper Bolsman and de Boer [44] examined photolysis of 'pseudonitrole' 1-nitro-1-nitrosocyclohexane with red light in the absence of oxygen. This is described in Chapter VIII.

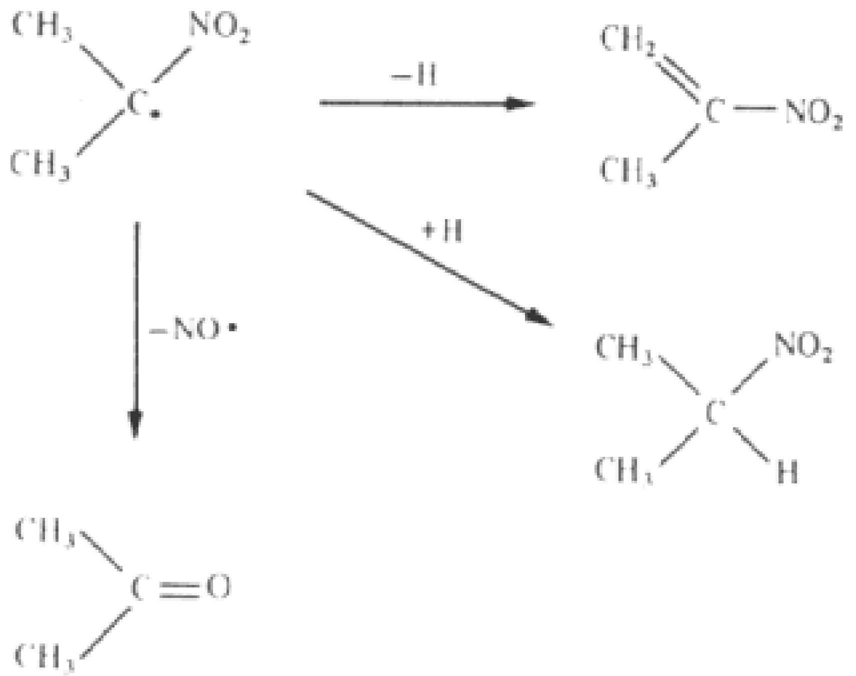
In further experiments Bolsman, de Boer and Verhoeven [45] examined the photochemical decomposition of 2-iodo-2-nitroadamantane in several hydrogen donating solvents and found the formation of α-nitroalkyl radical. This was extended to simple α-iodonitroalkanes in solution [46].

The formation of α-nitroalkyl radical can be depicted by reaction (15):

(15)

The evidence of the formation of the radicals was given by ESR signals.

Further reactions of a simple radical in inert solvents can be presented by scheme (16):



(16)

For more details on the photochemistry of nitro compounds see *Encyclopedia of Explosives* [47].

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CHAPTER 6

NITRO DERIVATIVES OF BENZENE

(Vol. I, p. 230),

TOLUENE (Vol. I, p. 265)

AND OTHER AROMATICS

The properties of higher nitrated derivatives of benzene and toluene were given in Vol. I (pp. 230, 265) and more detailed and modernised data in the monograph by Meyer [1]. Only those properties which have not been recorded in the said books or given in the literature recently will be mentioned here. With regard to the chemical properties, one of the most characteristic features of polynitro aromatics is their ability to nucleophilic substitution. This is discussed in Chapter IV in general terms and some features will be given here in the description of particular nitro compounds.

NITRATION OF BENZENE TO NITROBENZENE

The heterogeneous nitration of benzene has been reviewed by Albright, Hanson and co-workers [2]. They drew attention to the problem of diffusion control which has already been discussed in Chapter II. The differences between the results of various authors was partly due to insufficient appreciation of the problem of diffusion. It is true that nitration occurs mainly in the acid phase and at the interface between acid and organic phases. However, the role of diffusion and solubility of organic compounds in each phase can be decisive and so is adequate mixing. The authors also described their own work where they used a continuous flow stirred tank reactor of 50 ml capacity made of stainless steel and jacketed for temperature control. The agitator of 2.5 cm diameter was a four-blade operator at 3000 rpm. They found that the solubility of benzene in acids changed almost linearly as the concentration of nitric acid changed in the mixed acids. The solubility of benzene was about four times greater than that of toluene. Subsequently the nitration of benzene is only 5 times slower than the nitration of toluene, although earlier reports gave a figure of 20 times slower. The latter figure was based on one phase nitration systems and can be misleading for industrial reaction.

Nitrobenzene (Vol. I, p. 231)

Although it is not an explosive, nitrobenzene created an interest as an intermediate in the formation of di- and tri-nitrobenzene. Also it was known that at high temperature in the presence of an alkali it is subjected to explosive decomposition.

Powerful liquid explosives mixtures of nitrobenzene and liquid N_2O_4 were also known and in some use (Vol. III, p. 289). Recently pyrolysis of nitrobenzene was examined in the range of 275–630°C [3]. At lower temperatures nitrobenzene decomposes via direct rupture of the C–N bond to give free radicals $C_6H_5\cdot$ and $\cdot NO_2$. As the temperature was raised the yield of NO_2 considerably decreased and at 625°C the volatile products were composed of:

1.2%	NO_2
28.0%	NO
1.2%	N_2O
61%	CO
8%	CO_2

The liquid products contain: benzene (21%), phenol (19%), diphenyl (8%), benzonitrile (5%), dibenzofurane (8.5%), benzoquinoline (2.5%) among other less defined substances. Among earlier papers see also that of Fields and Meyerson [4] (see p. 113), Hand, Merrit and Di Pietro [5] which referred to phenyl free radical and nitrobenzene formed by pyrolysis.

Nucleophilic substitution of nitrobenzene with some carbanions was described in Chapter IV.

The industrial method for the nitration of benzene to nitrobenzene is described in the paragraph dedicated to nitration of toluene.

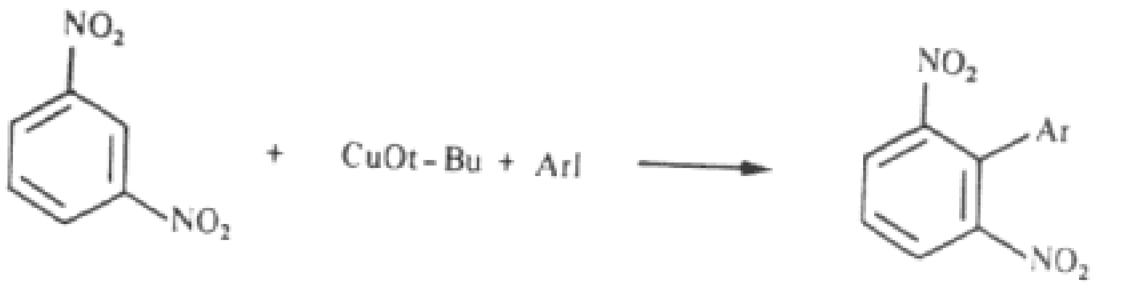
m-Dinitrobenzene

An early paper on the crystal structure of *m*-dinitrobenzene should be mentioned [6]. The method of Fourier series and a projection of the electron density gave the following result. Benzene ring is a regular hexagon of side 1.41 Å. C–N bonds do not lie in the plane of the ring but make an angle of 15° with it. The C–N distance is 1.54 Å, the N–O distance has been found to be 1.20 Å and O–O distance in the nitro groups is 2.17 Å.

An interesting synthesis of biaryl systems which is a modification of the Ullmann method was recently given by Cornforth and Wallace [7]. It consists in acting upon *m*-dinitrobenzene with aryl iodides under the influence of copper *t*-butoxide (1).

The yield of 2.6-dinitrodiphenyl derivatives varied from 10 to 96% depending on aryl.

New data have appeared on the vapour pressure of *m*-dinitrobenzene [1a] – p. 94. This is of importance because of the danger of handling this highly toxic



(1)

substance, particularly at high temperature. The report of H.M. Inspector of Explosives [8] describes fatal accidents in South Africa on 29 February 1932, when an old explosive was carried out in sacks on the bare backs of a dozen natives. Two of them suddenly collapsed and one was taken ill. One of the men died a few hours later. Casualties were caused by the absorption of DNB through the pores of the skin.

The problem of toxicity of *m*-dinitrobenzene has attracted the attention of physicians for a long time. It has been found that animals poisoned with the compound developed methaemoglobinaemia, anaemia, liver damage, convulsions and cerebral paralysis [82, 83]. The problem of metabolism of *m*-dinitrobenzene in a living organism was examined and reviewed by Parke [84]. By using *m*-dinitrobenzene labelled with ^{14}C he examined the metabolism of the substance in rabbit and found that major metabolites in the urine were: *m*-nitroanaline and *m*-phenylenediamine (14% and 21% respectively) 2,4-diaminophenol (31%) and 2-amino-4-nitrophenol (14%). The minor products (present in trace quantity, below 1%) were: unchanged *m*-dinitrobenzene, 2,4-dinitrophenol, 4-amino-2-nitrophenol, *m*-nitrophenylhydroxylamine and derivatives of this: 3,3-dinitroazoxybenzene and *m*-nitrosonitrobenzene.

Electrochemical properties

The ease of reduction of the nitro group of aromatic nitro compounds suggested using aromatic nitro compounds for electrochemical cells. The electrochemical cell Mg/*m*-DNB seems to be particularly suitable giving a high yield of 160 Wh/kg. The reaction requires an acid or neutral medium [85].

Isomeric dinitrobenzenes

High purity *o*- and *p*-dinitrobenzene can be obtained by the oxidation of *o*- and *p*-nitroaniline respectively. The oxidation was carried out with hydrogen peroxide (30%) in acetic acid [36].

Some attention was paid to *o*-dinitrobenzene as an oxidizing agent (Chapter IV).

sym-Trinitrobenzene (Vol. I, p. 248)

Some new data have been published [1] on the physical properties of *sym*-trinitrobenzene such as vapour pressure between 122°C (m.p.) and 270°C.

A few more charge–transfer complexes have been described of *sym*-trinitrobenzene with: phloroglucinol and nitrophloroglucinol [9], picric acid [10], ferrocene [11].

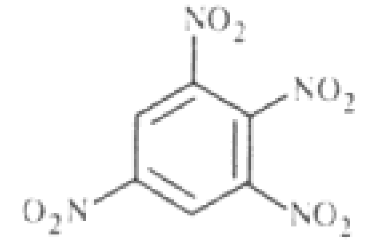
Although the compound possesses very good explosive properties an application could not be found for it owing to the difficulty of making it. A new laboratory method was given by Olah and Lin [12] of nitrating *m*-dinitrobenzene to *sym*-trinitrobenzene with nitronium tetrafluoroborate in fluorosulphuric acid solution. A short description of the method is given below.

Nitronium tetrafluoroborate and *m*-dinitrobenzene were added to fluorosulphuric acid and cooled in a dry ice/acetone bath. The temperature was gradually raised to 150°C. After three hours of heating the reaction mixture was poured on to crushed ice. The nitro product was extracted with dichloromethane, washed with sodium hydrogen carbonate solution and dried over magnesium sulphate. The yield of *sym*-trinitrobenzene was 61.6% with 5% unreacted *m*-dinitrobenzene.

The reaction time of 2.2 hours gave a 66% yield of *sym*-trinitrobenzene and 17% of unreacted substrate. A reaction time of 3.8 hours gave a 49.3% yield of high purity *sym*-trinitrobenzene.

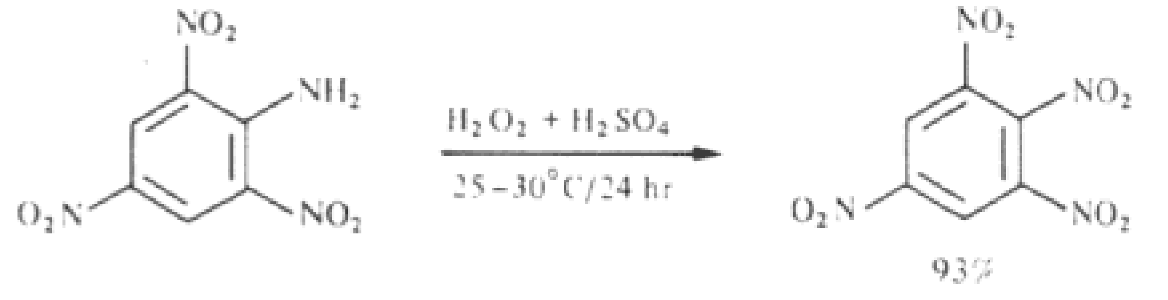
sym-Trinitrobenzene can be subject to a number of nucleophilic reactions. The known reaction for transformation of this compound into 3,4-dinitrophenol under the action of alkalis (Vol. I, p. 251, reaction 11) was facilitated by irradiation with ultraviolet [27, 28]. Pure 3,5-dinitrophenol without the azoxy compound resulted.

1,2,3,5-Tetranitrobenzene (Vol. I, p. 257)



m.p. 127–129°C

1,2,3,5-Tetranitrobenzene was obtained by a new method established by Nielsen and co-workers [13]. In general terms it consists in the oxidation of an amino group of polynitroanilines with concentrated (98%) hydrogen peroxide in 100% sulphuric acid. The reaction of picramide was carried out below 30°C with an excellent yield:



(2)

According to Nielsen [16] the method consists in the action of peroxydisulphuric acid $H_2S_2O_8$:

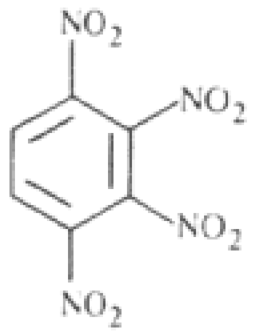
$$H_2O_2 + 2H_2SO_4 \longrightarrow H_2S_2O_8 + 2H_2O. \qquad (3)$$

Murto [14] examined the action of sodium ethoxide on 1,2,3,5-tetranitrobenzene. It produced a red colour attributed to the formation of a quinoid structure and eventually sodium picrate. A more detailed study of the action of nucleophiles on 1,2,3,5-tetranitrobenzene was made by Crampton and El Ghariani [15]. They obtained σ-complexes of Jackson–Meisenheimer type.

1,2,4,5-Tetranitrobenzene (Vol. I, p. 259)

Crampton and El Ghariani [15] examined the behaviour of 1,2,4,5-tetranitrobenzene (m.p. 188°C) towards nucleophile and found that σ-complexes were being readily formed. Nielsen and co-workers obtained [16] the same product of higher purity (m.p. 190–191°C) by the oxidation of 2,4,5-trinitroaniline with 90–98% H_2O_2 in oleum or 100% sulphuric acid.

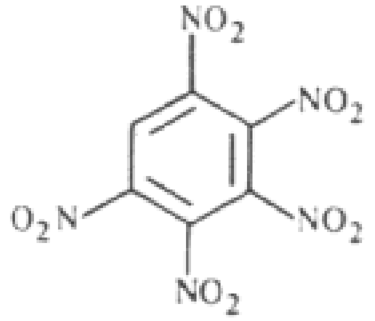
1,2,3,4-Tetranitrobenzene



m.p. 120–121°C

The new compound – 1,2,3,4,-tetranitrobenzene was obtained by Nielsen and co-workers [16] by the oxidation of 2,3,4-trinitroaniline with hydrogen peroxide (98%) in sulphuric acid (100%) at 10–18°C with a 78% yield. Oxidation with concentrated hydrogen peroxide in the presence of sulphuric acid forms a new modification of the method for the introduction of a nitro group, described earlier by Nielsen and co-workers [13], where no sulphuric acid was used.

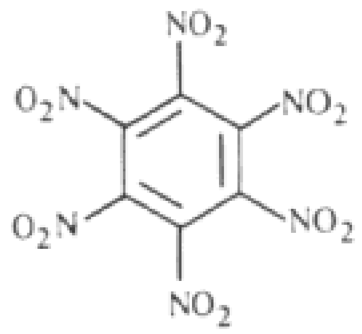
Pentanitrobenzene



m.p. 142–143°C

Tetranitroaniline (Vol. I, p. 560) was used by Nielsen and co-workers [13] to oxidize it with 98% H_2O_2 in the presence of 20% oleum at a temperature below 30°C. Pentanitrobenzene resulted.

Hexanitrobenzene (HNB) (Vol. I, p. 259)



m.p. 246–262°C

The method given in Vol. I could not be repeated. Also no data on the preparation were given and the only paper published until recently was on crystal structure [17] and some data on the properties [18]. It decomposes in air to yield trinitrophloroglucinol. Its density is *ca.* 2.0 and the rate of detonation (at $\rho = 1.9$) is 9500 m/s.

Nielsen and co-workers described in their remarkable papers [13, 16] the formation of hexanitrobenzene by oxidation of pentanitroaniline.

The reaction was carried out either (1) in fuming (20% SO_3) sulphuric acid at 25–30°C by adding 98% H_2O_2 or (2) in trifluoromethanesulphuric at 45–55°C with 90% H_2O_2. The product was extracted with dichloromethane and dried over magnesium sulphate (which also removed trifluoromethane sulphuric acid). Method (2) gave 90% yield.

A lower yield (58%) was obtained by method (1).

Also a relatively low yield was produced with potassium persulphate instead of hydrogen peroxide.

Wide range of m.p. is explained in terms of the formation of a few decomposition products in the course of heating near the m.p. of the substance. At 100°C nitro groups are transformed into phenolic groups yielding pentanitrophenol, tetranitroresorcinol and eventually trinitrophloroglucinol. In the absence of light HNB shows good stability at room temperature, but irradiation produces an interesting isomerization of nitro groups to nitrites which in turn are hydrolysed to phenolic groups [120]:

$$-NO_2 \xrightarrow{h\nu} -ONO \longrightarrow -OH$$

Other high nitrated derivatives of benzene obtained by the method of Nielsen [16]

The following were the compounds obtained by oxidation of the nitro derivatives of aniline:

1,2,3-trinitrobenzene (Vol. I),
1,3-difluoro-4,5,6-trinitrobenzene (m.p. 88–90°C)
1,3-difluoro-2,4,5,6-tetranitrobenzene (m.p. 99–100°C)
fluoro-pentanitrobenzene (m.p. 152–154°C)

The latter three compounds are new to the literature.

NITRO DERIVATIVES OF TOLUENE

Nitration of Toluene to Nitrotoluenes (Vol. I, p. 265)

Formation of nitrotoluenes is an important step in the manufacture of the trinitro product and has been the subject of some review articles: [19, 20] which were dedicated to the kinetics of mononitration.

Giles, Hanson and Ismail [19] found that in mononitration of toluene with a standard nitration mixture of nitric–sulphuric acid and water, the organic phase contained nitric and nitrous acids, but did not include sulphuric acid and water. The authors also studied the role of agitation. Their conclusion was similar to that reported previously [2] that mass transfer between the phases plays an important role, and a fast reaction takes place in a zone in the aqueous phase adjacent to the interface. It is important to know the diffusivity of the aromatic substrate in the aqueous phase which depends on the design of the nitrator. The paper by Strachan [20] also points out the importance of mass transfer in agreement with a previously described statement (Vol. I, p. 49).

As has been already pointed out (Vol. I, p. 265) and Chapter III, in the mononitration of toluene, nitrocresols are formed [21]. They can be further nitrated to yield trinitrocresol and oxidized to oxalic acid. The presence of trinitrocresol is most undesirable (formation of sensitive salts) and therefore mononitrotoluenes should be washed with alkali to remove the nitrocresols (Vol. I, p. 359).

Some efforts have been made to reduce the proportion of undesirable *m*-nitrotoluene. A general rule is that the lower the temperature of nitration the smaller the proportion of *meta* isomer (Vol. I, p. 273). Also the use of nitric acid acetic anhydride mixture at 0°C can assure a lower proportion of *m*-nitrotoluene, for example to reduce it to 1.6% [22]. This is in agreement with former findings (Vol. I, p. 274).

Isomer control in the mononitration and dinitration of toluene was studied by Harris [23, 24]. Both papers were dedicated to the increase of *p*-nitrotoluene which is an important intermediate in dyestuffs and pharmaceuticals manufacture, where both *o*- and *m*-isomers are waste products and the high proportion of 2,4-dinitrotoluene is desirable for isocyanate production. This aim was achieved by adding phosphoric acid to the nitration mixtures.

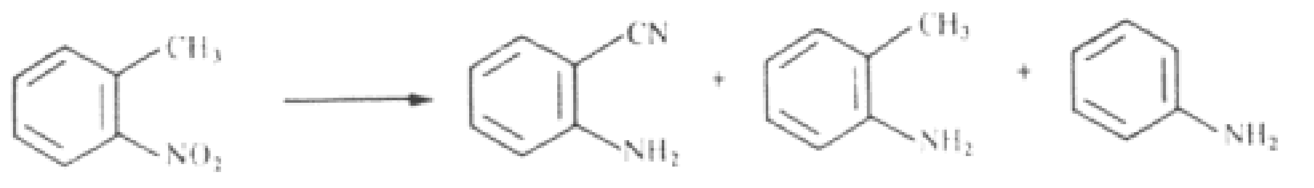
A number of papers (in addition to those mentioned in Vol. I) were given by Kobe, R. M. Roberts and co-workers [122–125] on the determination of the isomer distribution of the nitration of *o*-, *m*- and *p*-nitrotoluenes by the method of isotope dilution analysis.

The nitration of toluene to trinito products will be presented in a separate paragraph.

Mononitrotoluenes

A few unexpected reactions of nitrotoluenes have been recorded in recent years. Such is the reaction described by Hakanson and Nielsen [25] of the oxidation of *o*-nitrotoluene with dilute (35%) nitric acid at 190°C to yield (30%) picric acid. On the contrary *m*- and *p*-nitrotoluenes yield *m*- and *p*-nitrobenzoic acids. In addition to picric acid also nitro- and dinitrobenzoic and 3,5-dinitrosalicylic acids were formed. A large quantity of nitrogen was evolved and this led the authors to rationalize the reaction as passing through the formation of a diazo compound.

o-Nitrotoluene under action of ammonia in the presence of catalysts (Si-Mo-V-Bi-Base) at elevated temperature (4) was converted to *o*-cyanoaniline in addition to aniline and the expected *o*-toluidine.



(4)

INDUSTRIAL METHODS OF MONO-NITRATION OF BENZENE AND TOLUENE (Vol. I, p. 232 and Vol. I, p. 275)

Industrial methods of mono-nitration of benzene and toluene are either periodical or continuous. More attention is now given to continuous methods – safer and more economic when applied to a large, continuous production. Nevertheless, periodic nitration is still in use for smaller and less regular production.

Matasă and Matasă [29] in their monograph collected technical data on the nitration of benzene and toluene (Table 26).

TABLE 26. Mononitration

Components*	Benzene		Toluene	
	Nitrating acid	Spent acid	Nitrating acid	Spent acid
HNO_3	32	1	28	1
H_2SO_4	60	83	56	69
H_2O	8	15	16	29
NO_2	–	2	–	2
Temperature °C	40		60	
Reaction time min.	60		75	
Ratio HNO_3 : hydrocarbon	100:100		100:100	
Yield in % of theoretical	98		97	

* In weight per cent.

Removal of Phenolic By-products

To free the aromatic mononitro products from phenolic by-products the usual industrial procedure consists in washing the nitro compound with water to free it from acids and then washing with dilute sodium hydroxide (concentration 1–5% NaOH and an excess of 5–15%). The process is efficient as regards to purification of the nitro compound but produces a considerable amount of water containing sodium phenates and is an obnoxious effluent. This can be dealt with by acidification and extraction of phenols with organic solvent immiscible with water (such as benzene or more costly solvents). The method is expensive and led to the search for another method. Hanson and co-workers [30] developed a method of extracting phenolic compounds with a weak basic reagent such as phosphate salts. A mixture of trisodium and disodium hydrogen phosphate, for example 64.2 g/l of $Na_2HPO_4 . 2H_2O$ with 21.9 g/l of $Na_3PO_4 . 12H_2O$. After separation from the purified nitro compound the aqueous solution of phosphates and sodium phenates is mixed with benzene which dissociates the phenates and the liberated phenols are dissolved in benzene. The main constituent (*ca.* 80%) of phenolic fraction is 2,6-dinitro-*p*-cresol.

Periodic Nitration

Little can be added to the design of periodic nitrators as given in Vol. I, p. 155 (contrary to the continuous nitrators). An interesting innovation (which can also be used in continuous nitrators) deals with the control of the efficiency of stirring as given in the monograph by Chekalin, Passet and Ioffe [31]. It consists of a U-shaped glass tube on the lid of the nitrator. The tube is connected with a steel tube reaching the bottom of the nitrator (Fig. 16). The U-tube is filled with a coloured electrolyte solution and connected to an electric circuit. When the stirrer is in motion the pressure inside the nitrator increases and this is manifested by the difference of the levels in the U-tube. As a consequence the electric circuit is disconnected. When mixing stops (or is inadequate) the levels in the U-tube equalize, the circuit is closed and an acoustic or light signal gives a warning.

The emulsion of the nitro product and spent acid enters a separator which is designed on the principle of a laboratory separating funnel [31].

The nitro compound forms the upper layer. The spent acid is taken through the bottom valve and switched to another container when the upper layer appears in the 'lantern' situated just above the valve. The spent acid is further treated with a fresh hydrocarbon which goes to the nitrator and the nitro product is washed with aqueous alkaline solution to remove acids and phenols.

Continuous Nitration

The advantages of continuous method have already been pointed out in Vol. I, p. 366. It should be added that continuous nitration does not involve losses in time used for loading, emptying the nitrator and heating and cooling its contents as in periodic nitration. According to Soviet authors [31] the production of nitrobenzene can be increased 15 times, by changing periodic into continuous nitration.

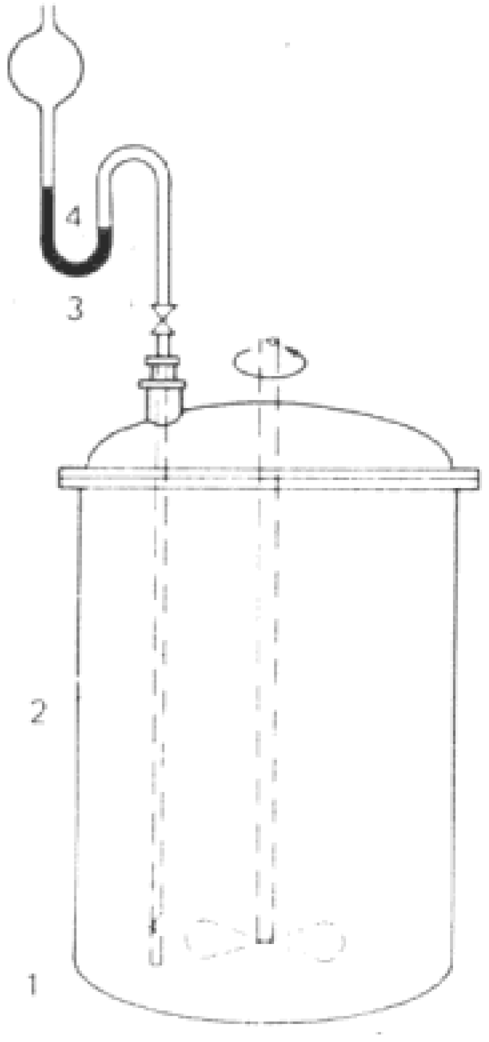


FIG. 16. Control of the efficiency of the stirrer according to Chekalin *et al.* [30]. 1 – Orifice in tube 2, 3 – electrodes, 4 – coloured electrolyte.

One of the popular designs for nitrators was given by Biazzi (Vol. I, p. 108, Fig. 47), originally designed for the nitration of glycerine and adapted with small changes for the nitration of aromatic compounds.

SOVIET METHOD (ACCORDING TO CHEKALIN, PASSET AND IOFFE [31])

The following is a diagrammatic presentation of a continuous nitrator made of stainless steel (Fig. 17).

The hydrocarbon enters through the top of the central, wide diameter tube where it is cooled, driven down and at the bottom meets the nitrating acid. Through energetic mixing the emulsion is formed and driven upwards through the stainless steel tube. Continuous outflow of the emulsion is achieved from the upper part of the nitrator.

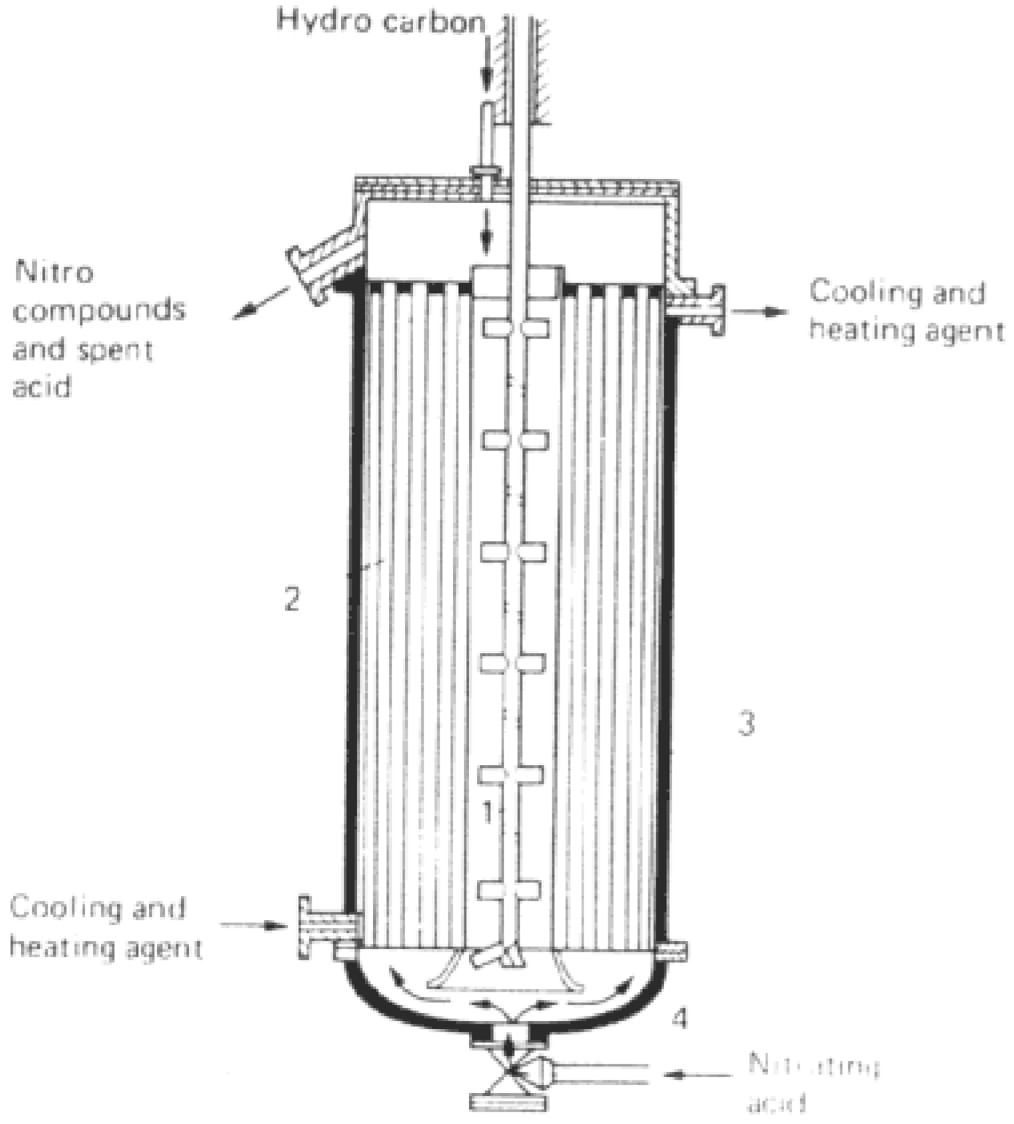


FIG. 17. Continuous nitrator according to Chekalin *et al.* [30]. 1 Stirrer, 2 tubular cooler and heater, 3 stainless steel plate, 4 regulation valve.

It is of great importance that the continuous nitrator should be completely air-tight.

The emulsion enters the continuous cylindrical separator (Fig. 18) near the middle of its height. The place of entrance is changed depending on the nitrated substance: it should correspond to the surface of the separation of phases.

The lighter nitro compound flows to the upper part of the cylinder and the heavier spent acid flows out through a syphon tube. It is advisable to fill the cylinder with Raschig-rings.

A general diagram of continuous nitration of benzene (and also toluene) according to Soviet sources (Chekalin, Passet and Ioffe [31]) is given in Fig. 19. The nitrator is provided with a cooling mantle, two cooling coils of different tube diameters, the stirrer has an upper turbine mixer driving the liquids downwards and a lower propeller. The supply of hydrocarbon, nitrating acids, spent acid and cooling liquid (usually water) is regulated in such a way as to keep the temperature of nitration at 65–68°C in the case of nitration of benzene. The concentration of nitrobenzene in the acid remains constant *ca.* 5%. The emulsion enters two spiral 'coolers' where the reaction is ended: 90% of nitric acid is used in the nitrator and 9–9.5% in the coolers, thus 99–99.5% of nitric acid is used for the

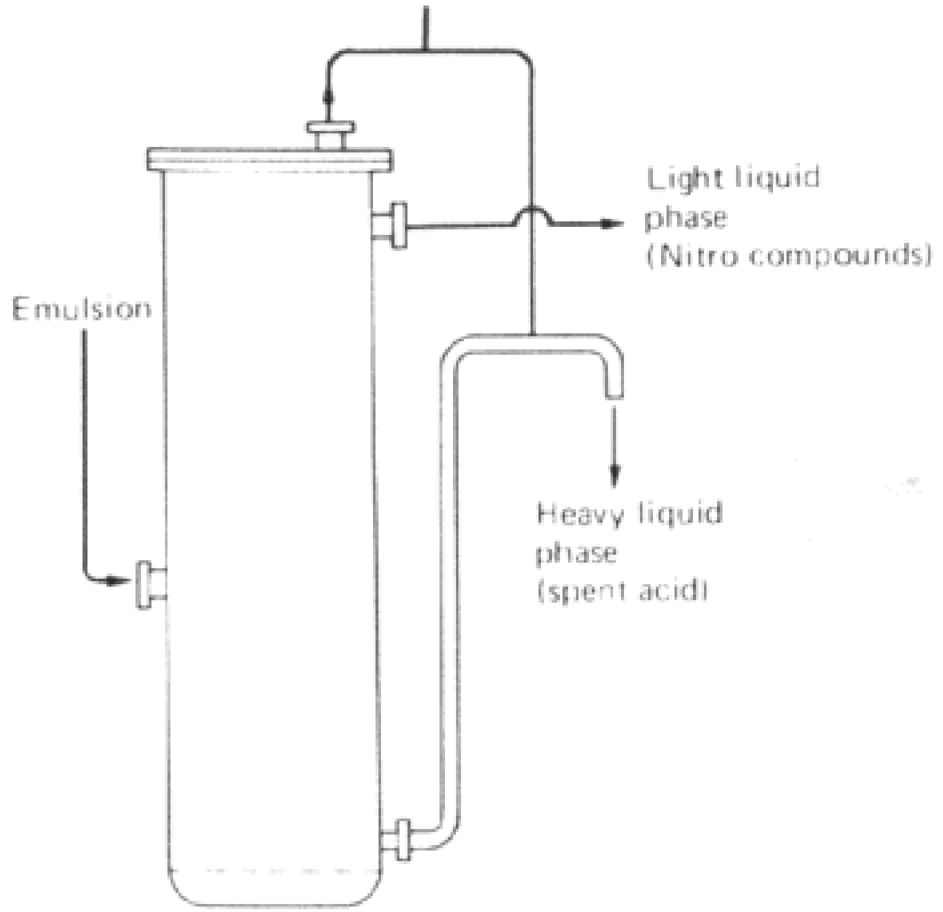


FIG. 18. Continuous separator according to Chekalin *et al.* [30].

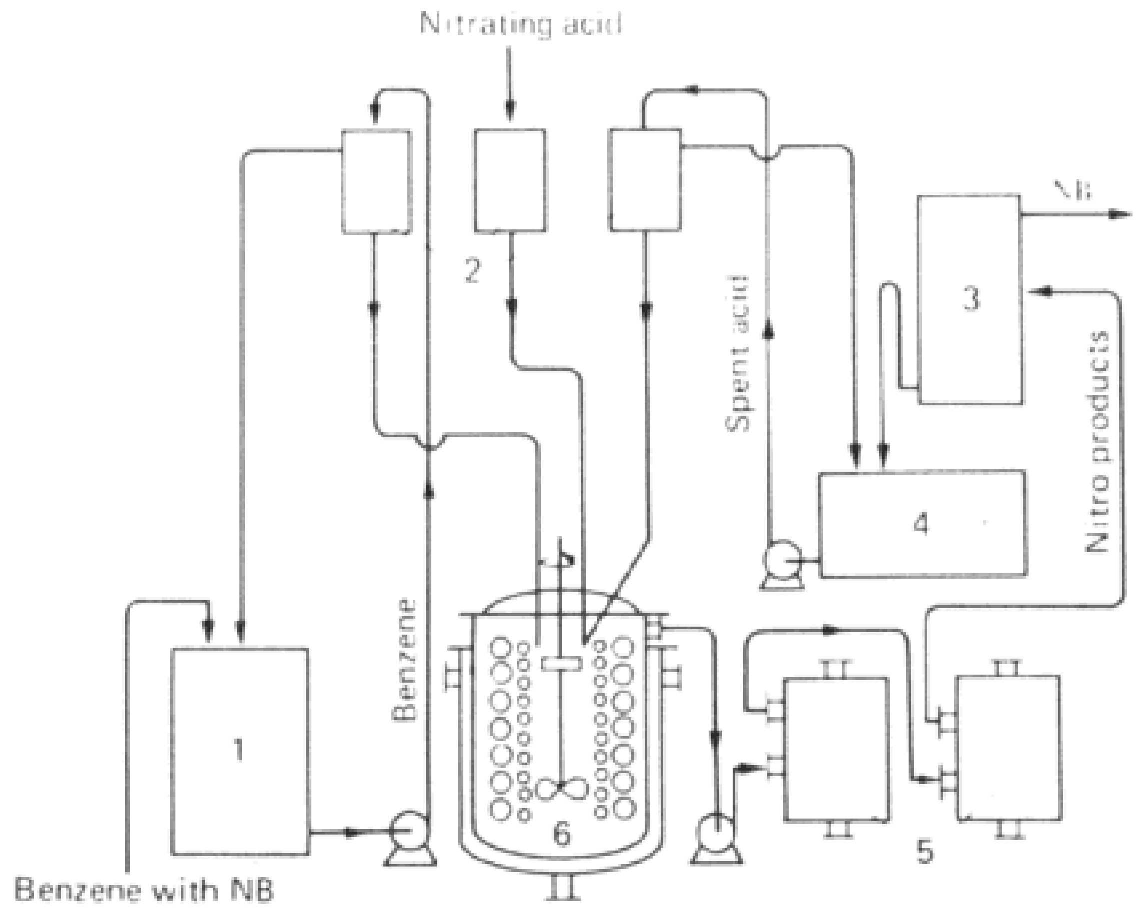


FIG. 19. General scheme of nitration of benzene or toluene according to Chekalin *et al.* [30]. 1 benzene or toluene storage tank, 2 measuring tanks for the hydrocarbon, nitration acid, spent acid, 3 continuous separator, 4 spent acid tank, 5 spiral coolers, 6 nitrator of continuous action.

nitration. In the second spiral cooler the reaction mass is cooled to 30°C. It should be understood that the spiral coolers are provided with stirrers. From there the emulsion enters the continuous separator. Due to the great difference of the density of nitrobenzene (or nitrotoluenes) and the spent acid, the separation takes 5–10 min.

Every 1000 kg of nitrobenzene gives 900–1000 kg of spent acid containing: 70–73% H_2SO_4, 1.5-2.2% nitrobenzene and 0.25–0.5% nitric acid. Nitrobenzene is extracted from the spent acid with benzene. The latter is partly nitrated with the residual nitric acid and the content of nitrobenzene and nitric acid after the extraction falls to 0.1–0.15% and 0.01–0.03% respectively. Benzene with a small quantity of nitrobenzene is sent to the storage tank and from there to the nitrator.

It is strongly emphasised that perfectly faultless automation is necessary for the safe and efficient process. Thus the ratio: hydrocarbon/acid is under automatic control according to the temperatures of the reaction, cooling liquid inflow is regulated according to the temperature of the cooling liquid leaving the nitrator. The cooling water entering the spiral coolers is also automatically controlled. If the mixing in the nitrator and supply of cooling liquid becomes inadequate, the flow of hydrocarbon into the nitrator is automatically stopped and the whole plant ceases to operate.

BOFORS-NOBEL-CHEMATUR METHOD OF NITRATING BENZENE AND TOLUENE TO MONONITRO PRODUCTS (FIG. 20) [32]

An innovation in the nitration technique was introduced by Bofors-Nobel-Chematur (Sweden). This is the so-called "Nitration Circuit". It consists in the ingenious use of a centrifugal pump as a nitrator. A cooler and a gravimetric separator are included in the circuit. Cooled acids and hydrocarbons are injected into the circuit. Hydrocarbons are: benzene or toluene used for the extraction of spent acid together with fresh hydrocarbons. The nitro compound and the spent acid overflow to the gravimetric separator and are split into streams of spent acid and a nitro compound. The spent acid is mixed with fresh hydrocarbon and subsequently the latter enters the circuit as mentioned above. The spent acid containing 70% H_2SO_4 is removed and can be used for fertilizer production or can be concentrated and recycled for nitration. The nitro compound is washed with dilute NaOH solution to remove phenols.

The advantages of the nitration circuit method are as follows: low oxidation due to the short contact time of the hydrocarbon with the acid, full nitric acid utilization, safety due to a very small quantity of the nitro compound in the circuit.

The following is the material balance given by Bofors-Nobel-Chematur (Table 27) [32]:

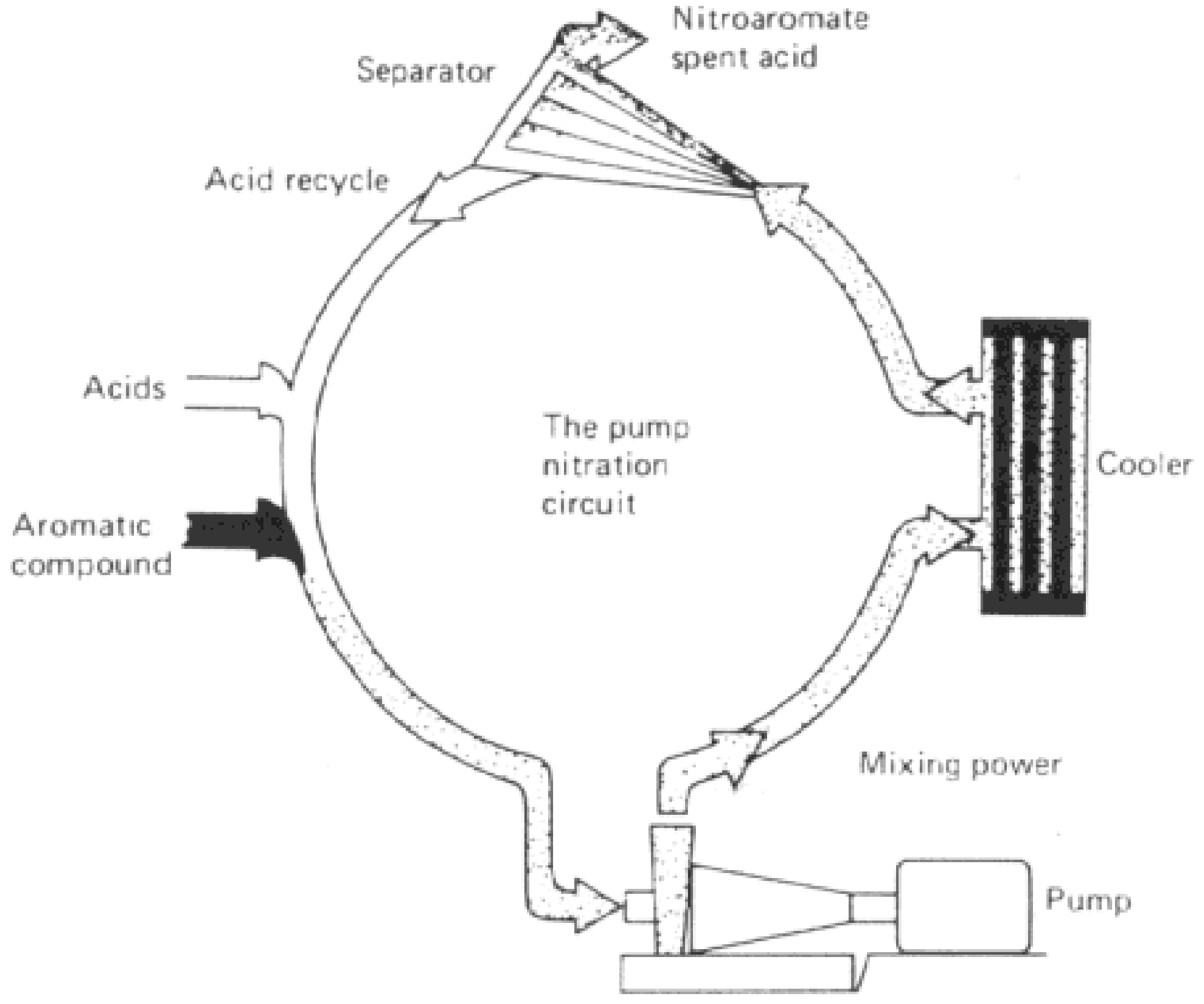


FIG. 20. Bofors-Nobel-Chematur. The Pump Nitration Circuit diagram. Courtesy Bofors-Nobel-Chematur.

TABLE 27. Consumption of materials in kg for production of 1000 kg of nitrobenzene and nitrotoluene

	Nitrobenzene	Nitrotoluenes
Hydrocarbon:		
benzene	650	
toluene		686
Nitric acid 98% as 100% HNO_3	537	486
Sulphuric acid 96% as 100% H_2SO_4	460*	390*
Sodium hydroxide as 100% NaOH	5	10.4

* If the spent acid is concentrated the consumption is only 5% of the above figure.

DINITROTOLUENES (Vol. 1, p. 281)

As is known dinitrotoluenes are not explosives by themselves but they are of course intermediates in the manufacture of TNT and are in use as ingredients of:

(1) mining explosives,
(2) some smokeless powders.

For mining explosives a low melting mixture of isomer is used. It is readily miscible with nitroglycerine and dissolves soluble nitrocellulose. For smokeless powder a relatively pure 2,4-dinitrotoluene is used. For further nitration, dinitrotoluene – a mixture (m.p. *ca.* 35°C) is used and after nitration to trinitroproduct, the latter is purified.

Physical (including thermochemical and explosive) Properties

The following are figures for main isomers of dinitrotoluene according to Meyer [1].

TABLE 28. Properties of dinitrotoluenes

	Dinitrotoluene	
	2.4-	2.6-
Density	1.521 g/cm^3	1.538 g/cm^3
Melting enthalpy	26.1 kcal/kg	22.5 kcal/kg
Enthalpy of formation	−89.5 kcal/kg	57.6 kcal/kg
Heat of detonation	1056 kcal/kg	1538 kcal/kg
Ignition temperature	360°C	
Volume of detonation gases	602/1/kg	
Lead block test	240 cm^3/10 g	

The same source [1] gives vapour pressure of the 2,4-isomer:

at	35°C	0.014 milibar
	70°C (m.p.)	0.111
	100°C	0.83
	150°C	8.5
	200°C	50.5
	300°C	300

The MAK-value (maximum permitted concentration in air at a workplace) is 1.5 mg/m^3.

The specification of commercial product is as follows:

moisture:	no more than 0.25%
benzene insoluble:	no more than 0.10%
acidity (as H_2SO_4):	no more than 0.02%
tetranitromethane:	absent
solidification point	
for smokeless powder grade:	68.0 ± 2.5°C
for commercial explosives:	liquid–solid mixture

Data for isomeric dinitrotoluenes are given in Vol. I, pp. 281–282.

Formation of Dinitrotoluenes from mononitrotoluenes (Vol. I, p. 285)

It is generally known that 2,4-dinitrotoluene is formed by nitration of *o*- and *p*-nitrotoluene and 2,6-dinitro isomer by nitration of *o*-nitrotoluene. It was accepted that 2,3-, 3,4- and 3,6-isomers are produced from *m*-nitrotoluene. Nevertheless it was firmly established that the nitration of *o*- and *p*-nitrotoluene can also produce a small proportion (below 0.5%) of 2,3- and 3,4-dinitrotoluene respectively [33]. Also small proportions of other isomeric dinitrotoluenes, such as 2,3-, 2,5- and 3,4- was proved from *o*- and *p*-nitrotoluene respectively [34]. Hill and co-workers [39] have found that the nitration of pure *o*- and *p*-nitrotoluene at −10°C with a nitrating mixture containing SO_3 yielded only 0.1% dinitro- and trinitroproducts deriving from *m*-nitrotoluene.

The formation of *m*-nitrotoluene derivatives from *o*- and *p*-nitrotoluene can be understood on the basis of the electron densities, free valencies and localization energies as depicted in Fig. 14. Also the formation of 3,5-dinitrotoluene seems to be possible by direct nitration of *m*-nitrotoluene [34].

The exact analysis of the nitration product has almost been perfected since the advent of chromatographic methods (t.l.c. and gas chromatography) and exact and reliable detection of isomers and impurities of lower and higher nitrated hydrocarbons [35–37] has been possible.

French authors [118] isolated pure isomeric dinitrotoluenes: 2,3, 2,5 and 3,4 from the product of the nitration of *m*-nitrotoluene by fractional distillation and repeated crystallization. 2,6-Dinitrotoluene was isolated by distillation of crude dinitrotoluene.

The following are setting points and distillation temperatures of isomeric dinitrotoluenes:

3,4	set pt. 58.3	, distilled under 10 mmHg	166–168°C
2,5	50.3	,	175–177°C
2,3	59.3	,	181–183°C

Recently 2,5-, 2,3- and 3,4-dinitrotoluenes were obtained by oxidation of 2-methyl-4-nitroaniline, 2-methyl-6-nitroaniline and 2-methyl-6-nitroaniline respectively [38]. The oxidation was carried out by hydrogen peroxide in acetic acid at 65–75°C. The yields were around 70% of theoretical.

As mentioned earlier low temperature nitration of toluene favours the reduction of the yield of *m*-nitrotoluene. This was examined in detail by Hill and co-workers [39]. They found that while lowering the nitration temperature from −5° to −35°C a reduction of 3,4-, 2,3- and 2,5-dinitrotoluenes occurred from 2.06% to 1.40% and the setting point of the product raised from 61.0 to 63.7°C. According to the same authors the use of trifluoromethanesulphonic acid with nitric acid made it possible to use a very low temperature on mononitration (−110° to −60°C) and the temperature 0° to 25°C on dinitration. When mononitration was carried out at −110°C and dinitration at 0° to 25°C, the content of isomeric dinitrotoluenes was as low as 0.33%. This figure is the lowest that has been recorded for dinitrotoluenes derived from toluene.

A problem was recently raised again on the production of high purity 2,4-dinitrotoluene not only because of its use in the manufacture of TNT but also for reduction to *p*-toluilenediamine which is an important starting material for polyurethane. The general tendency is to use high purity *p*-nitrotoluene to introduce the second nitro group. Thus Vinnik and co-workers [95], Leitman and Fedorova [96], found that the nitration of pure *p*-nitrotoluene produces pure 2,4-dinitro product. Nevertheless Ziółko and Matys [97] stated on the grounds of their experiments that the nitration of pure *p*-nitrotoluene yielded 2,4-dinitrotoluene containing 0.3–0.5% 3,4-dinitrotoluene. The conditions of the nitration were as follows:

Nitration acid contained 25% HNO_3
70% H_2SO_4
5% H_2O.

An excess of the acid over theoretical was 5%, the temperature of nitration between 75 and 95°C. The yield of 96% of the product with setting point over 69.5°C was obtained. Crystallization from ethanol or trichloroethylene yielded practically pure 2,4-dinitrotoluene.

INDUSTRIAL METHODS OF DINITRATION OF BENZENE AND TOLUENE

Matasă and Matasă [29] collected the technical data on dinitration of mononitro derivatives of benzene and toluene.

Modernized Pilot-plant and Industrial Production of DNT

Three modern methods of dinitration will be given here:

(1) Pilot-plant method by Haas and co-workers [40] of low temperature nitration of toluene,
(2) continuous method of Bofors-Nobel-Chematur two-step process with a pump nitrator [32, 41],
(3) continuous method of Biazzi S.A. [132].

Low Temperature Nitration of Toluene to DNT [40]. – Fig. 21

The principle was based on the nitration of toluene by anhydrous mixtures composed of nitric acid and oleum at temperatures between 0° and −10°C (freezing point of the solution) [39]. The dinitration was nearly quantitative (over 99%) when the molar ratio HNO_3/toluene was 2.1–2.2. With the increase of the ratio (e.g. to 4) the yield decreased (*ca.* 98%). The optimum was obtained with molecular proportion of reagents:

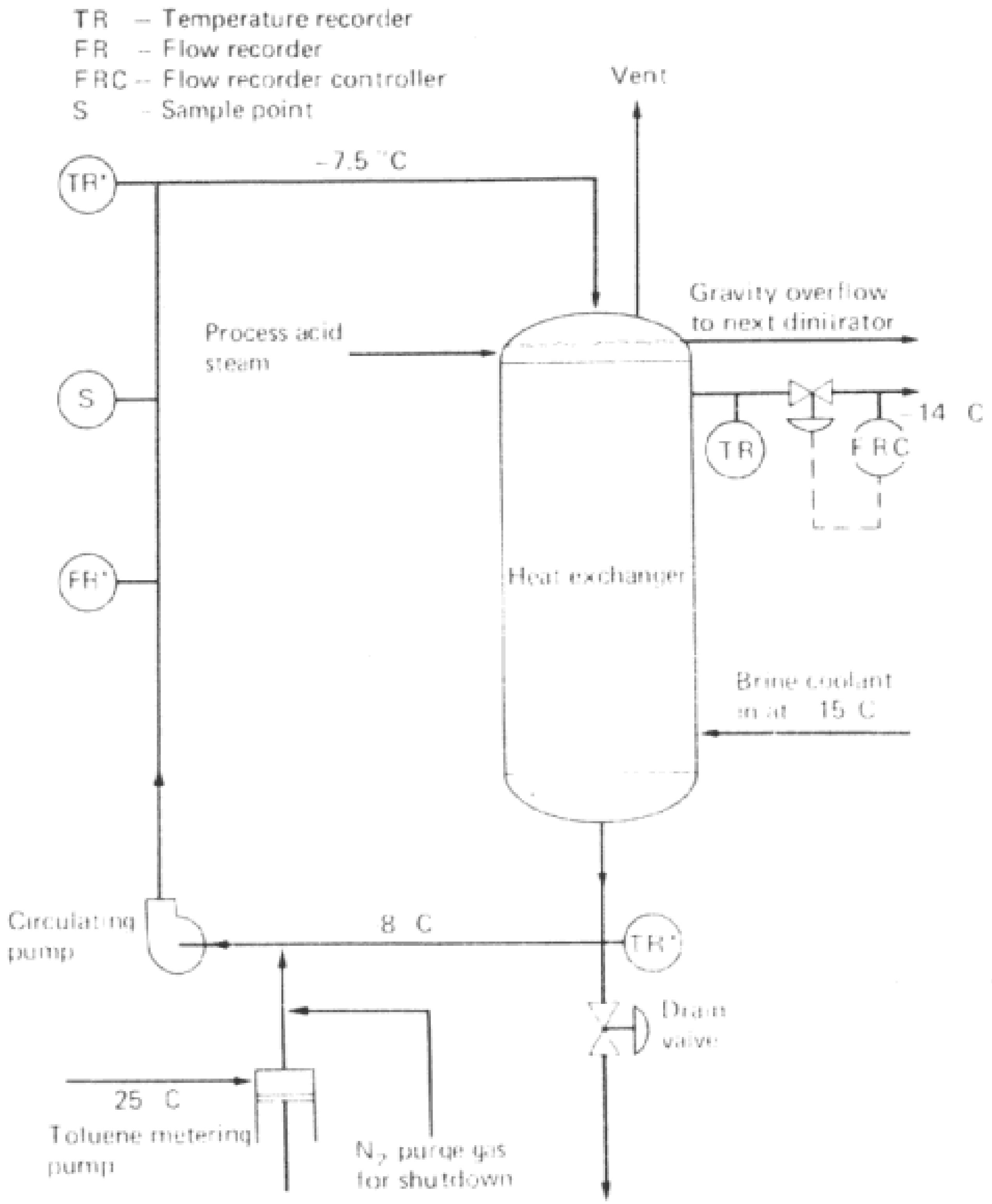


FIG. 21. Low temperature nitration of toluene to DNT according to Haas, Yee *et al.* [40].

toluene	1.0
HNO_3	2.11
SO_3 (as 20% oleum)	1.97
SO_3/HNO_3 ratio	0.93

The yield at −10°C was 99.4%.

These experiments served as a basis for DNT pilot plant development [40]. Toluene has a low solubility in nitratic acid, subsequently, toluene is added just ahead of the centrifugal pump. Toluene is dispersed into the anhydrous acid at −8°C.

The dinitration is carried out in four recycle nitrators. The acid stream moves through the reactors and toluene is added to each of the first three. The effluent from the last nitrator has the composition in wt %:

dinitrotoluene	12.5
trinitrotoluene	5.5
HNO_3	0.2
H_2SO_4	68.9
nitrozylsulphuric acid	12.8
HNO_2	0.1

The effluent is heated from −8° to 35°C in a tank where the product is divided into two phases. The upper phase enters the trinitrator and the lower acid phase is diluted with water to reduce the concentration to 70% H_2SO_4. The nitro compounds are separated and sent to the trinitrator and spent acid to the concentration unit.

The diagram of the system is given in the paragraph on trinitration.

Bofors-Nobel-Chematur Method of Manufacture of DNT (Fig. 22) [134]

This method is based on the principle of a circuit nitration pump for the production of nitrobenzene and nitrotoluene, as described already (p. 151). Each circuit is comprised of the nitration pump, cooler, separator and acid overflow vessel. The toluene fed to the mononitration circuit leaves the separator, is pumped as mainly mononitrotoluene to the dinitration circuit and leaves the separator as DNT ready for washing. The sulphuric acid fed to the dinitration step flows down-stream and leaves the mononitration circuit acid to overflow as spent acid. Nitric acid is fed to both circuits meeting the requirements of fully nitrated dinitro product and possibly complete consumption of nitric acid. The spent acid contains *ca*. 70% H_2SO_4 and less than 0.5% HNO_3 and does not require denitration.

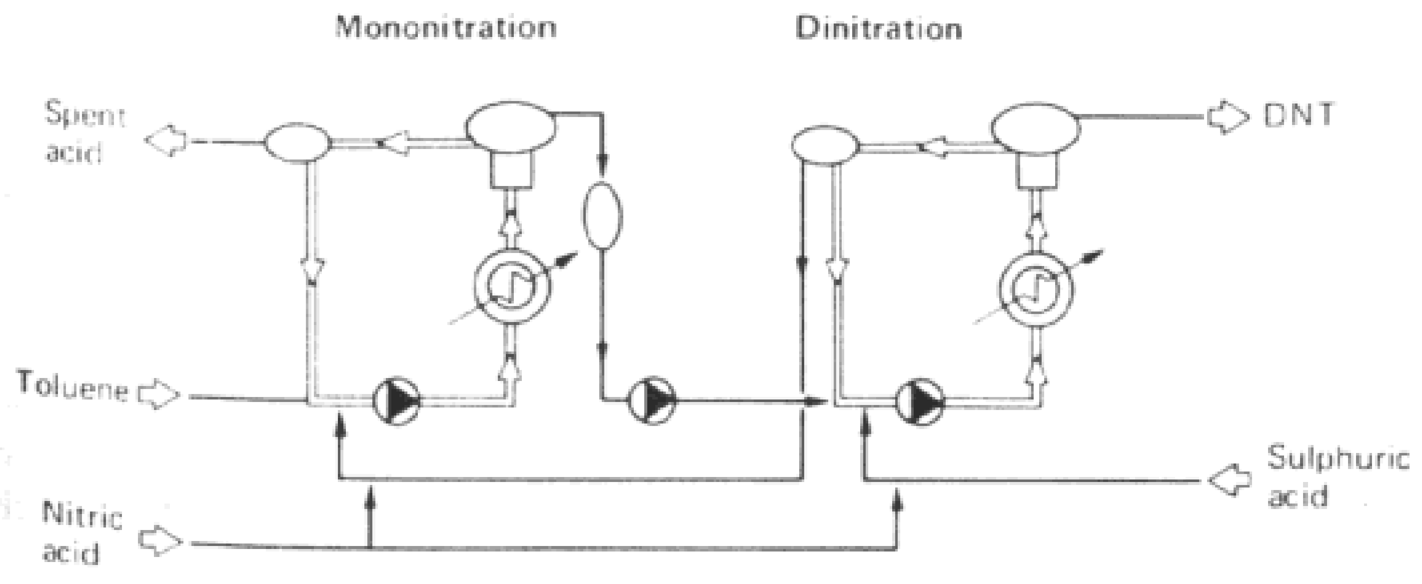


FIG. 22. Bofors-Nobel-Chematur method of manufacture of DNT (diagrammatic presentation). Courtesy A. B. Bofors-Nobel-Chematur.

An important innovation is the use of Bofors-Nobel centrifugal separator which minimizes the volume of the circuits and the size of the plant (Figs 23 and 24). It was originally designed in the 1960s for nitroglycerine manufacture, now it is accepted for DNT and TNT production. It changes the classical static separator, considerably reduces the amount of the explosive in the apparatus and is particularly suitable for use in continuous methods. It can be used to separate the nitro product from the spent acid and in the process of purification and washing of the nitro product. According to the manufacturer it can be easily cleaned. A relatively low operating speed of 500 1000 rpm is much below the critical figure. The separator can be installed in the nitrator this design is described in the paragraph dedicated to the manufacture of TNT.

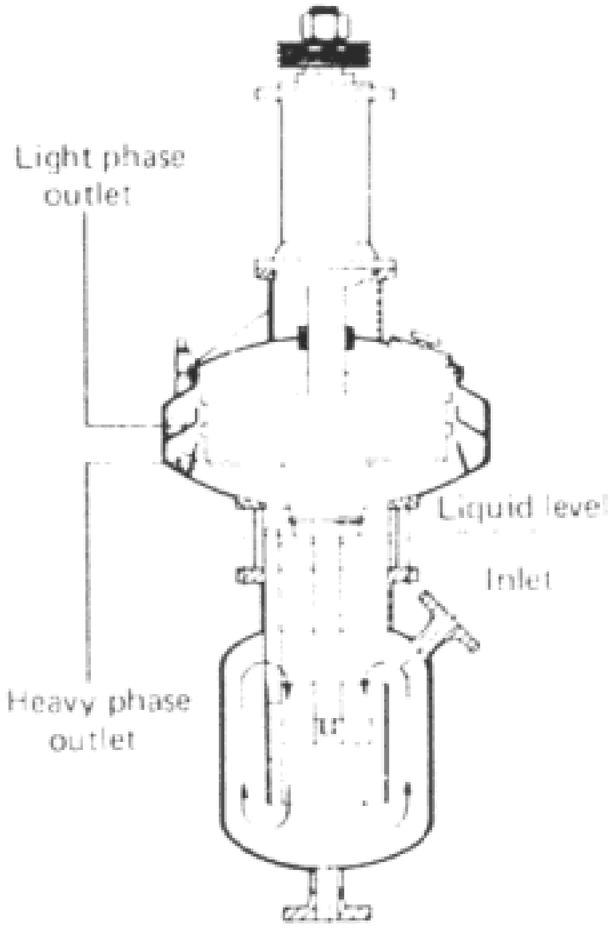


FIG. 23. Bofors-Norell Centrifugal Separator. Courtesy A. B. Bofors-Nobel-Chematur.

Biazzi S.A., Vevey Continuous Method [132]

The continuous Biazzi nitration process was used for the first time in 1935 for the manufacture of nitroglycerine. It soon became clear that many advantages were offered by this system such as the increased reaction speed, the high

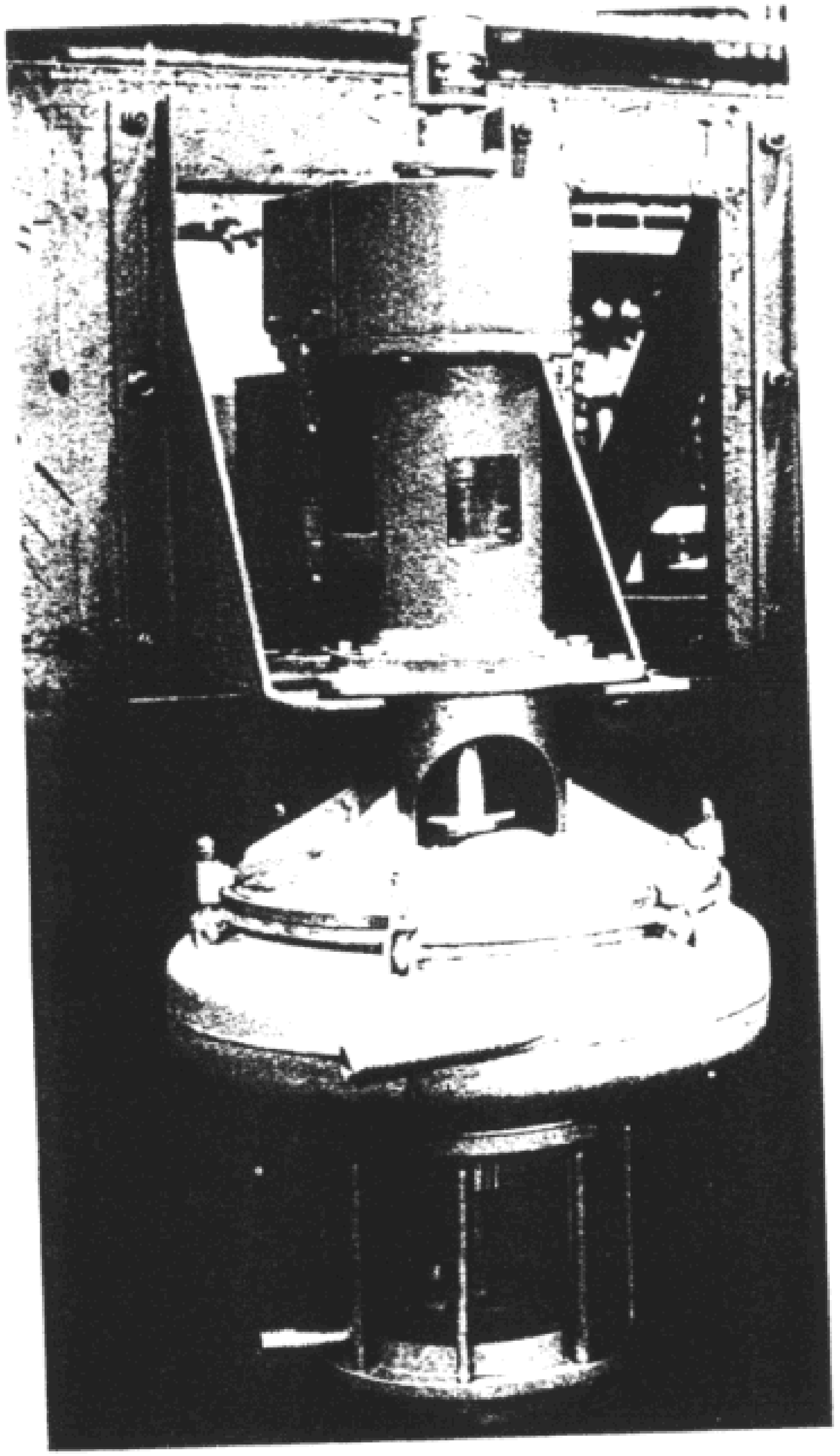


FIG. 24. Bofors-Norell Centrifugal Separator, General View. Courtesy A. B. Bofors-Nobel-Chematur.

heat transmission coefficient, the new method of separating the phases, washing by counter-current flow could be applied to the nitration of other organic products such as aromatic compounds.

A general scheme is presented in Fig. 25.

The reaction takes place in nitrators into which toluene and mixed acid is introduced continuously in exact proportion. The number of nitrators in the series varies from two to four. The temperature in each nitrator is kept constant

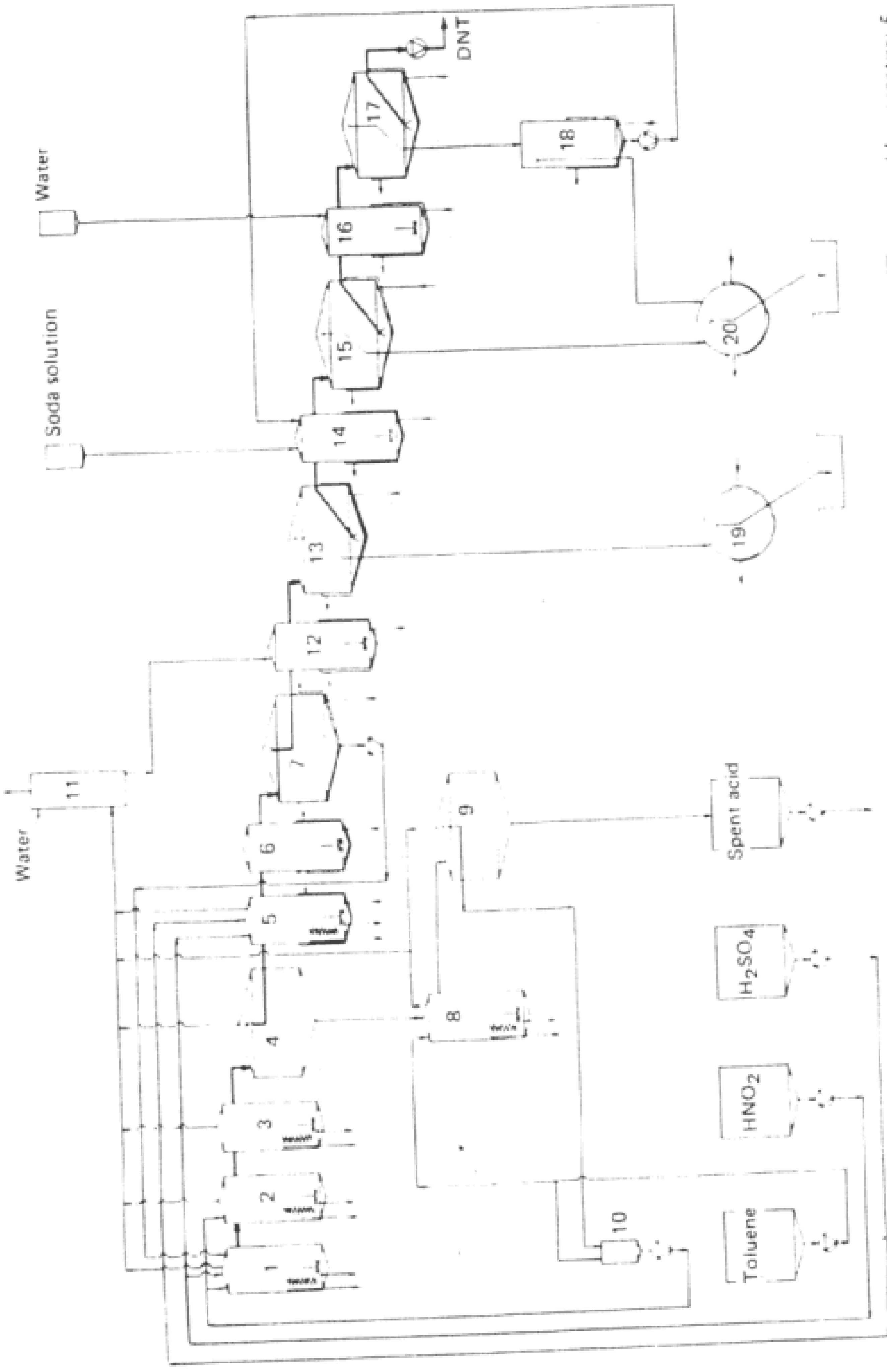


FIG. 25. DNT Biazzi S.A. plant for the manufacture of nitroaromatics. 1, 2, 3, Mononitrators; 4, MNT spent acid separator; 5, 6, Dinitrators; 7, DNT spent acid separator; 8, spent acid stripper; 9, final spent acid separator; 10, toluene feeding tank; 11, scrubbing column; 12, 14, 16, washers; 13, 15, 17, washing separators; 18, recycled waste-water feeding tank; 19, acidic waste-water catch tank; 20, alkaline waste-water catch tank.

by a thermostatic system. The stirring is achieved by a turbine acting as a pump. The emulsion from the nitrator enters a 'semistatic' Biazzi separator. The separated product is nitrated in next nitrators followed by a second separator.

The spent acid from the second separator is used as nitration acid for the previous stage.

The final spent acid is generally mixed with toluene to extract dissolved nitrobodies and use up the small remaining quantity of nitric acid.

The separated DNT is washed with water, with an alkaline solution and finally with fresh water. The water from the last wash is used again for the next wash. Between each wash the product is separated in a Biazzi separator.

The plant is made of stainless steel.

The manufacturing parameters are kept constant by automatic remote control. Among recorded parameters is the Redox value of the spent acid fully described in Chapter XI. In case of any irregularity the plant is automatically stopped and an alarm given in the control room.

TRINITROTOLUENE (Vol. I, p. 290)

2,4,6-Trinitrotoluene (TNT) remains the most popular explosive because of its stability, low sensitivity to impact, friction and high temperature and well developed methods of manufacture. It is widely used in commercial explosives as a good sensitizer and is much safer in production and handling than nitroglycerine. For commercial explosives lower grade purity of TNT is being used whereas the military grade TNT must be a highly pure compound.

Physical (including thermochemical and explosive) Properties

The setting point of TNT for military purposes should not be lower than 80.2°C. Chemically pure substance shows 80.8°C. TNT recrystallized from nitric acid is commercially available, its setting point is 80.6–80.7°C [1a].

The following are figures related to properties of TNT according to Meyer [1].

Thermal conductivity of 2,4,6-trinitrotoluene was determined by Belayev and Matushko [43]: $\lambda \times 10^4 = 4.8$ cal/cm sec grade for pressed substance and 3.5 cal/cm sec grade for powder. The temperature conductivity $a \times 10^4 = 8.5$ cm^2/sec and 11.5 cm^2/sec respectively.

The following are data for the velocity of detonation calculated for the infinite diameter and density ρ [42]:

$$D_\infty = 1872.7 + 3187.2\,\rho$$

when ρ = from 0.9 to 1.5343.

At higher densities: $\rho = 1.5543 - 1.636$

TABLE 29. Properties of 2,4,6-trinitrotoluene

Density (crystals) 1.654, molten 1.47 g/cm^3
Melting enthalpy 23.1 kcal/kg
Specific heat at 20°C 0.331 kcal/kg
Enthalpy of formation −62.5 kcal/kg
Heat of detonation 1080–1210 kcal/kg
Ignition temperature 300°C
Volume of detonation gases 730–620 l/kg
Lead block test 300 cm^3/10 g
Impact sensitivity 1.50 kpm
Friction sensitivity – no reaction up to 36 kp
Critial diameter in steel tube 5 mm

Vapour pressure:

at 81°C (m.p.)	0.057 millibar
100	0.14
150	4
200	14
250	
(beginning of decomposition)	86.5

$$D_\infty = 6752.5 + 3187.2\,(\rho - 1.53342) -$$
$$25102\,(\rho - 1.5342)^2 + 115056\,(\rho - 1.5342)^3.$$

The figures are valid for diameters from 0.7 to 7.8 cm. Meyer [1] gives 6900 m/s for $\rho = 1.60$.

The specification for commercial product is according to [1]:

Appearance: light yellow coloured flakes or crystals

Setting point for TNT of highest purity	min 80.6°C
for some commercial explosives	80.2 – 80.4°C
ammonium nitrate commercial explosives	various lower setting points
Volatiles	no more than 0.1%
Tetranitromethane	none
Acidity (as H_2SO_4)	no more than 0.005%
Alkalinity (as Na_2CO_3)	no more than 0.001%
Benzene insolubles	no more than 0.05%
Minerals (as ash)	no more than 0.01%

For a long time the setting point was the most common criterion of the purity of TNT. However, it has also been recognized for some time that it does not answer all the problems of the practical use of the explosive. One of the important problems is the exudation of a multicomponent eutectic mixture of isomeric trinitrotoluenes and dinitrotoluenes. Even a minute quantity of these substances can produce an inconvenience through the exudation.

This can occur in the course of the storage of projectiles with TNT particularly in summer time. The problem was recently reviewed by Reitsma [76]. Here are the main disadvantages produced by the exudation:

(1) it may affect the functioning of some components of the ammunition (e.g. initiators),
(2) cavities and cracks may be formed in the TNT casting and create a danger of premature detonation,
(3) the migration of explosive mixture to the screw thread of the fuse also creating a danger.

In the Federal Republic of Germany the exudation test consists in placing a cylinder of cast TNT on filter paper and keeping it at 70°C for 20 hours. The diameter is then determined by the stain on filter paper and also the loss of weight of the cylinder.

Reitsma examined different factors influencing the test, for example higher humidity favours the exudation. The test is not only influenced by impurities of TNT but also by the crystal size of the cast. Pressed cylinders of TNT do not show the exudation.

His conclusion is that the practical value of the test in its present form is limited.

Attention should be drawn to the microscopic examination of cast TNT. Thorpe and Connick [126] suggest polishing the cast sample with MgO powder and direct observation by reflected light. The previously suggested 'peal' method by Williamson [127] does not reveal sufficient structural detail.

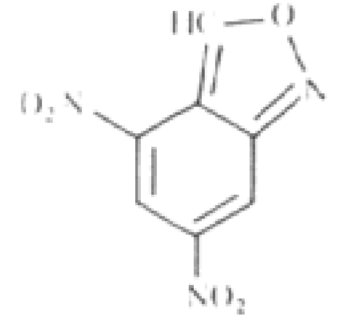
Thorpe and Connick suggested:

(1) preliminary polishing with wet silicon-carbide paper,
(2) intermediate polishing by hand on nylon velvet using MgO powder,
(3) finishing on vibratory polishing,
(4) an etch with bromoform shows up the grain orientation of the TNT matrix.

Among the properties of 2,4,6-trinitrotoluene related to its explosive character, very important is the sensitivity to high temperature. High sensitivity of molten TNT to impact was described in Vol. I, pp. 319–320.

Another problem is its thermal decomposition. T. Urbański and Rychter [44] examined the decomposition at temperatures near 400°C and above. The energy of activation between 380–440°C was of the order of 14 kcal/mol. Between 490 and 750°C trinitrotoluene took spherical shape and decomposed slowly with the evolution of a considerable amount of soot. The energy of activation in the range of temperatures 490–750°C was of the order of 8 kcal/mol and the shape of the curve: induction period against temperature was analogous to that shown for nitroglycerine in Vol. II, p. 50, Fig. 13.

Kamlet and co-workers [45] undertook the task of elucidating chemical changes of 2,4,6-trinitrotoluene which occurred during its isothermal decomposition at 200°C. 75–90% of TNT remained unchanged after 16 hours. The main products were: 4,6-dinitroanthranil (I) (2–4%), 2,4,6-trinitrobenzaldehyde (1–2%), 2,4,6-trinitrobenzyl alcohol (*ca.* 0.2%) and a minute amount (*ca.* 0.1%) of an azoxy compound of a probable structure (II).



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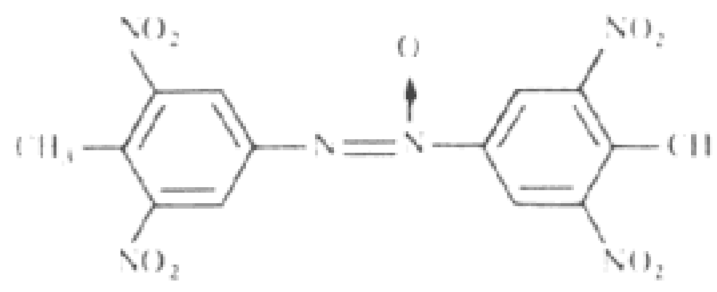


II

Camera and Biasutti [121] developed an interesting method of isothermal pressure metering for the determination of chemical stability of aromatic nitro compounds, as described in Chapter IV. It showed that a temperature as low as 200°C could be dangerous if DNT pure, or with TNT, is kept for less than 24 hours (e.g. 18 hours) at this temperature.

Also the addition of many foreign substances to molten TNT can create a great danger (see the paragraph on safety of manufacture and handling aromatic nitro compounds).

The formation of an azoxy compound is not surprising considering the ease of transformation of nitro compounds into benzazoxy derivatives. Among them is known an important by-product of the continuous methods of making TNT known as 'white substance' (p. 169). A few unidentified products of oxidation and reduction were isolated, all of which had high melting points. In up to 13% a polymeric substance was formed, insoluble in benzene, which did not melt below 300°C and burned when ignited by a flame. The substance was named 'explosive coke'. No *sym*-trinitrobenzene was found by Kamlet *et al.*, contrary to the statement by Rogers [46]. Kamlet suggested that a minor quantity of TNB could be produced through the oxidation of TNT to trinitrobenzoic acid followed by a loss of CO_2 (the usual reaction leading to TNB) and after that TNB was lost in the 'explosive coke'.

An important finding of Kamlet and co-workers was that at 210°C a spontaneous self-ignition of TNT occurred after 14–16 hours (or less) of heating.

The thermal decomposition of TNT is accompanied by the formation of free radicals. Jantzen [108] found free radicals at 240°C.

Hara, Kamei and Osada [109] described a detailed study of the thermal decomposition of TNT. They examined the decomposition by differential thermal analysis, thermogravimetry, infra-red spectroscopy, ESR and mass spectrometry. One of their most important findings was that TNT produced free radicals already in the vicinity of the melting point, that is 80°C. The substances which promote the decomposition of TNT are free radicals which are stable at room temperature. They are insoluble in benzene or chloroform and are partly oxidized polymeric substances.

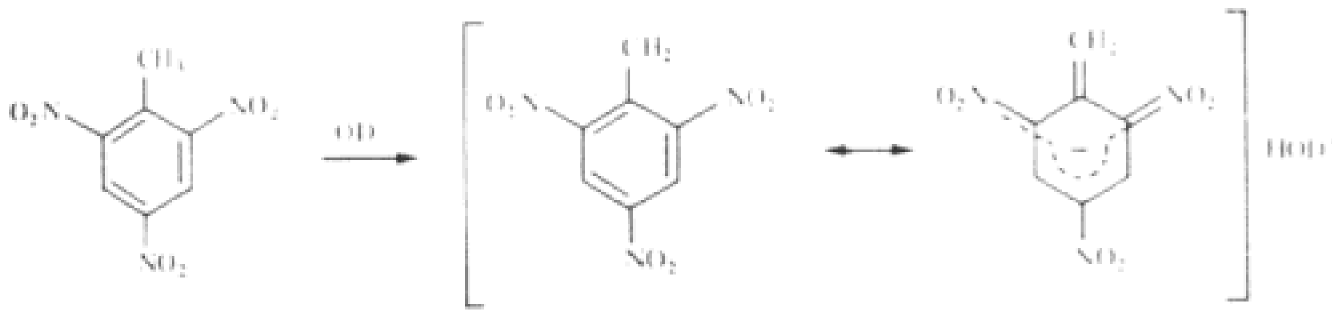
Chemical Properties of 2,4,6-Trinitrotoluene

Acid properties. The acid properties of 2,4,6-trinitrotoluene were discussed in Vol. I (p. 300). This problem was reviewed with the reactions of the formation of σ-complexes (Chapter IV). Acid properties were also examined by modern methods. Thus Schaal [47] gave the following figures for pK_a of trinitrotoluene, as compared with dinitrotoluenes:

2,4,6-trinitrotoluene	pK_a = 14.45
2,4-dinitrotoluene	17.12
2,6-dinitrotoluene	19.00

Therefore, 2,6-dinitrotoluene is the weakest acid.

Buncel and co-workers [48] also came to the conclusion that 2,4,6-trinitrotoluene has acid properties. They based it on their report of a ready exchange of CH_3 protons of the compound in basic medium of deuterium oxide:



(5)

Fyfe, Malkiewich and Norris [94] examined intermediates formed by the action of bases on TNT using high resolution NMR spectroscopy. Within 0.5 sec of mixing equimolar proportions of TNT and methoxide in DSO and CH_3OH the Jackson–Meisenheimer complex is formed. It decayed over 8 sec and the spectrum of anion according to (5) slowly appeared.

Salts of TNT were described in Vol. I, p. 304. A patent [79] claimed the use of salts of TNT for delay compositions.

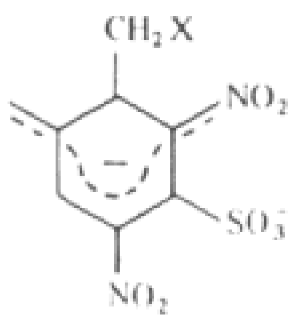
Action of light. This was described in Chapter V on the photochemistry of nitro compounds.

Reaction with Sodium Sulphite

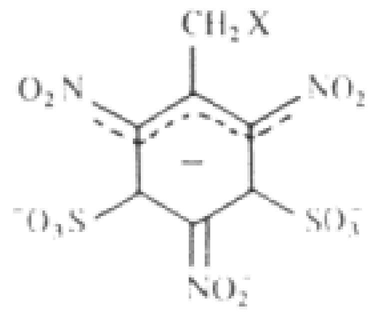
Reaction of 2,4,6-trinitrotoluene with sodium sulphite was extensively studied and reviewed by Crampton and co-workers [49], Strauss [50], Buncel and co-workers [51], Bernasconi and co-workers [52].

σ-Complexes with sulphonic groups are the products of the reaction of 2,4,6-trinitrotoluene (X = H) or trinitrobenzyl chloride (X = Cl) with one and two moles of sodium sulphite at 25°C: IIIa and b respectively.

According to Crampton [49b, d] dimethyl sulphoxide stabilizes the adduct 1:1. The compounds are soluble in water with a deep colour (440–460 nm and 550 nm).



III a



III b

The reaction of sodium sulphite with unsymmetrical trinitrotoluenes is much more vigorous replacing *meta* nitro with sulphonic group (Vol. I, p. 332).

Oxidation of 2,4,6-Trinitrotoluene

Kamlet and co-workers [53] made an interesting and important observation that the oxidation of 2,4,6-trinitrotoluene with dichromate-sulphuric acid in the presence of nitric acid gave a high yield (*ca.* 85%) of picric acid, that is the methyl group is replaced by phenolic group, whereas the oxidation with pure dichromate-sulphuric acid yields, as known (Vol. I, p. 255), 2,4,6-trinitrobenzoic acid. The formation of picric acid was rationalized according to Kamlet as the result of oxidative aromatic nucleophilic substitution which passes through the intermediate formation of 2,4,6-trinitrobenzoic acid.

Thus, the oxidation of 2,4,6-trinitrobenzoic acid with dichromate–20% oleum in acetic acid solution yielded 71% picric acid.

Using acetic acid instead of nitric acid Kamlet *et al.* [53b] was also able to obtain picric acid from 2,4,6-trinitrotoluene. The yield was 70% by using chromium trioxide-sulphuric acid in acetic acid medium.

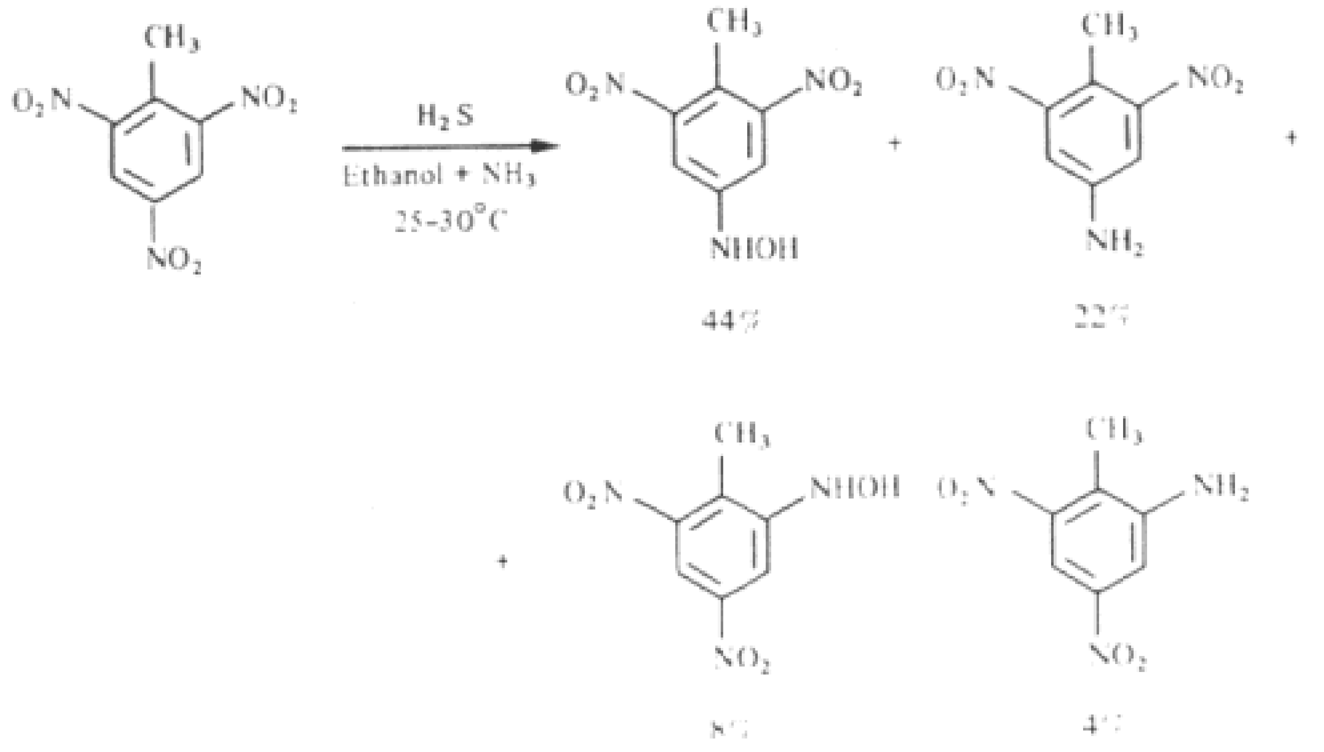
The oxidation of 2,4-dinitrotoluene [53a] with sodium dichromate in sulphuric acid in the presence of nitric acid yielded up to 45% of picric acid together with *ca.* 18% of 2,4-dinitrobenzoic acid. These authors found that 2,4-dinitrotoluene is more sensitive than 2,4,6-trinitrotoluene.

The oxidation–reduction process is involved in the formation of the 'white compound', a by-product of continuous production of TNT [54]. The formation of this compound is discussed in the paragraph on by-products of nitration of toluene to TNT.

Reduction of 2,4,6-Trinitrotoluene

An extensive study of the reduction of 2,4,6-trinitrotoluene was made by Nielsen, Coon and co-workers [55]. They also reviewed the existing literature. So far the use of different reducing agents produced mainly 4-amino-2,6-dinitrotoluene. Nielsen, Coon *et al.*, examined the use of hydrogen sulphide in the presence of a catalytic amount of ammonia and found the reaction to be solvent dependent: in dioxane both 4-amino-2,6- and 2-amino-4,6-dinitrotoluenes being formed. In ethanol the attack at position 4 is favoured but incomplete reduction to hydroxylamine derivatives also occurred.

The results can be summarized as follows (6):



(6)

Methylation of 2,4,6-Trinitrotoluene (Vol. I, p. 212)

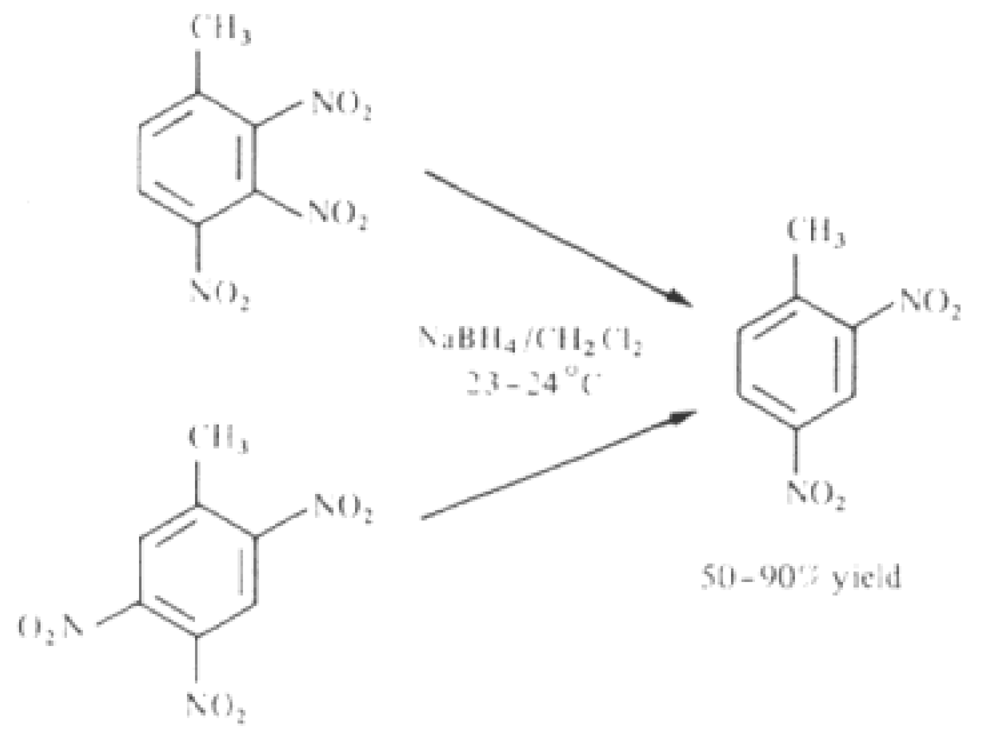
In addition to the reaction of methylation reported by Fieser (Vol. I, p. 212), a more recent observation was reported by Sauermilch [56]. It consists in warming 2,4,6-trinitrotoluene and *sym*-trinitrobenzene with an aqueous 50% solution of acetic acid and Ce(IV) ammonium nitrate. At 90–95°C an evolution of CO_2 occurred with the formation of 2,4,6-trinitro-*m*-xylene with yields of 67% and 84% respectively.

By using propionic acid instead of acetic acid nitro derivatives of ethylbenzene resulted.

Unsymmetrical Isomers of Trinitrotoluene and By-products of Nitration of Toluene

A number of analytical papers have been dedicated to the detection of isomers of trinitrotoluene and by-products by gas chromatography [57], NMR [58] and by TLC [59].

Some new reactions have been reported of unsymmetrical trinitrotoluenes. Okamoto and Attarwala [60] described the reaction of denitration of *meta* nitro group by acting with sodium borohydride in the atmosphere of nitrogen at 23–24°C in CH_2Cl_2.

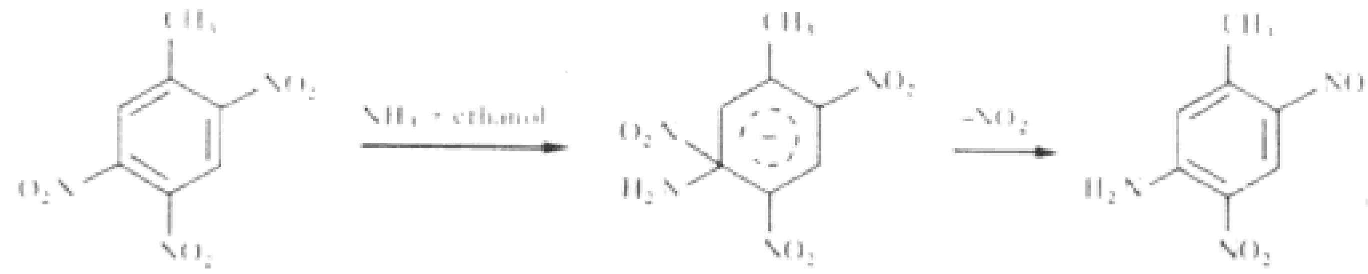


(7)

Another extensive paper on the reaction of unsymmetrical trinitrotoluenes with ammonia leading to aminodinitrotoluenes was that by Nielsen, Coon and co-workers [55]. The main purpose of this work was to identify the major components of waste waters which are formed through ammonolysis and reduction of TNT isomers, and to determine their toxicity.

The method of Hepp (Vol. I, p. 331) was also used: the action of ethanolic solution of ammonia.

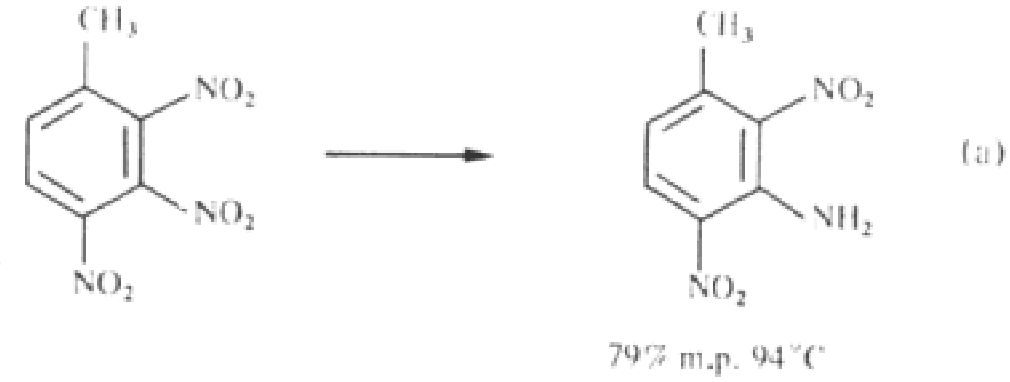
The mechanism consists of the initial formation of σ-adduct followed by splitting off NO_2 group in the form of the anion NO_2^- as depicted in scheme (8). It is referred to as the main unsymmetrical product — 2,4,5-trinitrotoluene:



(8)

The other isomers reacted in a similar way (9) with the exception of 2,3,6-isomer which gave a mixture of isomers.

Some of the aminodinitrotoluenes can be made by nucleophilic amination of 2,6-dinitrotoluene with hydroxylamine in basic medium [61, 62].



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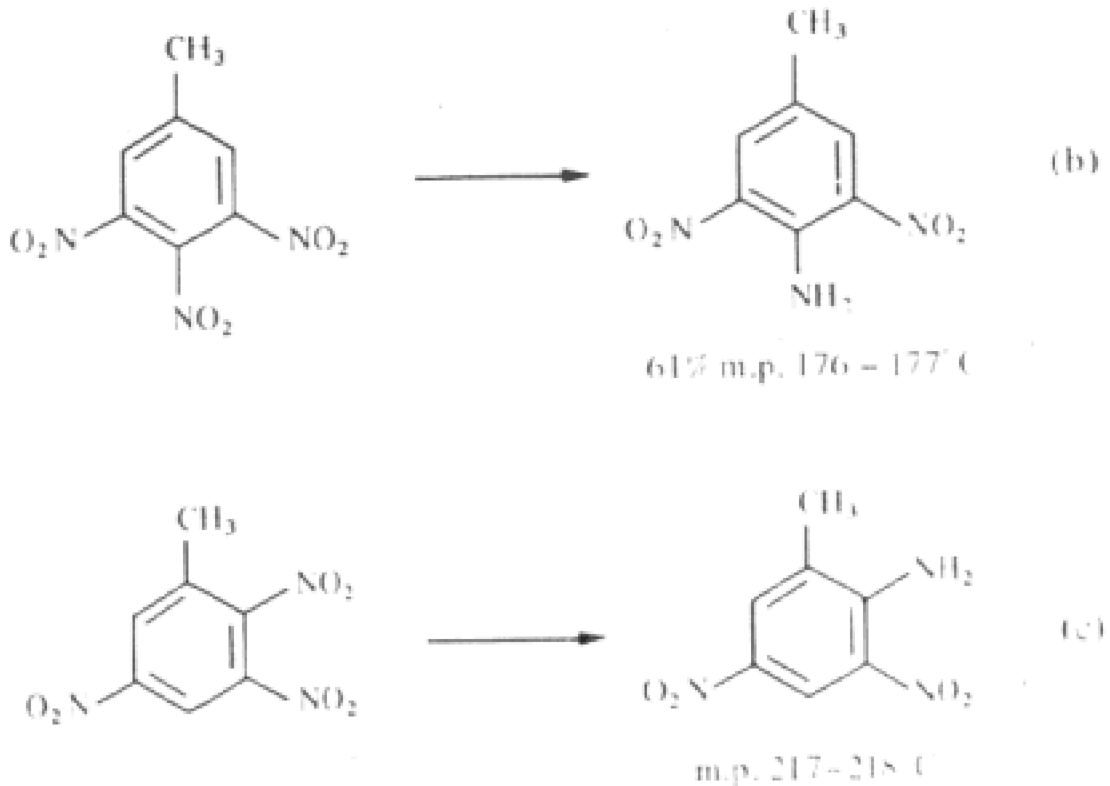

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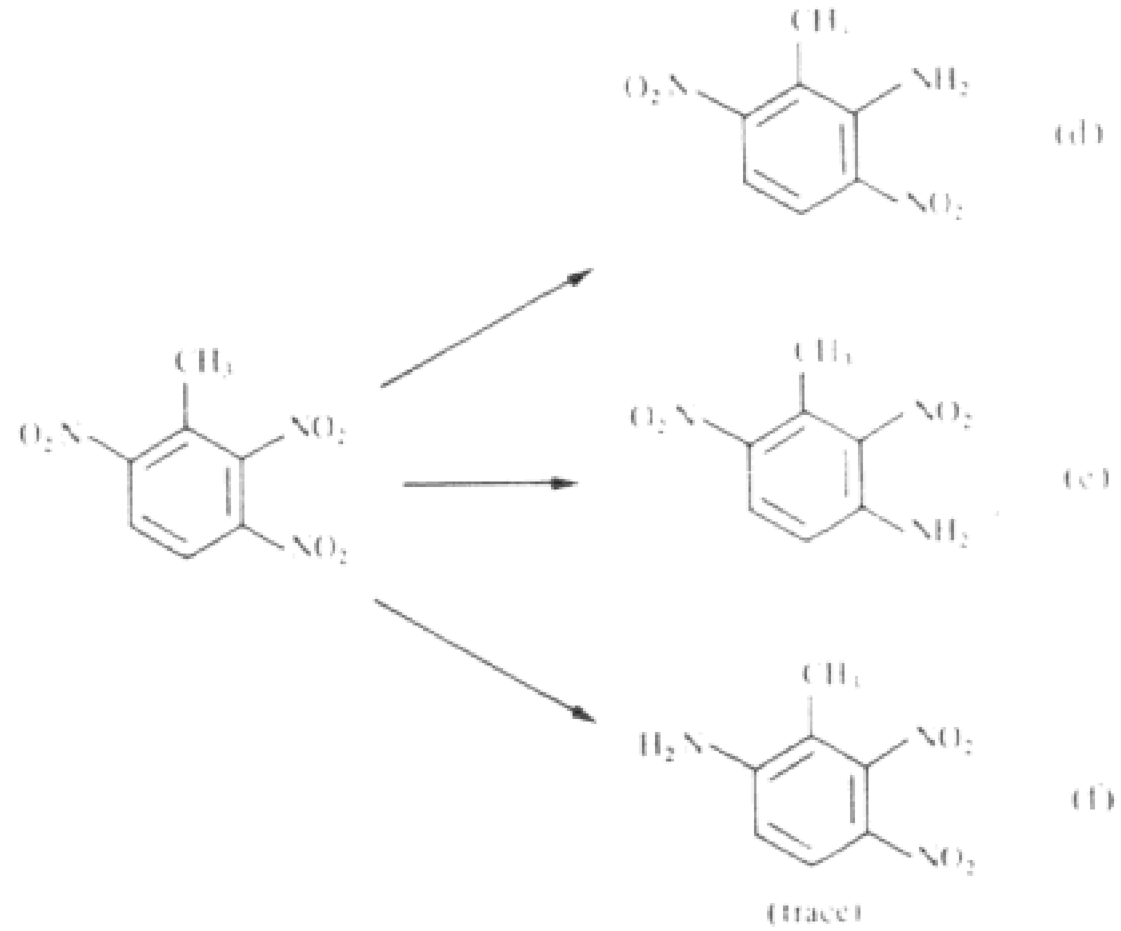


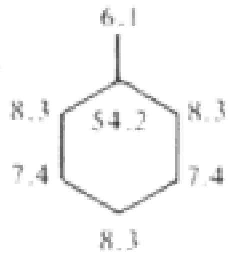
(9)

Tetranitromethane (TNM) (Vol. I, p. 337)

An important work was carried out by chemists of Picatinny Arsenal [63] who elucidated the problem of which part of the molecule of toluene is responsible for the formation of tetranitromethane.

Using carbon-14 as a tracer it was found that most TNM originates from the

aromatic ring carbons with over 50% being contributed by the ring carbon attached to CH_3 group. The distribution of carbon atoms taking part in the formation of TNM is given in diagram IV.



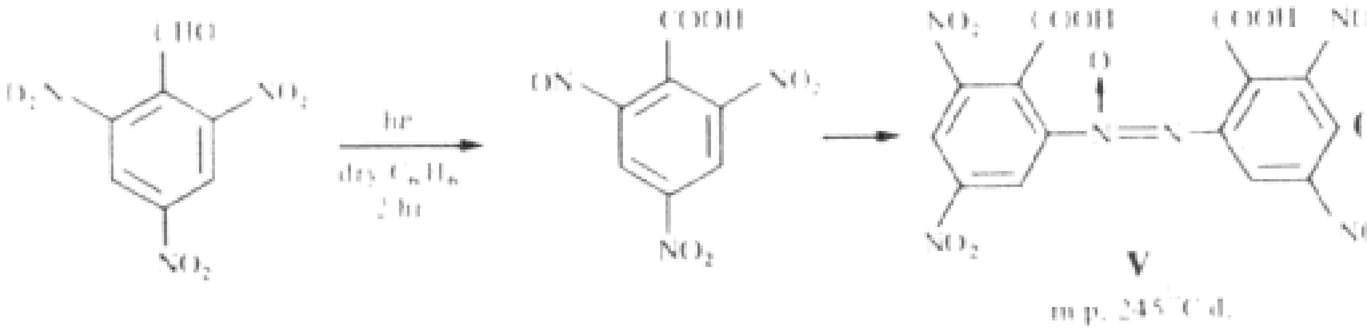
IV

It was found that over 80% of all the TNM can be traced to the dinitrotoluene isomers deriving from *m*-nitrotoluene. The ultimate formation of TNM is attributed to DNT oxidation reactions in competition with the reaction of nitration.

White Compound

It was found as early as 1950 that continuous methods of making TNT produce an as yet unknown compound named 'white compound'.

It was characterized by high m.p., white colour and a low solubility in nitrating acids. It readily crystallized out in various parts of the apparatus. Joshi and Patwardhan [54] established its structure as being 2,2′-dicarboxy-3,3′,5,5′-tetranitroazoxybenzene (V). They established it by synthetic route from 2,4,6-trinitrobenzaldehyde which was subjected in the light to the known reaction of Ciamician and Silber (Chapter V) yielding 2,4-dinitro-6-nitrosobenzoic acid. The latter on warming with water gave V (10):

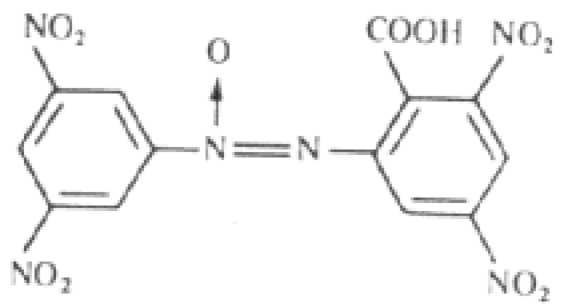


(10)

The synthetic product was identical to that produced by continuous nitration.

The structure of V was confirmed by Kamlet and co-workers [53]. Kotarski, Krasiejko and co-workers [64] also confirmed the structure V given by Joshi and Patwardhan by using infra-red, NMR spectroscopy and mass spectrography. Recently Ziółko, Krasiejko and Dębowski [65] established that 'white compound' exists in two crystalline forms differing by their m.p.: 268 269°C and

239–240°C. The raw product is also accompanied by a monocarboxylic azoxy compound (VI) [53b] which can further be decarboxylated to tetranitroazoxybenzene while boiling in ethylene glycol [65].



VI

m.p. 205–206°C

Ziółko and co-workers [65] established the solubility of white compound in organic solvents, in nitrating mixtures and spent acids: Tables 30 and 31.

White compound is soluble in aqueous (5%) sodium carbonate and in 10% solution of Na_2SO_3 at 90°C. Sulphuric acid does not precipitate the substance from the latter solution.

TABLE 30. Solubility of white compound in organic solvents (in 100 g of solvents)

Solvent	Temperature (°C)	
	20°C	Higher
Acetone	13.55	15.40 at 40°
Ethanol	6.80	7.85 at 50°
Benzene	0.0003	0.04 at 75°
Toluene	0.018	0.081 at 95°

TABLE 31. Solubility of white compound in water and acids (in 100 g of solvents)

Solvent		Temperatures (°C)	
		20°	70°
Water		0.22	0.393
Sulphuric acid (96%)		0.433	0.581
Nitric acid (91%)		0.162	0.189
Nitration acid:			
HNO_3	41.5%	0.201	0.417
H_2SO_4	54.5%		
H_2O	4.0%		
Spent acid:			
HNO_3	0.2%	0.026	0.099
H_2SO_4	79.7%		
H_2O	20.1%		

The white compound was examined by the same authors with regard to its sensitivity to impact and high temperature.

The results are as follows:

Sensitivity to impact is of the order of that of PETN and much above TNT, thus:

5 kg from a height of 10 cm gave 100% explosion,
and 2 kg from a height of 25 cm gave 100% explosion
(the figures for PETN are: 10 cm and 23 cm respectively)

At 300°C the explosion occurred after 10 s,
320°C the explosion occurred after 5 s
(the figures for TNT are 95 and 60 s respectively).

An attempt was made to establish in which stage of nitration white compound is formed. According to de Cazanove and co-workers [66] the amount of white compound increases with the time of the reaction. Ziółko, Krasiejko and Dębowski [65] established that white compound composed mainly of V with a possible admixture of VI is formed in the course of trinitration and is dissolved in the acid which passes to di- and mononitration. There, in more dilute acids it is precipitated in various parts of nitrators, pipes, valves etc. The precipitate can disturb the regular trend of the process.

It is advisable to determine the presence of white compound in the products of nitration of toluene. It is also advised [65] to use the TLC technique on silica-gel: the solution of nitro compounds in acetone is put on the starting line and the chromatogram is developed with vapours of benzene–acetone–methanol–dioxane (50:5:30:15 vol.%). The chromatogram is treated with ethylene diamine solution in acetone (50/50). White compound can be detected as a magenta coloured spot of R_f = 0.68. (Nitro derivatives give a reddish-brown coloured spot at $R_f = 0.80$).

IMPURITIES OF TNT

As previously mentioned, Yasuda [59] examined TNT by TLC. Among unsymmetrical trinitrotoluenes he found dinitrotoluenes: 2,4-, 2,6-, 2,5- and 3,5.

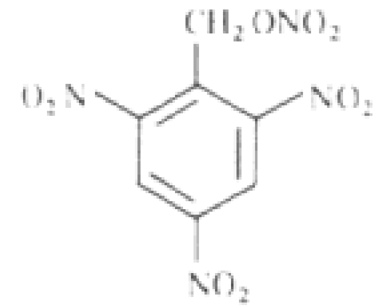
Gehring [67] undertook the task of examining non-volatile impurities of TNT by NMR technique. He found compounds in crude TNT as given in Table 32.

None of these substances were detected in purified TNT in quantities over 0.03%.

Special attention should be paid to 'α-Nitrato-TNT' which appears to have been detected by Yasuda [59], but no structure was given. Gehring [67] suggests the structure (VII):

TABLE 32. Impurities of crude TNT [67]

The substance	Quantity present in TNT in weight %
2,4,5-TNT	1.80–2.20
2,3,4-TNT	1.50–1.70
2,3,6-TNT	1.25–1.40
2,3,5-TNT	0.05–0.06
2,4-DNT	0.20–0.25
α-Nitrato-TNT	0.30–0.35
2,4,6-Trinitrobenzoic acid (TNBA)	0.20–0.22
2,4-Dinitrobenzoic acid	0.05–0.06
3,4-Dinitrobenzoic acid	0.01
2,4,6-Trinitrobenzaldehyde (TNBal)	0.20–0.24
m-DNB	0.003–0.005



VII

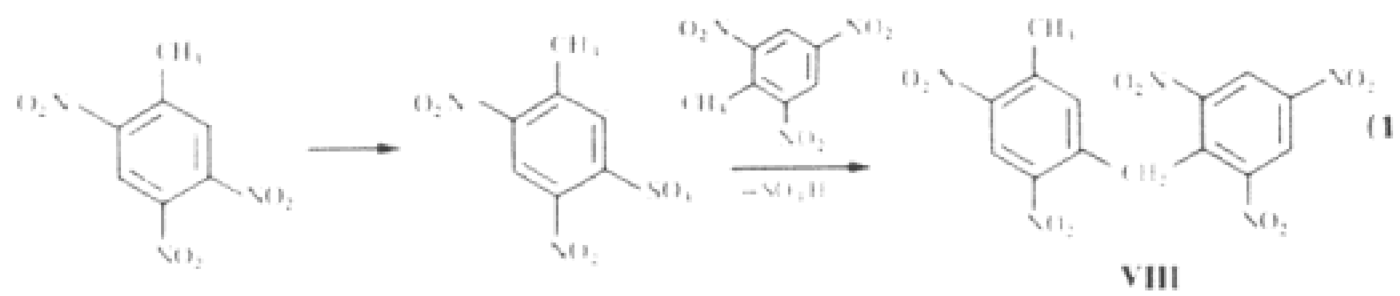
Kohlbeck and co-workers [68a] detected by TLC: trinitrobenzaldehyde, trinitrobenzylalcohol, hexanitrobibenzyl and azoxybenzene derivatives related to the 'white compound': tetranitroazoxybenzene and dimethyltetranitroazoxybenzene.

Sulphitation of Crude TNT ('Sellite' Process)

As known (Vol. I, p. 332) the reaction of sodium sulphite with unsymmetrical trinitrotoluenes is a major reaction in the purification of crude TNT, known under the name of 'Sellite Process' – 'sellite' being the name of sodium sulphite solution. Sodium sulphite solutions have pH > 8.0. It is known how sensitive higher nitrated aromatic compounds are to bases and sodium sulphite (particularly at a temperature, for example, above 40–45°C) can produce a damaging effect on TNT. It is therefore advisable to add a certain amount of sodium bisulphite to sodium sulphite to keep the pH value as low as possible. According to Clift and Fedoroff [71] 0.1–0.3% $NaHSO_3$ was added in the U.S.A. as a buffer to keep the pH value down.

By-products Formed in the Course of Purification of TNT with Sodium Sulphite

The excellent paper by Chandler, Kohlbeck and Bolleter [68b] has drawn attention to the possible formation of the 'new' by-products in the course of sulphitation of crude TNT ('sellite purification'). The authors noted a high reactivity of sulphonic group in *meta* position which derives from the sulphitation of unsymmetrical trinitrotoluenes. They explain the formation of 3-methyl-2,4,4',6,6'-pentanitrodiphenylmethane (MPDM) (VIII) from 2,4,5-trinitrotoluene by the reactions (11):



(11)

VIII

Another impurity previously reported [67, 68a] is 2,2',4,4',6,6'-hexanitrobibenzyl (HNBB):

The same authors [68b] also reported the difference between the quantity of both products – MPDM and HNBB – in continuous and batch processes of the manufacture of TNT:

	Continuous methods:	Batch processes:
MPDM	0.1–0.3%	0.06%
HNBB	0.1–0.5%	0.01%

Industrial nitration of toluene to trinitrotoluene (Vol. I, p. 312) is described in the next paragraph.

Utilization of Dinitrosulphonic Acids Formed in Sellite Process (Vol. I, p. 389)

In the widely used sellite process vast amounts of aqueous sulphite effluents ('red waters') are present. Some efforts were made to recover the compounds and at the same time to remove them from red waters, as they are harmful to the environment.

Red water is alkaline (pH 8.4) [98] and the products dissolved, slowly decompose on standing. Stabilization was achieved by acidifying with 25% sulphuric acid, allowing to stand for one week and then filtering [99]. The filtrate was extracted successively with benzene and ether and the solvent was evaporated. The precipitate from filtration and solid from evaporation amounted to 0.47% of the weight of the red water and proved to be mainly 2,4,6-trinitrotoluene. The stabilized (acidified) red water contains *ca.* 20% dissolved substances:

inorganics	5–8%
dinitrotoluene-sulphonic acids	4.5%
'Red Tar'	8.5%

According to Hall and Lawrence [99] Red Tar is composed mainly (90%) of sulphates. Gilbert [98] found that *ca.* 60% is composed of 2,4-dinitro-5-sulphonic and 40% of 2,4-dinitro-3-sulphonic acid.

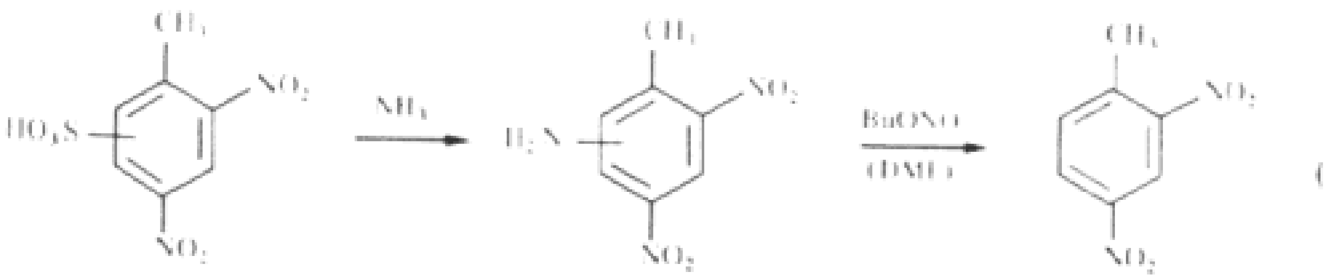
In another series of experiments [98] desulphonation was carried out on dinitrosulphonic acids. It is known that aromatic sulphonic acids can be desulphonated by heating with aqueous sulphuric and phosphoric acid but the data for dinitrosulphonic acid are very controversial and it appears that dinitrosulphonic acid cannot be readily desulphonated [98].

Subsequently reductive desulphonation was tried by methods which do not involve the reduction of nitro groups. A small yield (*ca.* 5%) was obtained [100] of 2,4-dinitrotoluene on desulphonation of 2,4-dinitro-5-sulphonic acid with sodium borohydride.

Reductive desulphonation was reported for 2,6-dinitrobenzenesulphonic [101] and 2,4,6-trinitrobenzenesulphonic to *m*-dinitrobenzene [101] and trinitrobenzene [102] respectively. In both reactions *N*-benzyldihydronicotinamide (the nicotinamide co-enzyme) was used.

Among the most important methods of transformation of the sulphonic group the following were reviewed by Gilbert [98].

Amination with ammonia under pressure [103] (12):

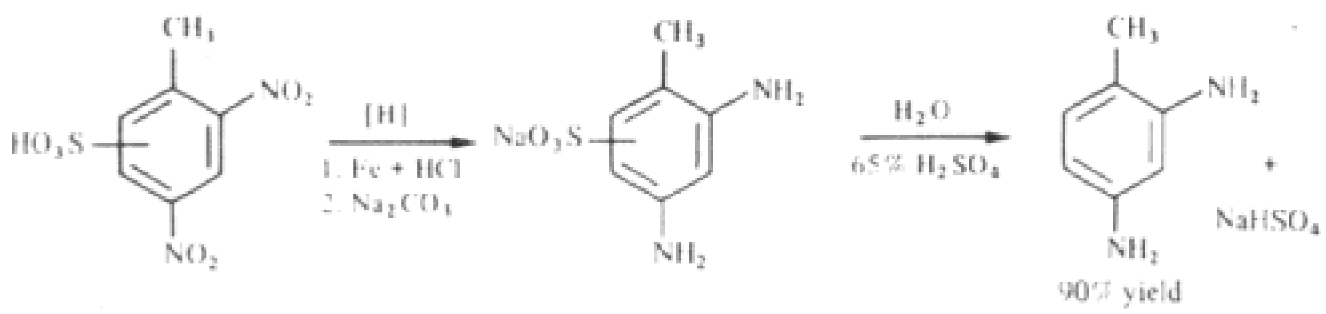


(12)

This method seems to be too expensive owing to the use of butyl nitrate as a diazotization and reduction agent. Substitution of the sulphonic group with hydrazine [104, 105] gave poor yield and was not economically justified owing to the expensive hydrazine.

Substitution of SO_3H with chlorine by reacting with $POCl_3$ and then removing chlorine with copper. The method was described for 2,4,6-trinitrobenzene [106] and 2,4-dinitrobenzenesulphonic [107] acids but it does not give the desired results with dinitrotoluene sulphonic acids [98].

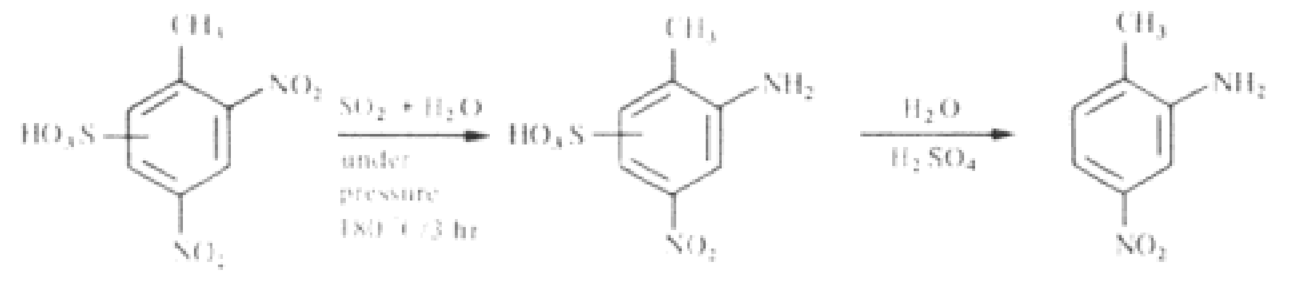
More promising is the reduction of the nitro groups followed by hydrolysis of the sulphonic group [98] (13):



(13)

Reaction (13) may possess a commercial significance owing to the value of *m*-toluylenediamine as a starting substance for urethane manufacture.

Another promising reaction is the partial reduction of the dinitro compounds followed by hydrolysis of the sulphonic group [98] (14):



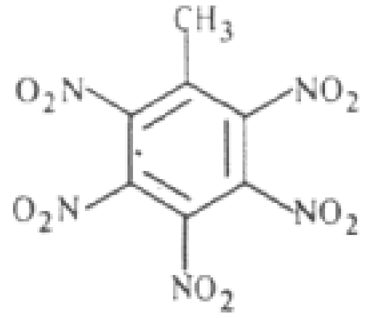
(14)

The reaction was tried with stabilized red water. The yield was 43% of the reacted sulphates present in the waters.

Recently a work has been reported on the treatment of red water with surfactants containing amino and quaternary ammonium groups which can form insoluble products with TNT (and probably with sulphonic acids salts formed in the course of the sellite process) [75].

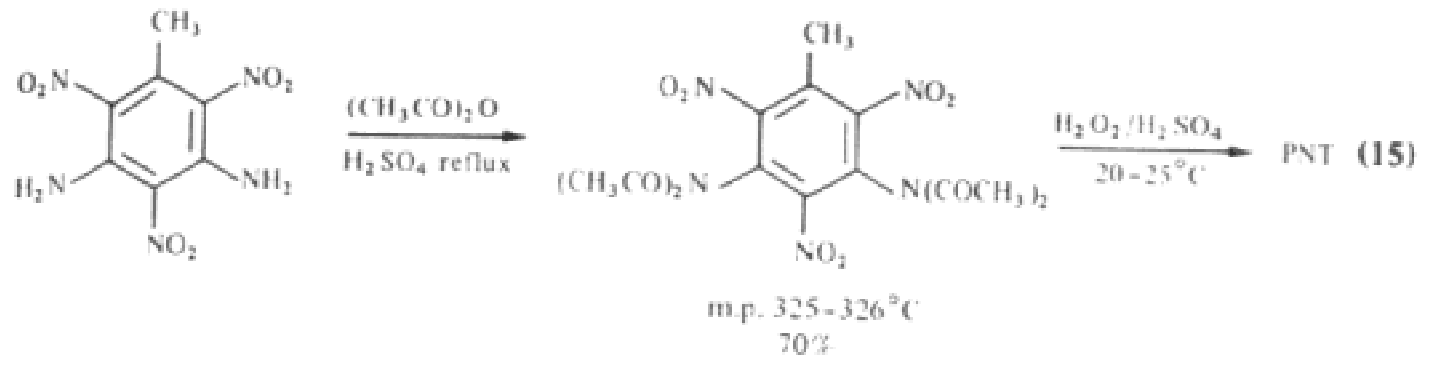
So far an adequate economic solution for the problem of utilization of sulphonic acids present in red water has not been found (see manufacture of TNT by Bofors-Chematur method [72] p. 177).

PENTANITROTOLUENE (PNT)



m.p. 225–240°C

The compound was prepared by Nielsen, Coon and co-workers [16] by oxidation of 3,5-bis (diacetylamino)-2,4,6-trinitrotoluene in 30% oleum with 90% hydrogen peroxide at 20–25°C (15):



(15)

3,5-Diamino-2,4,6-trinitrotoluene was made according to the improved method of Palmer [69].

The wide range of melting points of HNB and PNT has recently been explained by Coon [110] as the result of the isomerization of some of the nitro groups in the course of melting ($NO_2 \rightarrow ONO$). Subsequently a lower melting mixture occurred.

TNT MANUFACTURE (Vol. I, p. 345)

Continuous methods are now prevalent in the industrial methods of the manufacture of TNT. A general tendency is to use:

(1) relatively low temperature,
(2) high concentration of acids.

The first requirement ensures less by-products and particularly those produced by oxidation, and the second can help to obtain higher yield at lower temperature.

Nevertheless, batch processes are still in use. Matasă and Matasă [29] give parameters for the trinitration of dinitrotoluene – Table 33.

TABLE 33. Trinitration of dinitrotoluene

Composition of the acid	Nitrating mixture	Spent acid
HNO_3	49	1.5
H_2SO_4	49	92.0
H_2O	2	4.0
NO_2		2.5
Temperature °C	110	
Ratio HNO_3: DNT	120:100	
Yield in % of DNT	92	

It should be mentioned here that a paper on the nitration of DNT to TNT by anhydrous nitrating mixtures was given by Heertjes as early as 1953 [70]. He used nitric acid mixed with 40–72% SO_3 and a very good result was obtained by using the composition of the nitrating acid:

45–58% SO_3
51–28% HNO_3.

With an excess of 103% HNO_3 (i.e. 203% HNO_3 as compared to theoretical 100%) he obtained a yield of 98% while the temperature of nitration was kept at 81°C on mixing for 100 min, followed by heating at 109°C for a further 210 min.

Bofors-Chematur Continuous Method

The Bofors-Chematur method is now widely in use in many parts of the world. It emerged from Swedish–Norwegian Chematur and Norsk Spraengstoffindustrie (Vol. I, p. 371) incorporated by Bofors in 1968 [72].

The principle was given in Vol. I, but it is being continuously improved, the present process includes:

(1) nitration,
(2) washing with water ('presellite washing'),
(3) washing with sodium sulphite and bisulphite ('sellite purification'),
(4) 'post sellite' washing,
(5) drying,
(6) flaking.

1. Nitration. Raw materials: toluene or *o*-nitrotoluene, nitric acid (98% and 55%) oleum and sulphuric acid are stored in tanks from which they are fed to the process by metering pumps.

Nitration can start from toluene or *o*-nitrotoluene, *p*-nitrotoluene being isolated as an important intermediate for dyes and medicinal products – (Vol. I, p. 277). Nitration is carried out continuously in a series of nitrators through which the toluene or *o*-nitrotoluene and the nitrating acids flow in a countercurrent. In front of the first nitrator is placed an extraction vessel (not shown on the diagram) in which the residual nitric acid and nitro compounds are extracted from the spent acid by toluene. After extraction, the spent acid/toluene mixture enters the cooling unit. Toluene which now contains some nitrotoluene and acid is separated from the spent acid and enters the nitrator. The spent acid is sent for distillation.

All nitrators, extractors and spent acid coolers are equipped with 'dynamic' separators which have been described above – Fig. 23.

2. Presellite washing. TNT is continuously washed, in several washing vessels, by pure water to remove the acids. The washers are equipped with dynamic separators. The waste water, known as 'Yellow Water' is either sent to the washing system or to the absorbers, retaining the acids and organic products.

3. Sellite purification. The TNT is continuously treated with sellite solution in a series of washers. The pH level is controlled by pH meters. The washers are equipped with dynamic separators. The waste water, called 'Red Water' is transferred to a special destruction unit where water is evaporated and the remaining organic material is burnt.

4. *Post sellite washing*. The purified TNT is treated continuously in a washing system with pure water. The washers are equipped with dynamic separators. The waste water is transferred to Sellite purification. The washed TNT is transferred either in water emulsion or in molten form to the drying unit.

5. *Drying*. TNT is dried by heating with steam to 85–90°C and passing hot (75°C) air to agitate the molten substance.

6. *Flaking*. The dried TNT flows by gravity to the flaker which is a standard apparatus (Vol. I, p. 380, Fig. 38). It consists of an iron or steel drum rotating at constant speed and cooled inside by cold running water. By regulating the depth of immersion of the drum in the molten TNT the thickness of flakes can be controlled.

Design of Nitrators equipped with Centrifugal Separators.

The centrifugal separators which are usually given as an addition to the nitrators or washers (Fig. 23, 24), can be installed inside the reactor or washer. This is depicted in Fig. 26. It can be used for the capacity of the nitrator below 1250 kg/hr.

TABLE 34

The raw materials required for the production of 1000 kg of TNT are:

Toluene	485 kg
Oleum 20%	2250 kg
Nitric acid 55% and 98% calculated as 100%	1100 kg
Sodium sulphite	65 kg
Sodium bisulphite	10 kg
Sulphur dioxide	1 kg
Energy consumption per 1000 kg TNT are:	
HT Electricity and LT Emergency	135 kWh
Cooling water 28°C	50 m^3
Cooling water 15°C	50 m^3
Steam	1150 kg
Processed water	2 m^3

Low Temperature Process for TNT Manufacture

Haas, Yee and co-workers [40] developed a method of low temperature production of TNT. The main features of the method consist of:

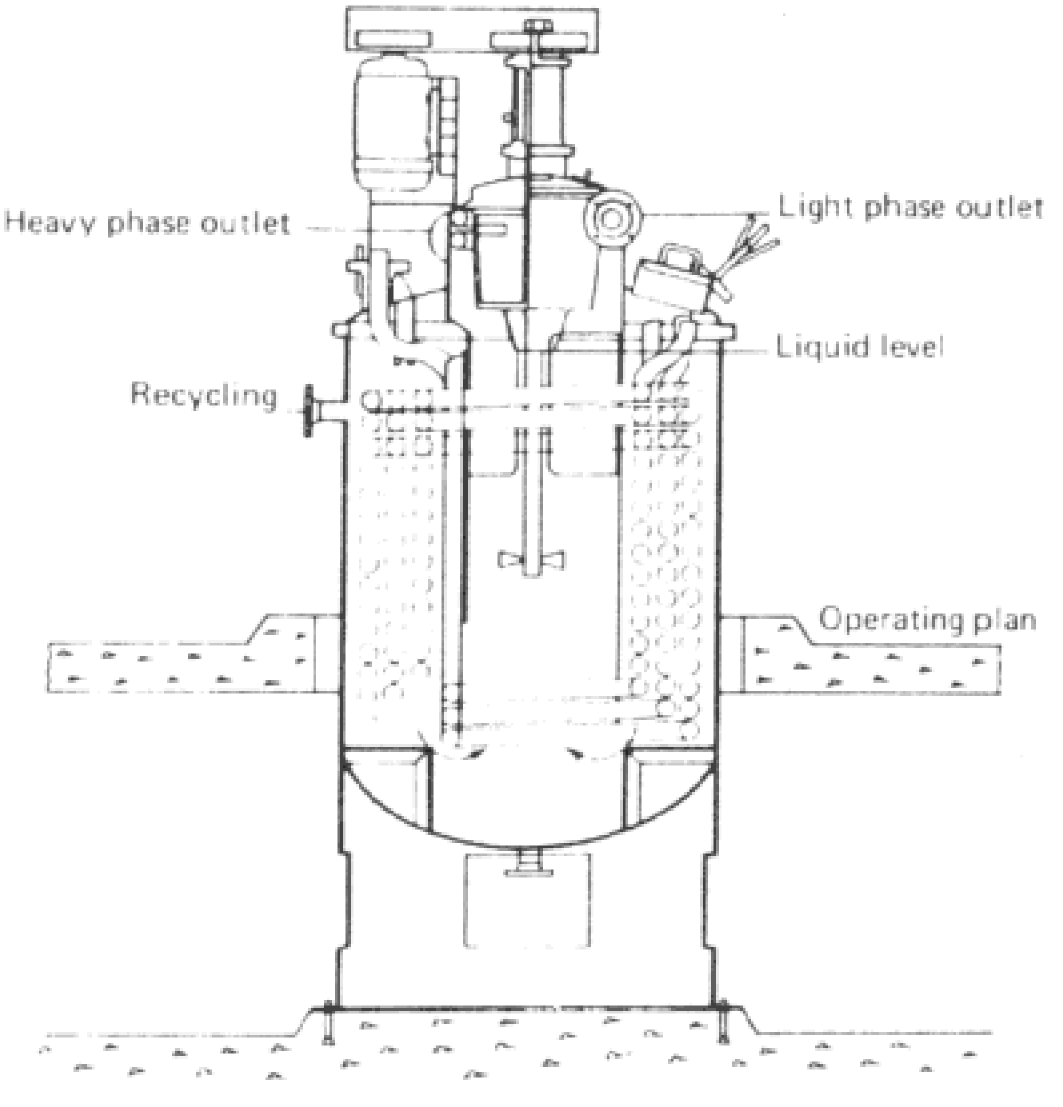


FIG. 26. Bofors-Norell Centrifugal Separator installed in a reactor. Courtesy A. B. Bofors-Nobel-Chematur.

(1) co-current flow of single phase the anhydrous acid and the nitro compounds,
(2) low temperature (−10°C) of dinitration,
(3) crystallization and filtration of TNT from the anhydrous nitrating acid.

A diagram of the system is given in Fig. 27. Dinitration has already been described and a diagram of the nitrating system given in Fig. 21. Trinitration occurred at 90°C, below 60°C it was insignificant, at 90°C the complete reaction of trinitration of DNT occurred at a batch process in *ca*. 1 hour. At 90°C an excess of oxidation occurred. The following feed material is added at a continuous rate to produce *ca*. 22 kg TNT/hr:

93 kg/hr of mixed acid,
85 kg/hr of dinitroeffluent containing DNT,
13 kg/hr of DNT from the dinitrator.

The composition and flow rate in the continuous method are given in Table 35.

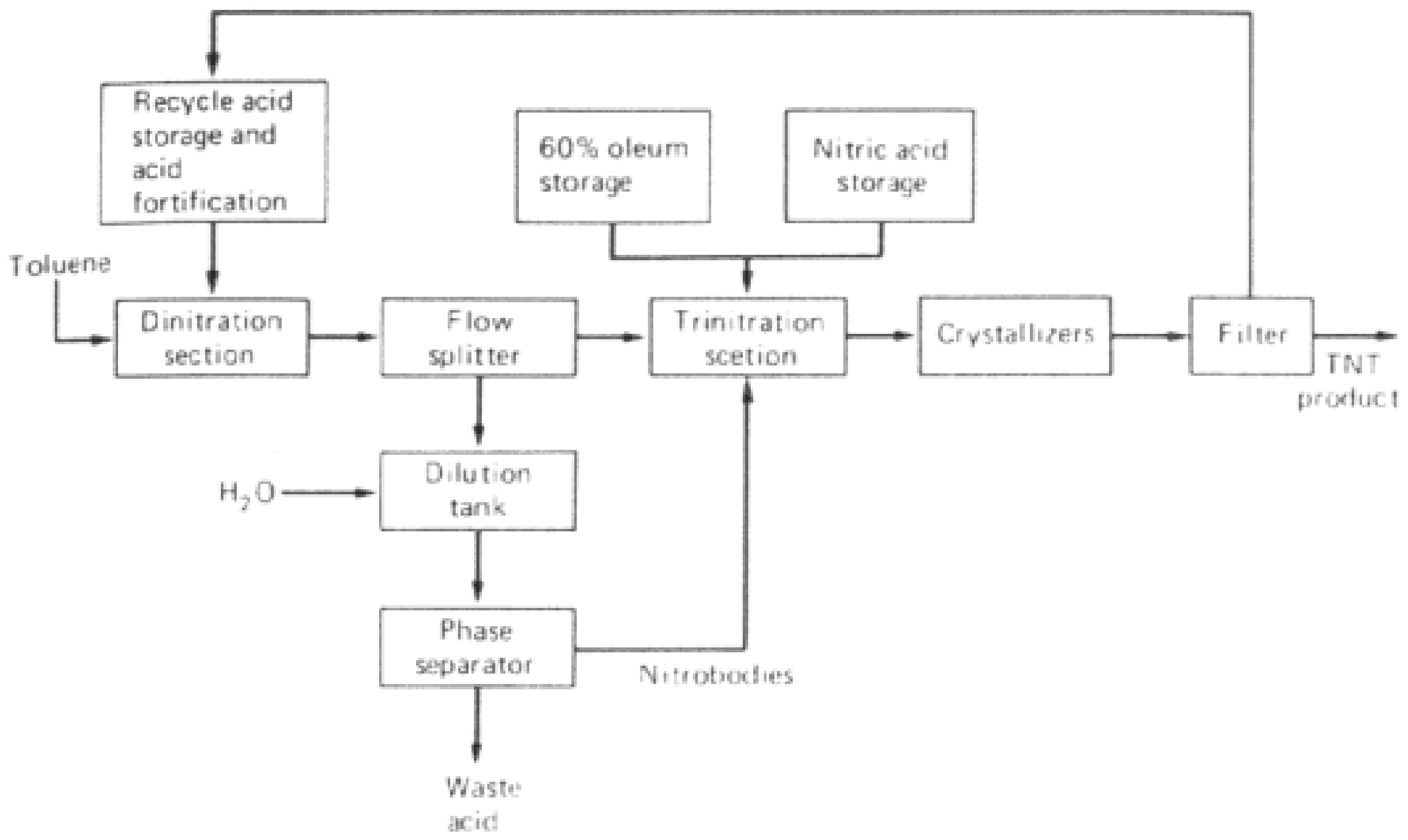


FIG. 27. Diagram of low temperature TNT process, according to Haas, Yee *et al.* [40].

TABLE 35. Composition of trinitration effluent

Compound	Flow kg/kg TNT	Wt %
TNT	1.4	16.5
HNO_3	0.65	7.7
H_2SO_4	4.6	54.3
SO_3	0.8	9.5
$NOHSO_3$	1.0	12.0

Crystallization. A diagrammatic presentation of the process is given in Fig. 28. The solvent was the trinitration acid of the composition: 10.6% HNO_3, 75.8% H_2SO_4, 10.6% SO_3. The solubility at different temperatures is collected in Table 36.

The process is diagrammatically depicted by a scheme Fig. 28. The first three vessels are cooled with water of 50, 30 and 10°C and the last two with a brine containing 25% $NaNO_3$ at temperatures of −5 and −15°C. The acid for the crystallization should not be too cold, as it would produce crystals which were too small and could block the pipes connecting the vessels.

The acid flowing from the crystallizer contains *ca.* 5.3% dissolved TNT and *ca.* 9.7% HNO_3 the rest being sulphuric acid, SO_3 and nitrosylsulphuric acid. It passes to the first (hot) crystallizer, after the draining of TNT, it is washed with 70% sulphuric acid, followed by washing with water.

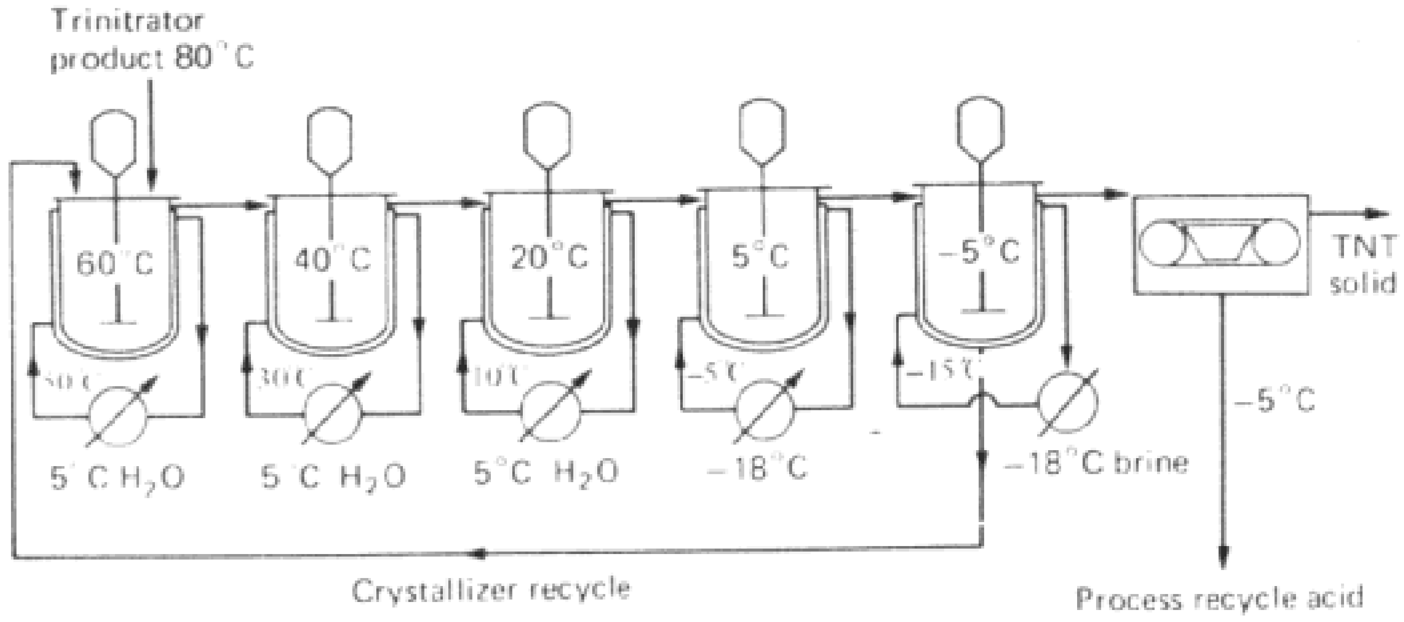


FIG. 28. TNT pilot crystallization unit, according to Haas, Yee *et al.* [40].

TABLE 36. Solubility of TNT in the trinitration acid

Temperatures	Dissolved concentration wt %
70	17.1
60	14.7
45	10.8
25	7.75
0	5.8
10	5.3
30	3.65

The filtrate removed from TNT contains *ca.* 66% of nitric and sulphuric acid and SO_3 used for the trinitration and is recycled to trinitration after the addition of acids.

Manufacture of TNT in the U.S.A. during World War II

Fedoroff [73] reviewed the methods of the manufacture of TNT in the U.S.A., after the description was declassified in the late 1960s. Some parts of the description possess an historical significance, but can create a good insight into the development of technology of one of the most important explosives.

One-stage Nitration of Toluene

During World War I, one stage nitration of toluene to TNT was carried out using a Hough nitrator (Vol. I, p. 157, Fig. 31). The nitrator was filled with

25,000 lb of the nitrating mixture (no composition was given). Toluene (2500 lb) was slowly introduced through a spray at 50°C. Gradually the temperature was raised to 110°C. The total time was 3 hours giving 5300 lb of TNT (85% yield).

Two-stage Process of Nitration

This method was in use at the Barksdale, Wisconsin plant, of the du Pont Co., the only TNT factory in the country between the two world wars. It consisted of mononitration and combined bi-tri-nitration.

Mononitration: toluene in a very thin stream was introduced to mono-mix for 3 hours at *ca.* 57°C. The charge was 'cooked' for 1 hour and then settled to separate mono-oil from the acid.

Combined bi-trinitration: mono-oil was added very slowly to a mixed acid containing 16% HNO_3, 82% H_2SO_4 and 2% H_2O. The ratio acid/mononitro was 9.5. During 2.5 hours of mixing, the temperature gradually rose to 120–125°C. The separated crude tri-oil was washed by agitating with hot water, dried and purified by crystallization with carbon tetrachloride.

Three-stage Process

This method was used from 1941 at Glen Wilton, Virginia and did not deviate from, at that time, the existing practice. The mono-nitration and di-nitration were carried out with the spent acids of dinitration and trinitration respectively mixed with 60–62% nitric acid. Mononitration was usually carried out in two stages to avoid the vigorous reaction of toluene with nitric acid. The idea was similar to that used in Germany (Vol. I, pp. 357–359). In Glen Wilton toluene was 'pre-mixed' in a mononitrator with a large quantity of acid composed of 7% HNO_3, 55% H_2SO_4 and 38% H_2O. After that mononitration acid was added to complete the nitration. The spent acid from mononitration was sent to the 'Recovery House' where nitric acid was distilled off (see Chapter on Denitration).

Trinitration was achieved with mixed acid composed of 97–100% nitric acid, sulphuric acid and oleum. It contained *ca.* 60% H_2SO_4, *ca.* 40% HNO_3 and a small amount (*ca.* 0.3%) of NO_2.

Direct Nitration Process

The so-called 'Direct Nitration' method was developed during 1942–45 in Beloeil, Quebec under collaboration between Canadian Industries Ltd and du Pont Co. (It was erroneously described [74] as being placed in Plum Brook Ordnance Work.)

This is a three stage process using essentially the method with three concentrations of mixed acid. The factory in Beloeil was making over 450,000 t of TNT per month. Later in 1942 another factory in Keystone Ordnance Work, U.S.A. started using exactly the same method as that in Beloeil. The main data on the method can be seen in Tables 37, 38, 39 and 40.

The advantages of the 'new' method called 'Direct Nitration' are given below.

1. Better heat control is possible, because the addition of toluene to 7–8 times its mass of nitrating acid, allows more efficient dissipation of heat of re-

TABLE 37. Compositions of acids

Type of acid	HNO_3	H_2SO_4	Nitrosyl-sulphuric acid	Nitro compounds soluble in ether	H_2O	Density at 25°C
Mononitration	14.2	48.2	16.6	1.8	19.2	1.68
Spent acid after mononitration	3.5	55.7	16.8	0.3	24.0	1.67
Dinitration	13.0	54.3	16.9	9.0	7.8	1.78
Spent acid after dinitration	4.4	62.4	15.8	2.7	14.7	1.78
Trinitration						
1. Oleum	4.9	103.7	0.3	–	–	1.95
2. 'Semi-mix'	62.0	43.0	0.3	–	−5.0*	1.83
3. Final Composition	23.3	82.7	0.4	0.2	−6.2*	1.93
Spent acid after trinitration	3.4	63.5	17.6	13.5	2.0	1.87

* Maximum amount of water which can be added to obtain a mixture free of water. It can be used as a criterion of the concentration of water in the acid mixture.

TABLE 38. Main parameters of the nitration

	Weight ratio	Temperatures of nitration (°C)	Time of nitration (min)
Mononitration	Acid/Toluene 7.8	1. 35–38° 2. 54–57° cooling to 38°	40–45
Dinitration	Acid/MNT 3.7	1. 82° 2. 84–86° cooling to 65°	45
Trinitration	Acid/DNT 2.4	1. 79–80° 2. 90–91° 3. 110–111° cooling to 93–96°	90

TABLE 39. Material balance in 'direct nitration' at Keystone, June 1945

Yield of TNT in kg for 100 kg of toluene	209.84 kg
Raw materials for 100 kg TNT	
Toluene	47.66
Sulphuric acid	211.67
Nitric acid	145.19
Sellite*	10.29
Sodium carbonate	5.02
Acid consumed and lost for 100 kg TNT	
Nitric acid consumed and lost	105.72
Nitric acid recovered	37.45
Sulphuric acid lost	1.72
Sulphuric acid recovered	209.95
Mean setting point of TNT	80.4

* Sodium sulphite.

TABLE 40. Acid consumption and losses per 100 kg toluene

Nitric acid in mononitration	90 kg
Nitric acid in dinitration	90 kg
Nitric acid in trinitration	125 kg
Sulphuric acid	450 kg

action in the large mass of high specific heat acid, than was possible in the methods where a small amount of low specific heat toluene was used. The difficulty in the nitrator at the beginning of mononitration, was partially overcome by mixing the toluene, prior to nitration, with large amounts of cyclic acid, and in cases of trinitration by mixing the bi-oil with oleum.

2. The time cycle of nitration is considerably shortened by using the new method, because the addition of a small mass of toluene or oil to a large mass of acid in the nitrator, obviously requires less time, than the addition of a large amount of acid to a small amount of toluene or nitrated oil, as in the older processes.

3. The new method is safer, because even with a rapid increase in the temperature of nitration the possibility of formation of gaseous explosives mixtures is very slight. These gases, consisting of toluene vapours (or volatile nitro compounds) mixed with air or tetranitromethane. They accumulated in the dead space above the nitrated material and could be ignited by a spark of static electricity or local overheating due to the too rapid feeding of acid, thereby causing very dangerous explosions. Two such explosions are described in the chapter dedicated to accidents in the manufacture of nitro compounds.

The new method is also safer because there is practically no accumulation, on

the surface of the acid layer, of large quantities of unnitrated organic cor pounds. Every new portion of organic substance introduced under the surfa of acid, nitrates almost completely, except in trinitration, before it rises to th surface. If the feed is too fast and the temperature starts to rise above pe missible limits, overheating may be easily checked by simply halting the additio of organic substance. Also the proportion of organic compounds to acids at an time during nitration, except at the end of nitration, is much smaller than in th older methods. This is especially important at the beginning of nitration, whe the reaction is most vigorous.

4. Dangerous foaming often observed at the beginning of trinitration by th older methods is practically eliminated by the new method.

5. 'Burned' charges, often occurring in the older procedures and caused by too rapid temperature rise during nitration, were not as numerous after the ne method was introduced.

6. The new method is easier to operate and does not require such highl skilled workers as in the older methods. Because of increased production pe line, labour requirements are much reduced.

7. The introduction of strong downward agitation and the use of undersurface toluene (or MNT) feed to the nitrating acid results in rapid and practicall complete (except in trinitration) nitration during the time that the oil phase is below the surface of the acid in the nitrator. This type of 'bubble nitration' is particularly efficient when a strong downward agitation is used, and the time for the oil to rise to the surface is increased by the correct design of the organic substance feeder tube. In the old process, nitration occurred at the interface between the acid and oil layers – and delayed reactions ('sleeper charges'), excessive heats, etc., were rather common. At the same time improvement in uniformity of nitration was obtained, the improved agitation allowed better temperature control by more efficient distribution of the heat of reaction.

8. The advantage obtained by increased production and decreased cost of TNT was important.

It is interesting to note that the direct method of nitration was attempted in Europe as well as in the U.S.A. (Barksdale Plant), long before the Canadian and Keystone Ordnance Works trials indicated the great benefits derived from this process. However, the early European experimentation indicated that the method was unsafe and that it was difficult to control the important temperature and time factors. It seems highly probable that the difficulties encountered were due to improper feeding of toluene or MNT or DNT to the acid in the nitrator, poor agitation, inefficient cooling and the use of incorrect acid compositions.

Purification of Crude TNT

Three methods of crude TNT purification were in use in the U.S.A.:

(1) 'Soda-Ash' (sodium carbonate) process introduced by du Pont Co.,
(2) Ammoniacal 'Sellite' (ammonium–sodium sulphite) process introduced by the West Virginia Ordnance Works of General Chemical Co.,
(3) The alkaline 'Sellite' (sodium sulphite) process of Hercules Powder Co.

All three methods were designed to shorten the time of the operation and to reduce the quantity of water used. The latter requirement was dictated by the necessity to reduce the pollution of streams and water-ways with toxic sulphite solutions. To accomplish this completely the sulphite solutions were evaporated in a quadruple-effect evaporater to a thick syrup, the syrup was then fired in a rotary kiln incinerator to give an ash which was harmless to fish and animal life. The number of water washes of TNT was also reduced.

Soda-Ash Process

Crude 'Tri-oil' was washed with a small amount of hot water, followed by adding cold water to reduce the temperature in the wash-tank to 68°C. TNT solidified as fine crystals.

Sodium carbonate 20% solution was added to neutral (on litmus) reaction and care was taken to avoid an excess of alkali harmful to TNT. A solution of 16–17% NO_2SO_3 and 0.1–0.3% $NaHSO_3$ was added. The sodium–hydrogen sulphite was used to avoid alkaline reaction and also served as a buffer. Cold water was added to thicken the charge, the whole operation lasted 45 min. The product was screened through a 10 mesh sieve, centrifuged and washed with water. Larger particles were returned for reworking.

The washed TNT was dried (at 110°C) and flaked (Vol. I, p. 380, Figs 93, 94). The 'Flaker' is a steel drum rotating at constant speed and cooled on the inside by cold running water. By regulating the immersion of the drum in the molten TNT in the pan, the thickness of the solid product on the drum is controlled. A steel scraper removes the adhering TNT. It seems however (for safety purposes) preferable to use a bronze scraper as in the French method (Vol. I, p. 379).

Ammoniacal Sellite Process

This method is similar to the 'Soda-Ash' process. The difference consisted of using a solution of sodium sulphite (16–17% Na_2SO_3) added with ammonia gas by bubbling it to 2% free NH_3. The solution should have pH = 5. The pH value rose to 8.5 after mixing the solution with TNT (15 min). The solution contains: ammonium nitrate, sulphate and sulphite. Free sodium sulphite causes the formation of a red colour in the slurry of TNT with the aqueous solution. TNT made by this method is slightly darker owing to the action of ammonia on β- and γ-trinitrotoluene producing traces of 2,4- and 4,6-dinitro-3-toluidine. Traces of

these impurities have not been found to adversely affect the quality of TNT.

The aqueous solution removed from TNT was not evaporated to incinerate owing to the presence of explosive ammonium nitrate in the solution.

Alkaline Sellite Method

Crude TNT is mixed with hot water and cold water is added to crystallize the product at 71°C. After washing to reduce the acidity to *ca.* 0.3% H_2SO_4, a calculated amount of Sellite solution was added containing 14.8–15.2% Na_2SO_3 and 1.1–1.6% Na_2CO_3. Mixing at 71°C lasted for 6 min after which the TNT was filtered. The washing, remelting, drying and flaking operations were carried out in the usual manner.

SAFETY OF MANUFACTURE AND HANDLING OF AROMATIC NITRO COMPOUNDS, PARTICULARLY OF BENZENE AND TOLUENE

(Vol. I, p. 391)

Although the number of accidents in the nitration of aromatic hydrocarbons is relatively small, the danger of the processes should not be underestimated.

As regards benzene and toluene the first and last steps of the reaction are particularly dangerous, i.e. the vigorous reaction of the hydrocarbon and the final nitration to introduce the second and third nitro group into benzene and toluene respectively.

An instructive description of a considerable number of accidents is given by Biasutti [76b].

In addition to those reported in Volume I, two accidents are described here.

In 1944 in a German factory which was built to the pattern of that of Krümmel (Vol. I, p. 357) an explosion took place during the nitration of benzene to nitrobenzene for the further nitration to dinitrobenzene. The reaction was carried out in a nitrator of 15 m^3 capacity. The nitrating mixture was added to benzene.

The explosion took place at the beginning of the reaction and demolished the building, although the nitrator suffered only slight damage. The conclusion of the investigation was that the explosion was produced by a gas mixture of benzene/air due to benzene leaking from the nitrator. This was probably the result of overheating the surface of the liquid in the nitrator. This in turn was the result of inadequate mixing produced by the incorrect design of the propellant stirrer (too small and too slow) and leaks from the nitrator which filled the building with explosive vapours of benzene/air.

The explosion took place through the discharge of static electricity.

As a result of the accident it was decided:

(1) to change the design of the stirrer to achieve better efficiency;

(2) to introduce nitrating mixture to the hydrocarbon,
(3) in both systems of adding acid to the hydrocarbon or vice versa it is advisable to introduce the acid and hydrocarbon respectively well below (0.5–1.0 m) the surface of the liquid in the nitrator. In this way, the hydrocarbon will be nitrated below the surface and its vapour pressure over the surface will be diminished.
(4) If acid is added to hydrocarbon a neutral gas (e.g. nitrogen) should be introduced into the nitrator to give a non-inflammable mixture over the surface of the liquid.

In another factory which used the same kind of nitrating system as in Krümmel, a major accident occurred in 1952. The whole building was destroyed together with several nitrators used solely for the nitration of DNT to TNT. Altogether *ca.* 80 tons of DNT/TNT exploded. The nitrators were at different stages of the process, in some of them the nitration proceeded at 95°C, in others with the stirrer stationary separation of the nitro compounds from the acid occurred. The accident began when a fire started in one of the nitrators where the separation of *ca.* 5 tons of TNT was in progress. The operators tried to quench the fire with a carbon dioxide fire extinguisher. This was unsuccessful and the whole team left the building. A fire-brigade arrived and at that moment the detonation occurred, 6 min after the fire started. A detailed examination of the cause of the fire and the detonation and an examination of analogous nitrators in other buildings lead to the conclusion that the fire was caused by drops of paraffin oil, which was used as a lubricant to impregnate asbestos washers tightening the axis of the stirrer. Laboratory experiments have shown that at a temperature of 95°C the vapours of nitric acid, containing of course nitrogen dioxide, can readily ignite paraffin oil present in a suspended string of asbestos. Burning gave a temperature of over 260°C which was sufficiently high to bring molten TNT (temperature 95°C) to an explosive decomposition.

A few laboratory experiments have shown that fire in the nitrator separator can be extinguished by resuming the work of the stirrer. This is due to a considerable amount of mixed acid which can act as a cooling and extinguishing liquid.

In a few instances disastrous effects have been produced by foreign bodies entering the nitrator or spent acid of trinitration. Such was the case of a rubber glove which had fallen into spent acid (Vol. I, p. 391) or rubber tubing which entered the nitrator (Radford, 1974) according to [76].

In a factory a small explosion occurred when turning a stop-cock of the apparatus for sulphitation of molten TNT. It was found that deposits of picric acid or trinitrocresols and metal picrates (or trinitrocresates) were present in similar stop-cocks. An instruction was given that careful periodic cleaning of stop-cocks should be implemented.

The danger of keeping molten TNT at a high temperature has already been

1700 kg of the
It was estimated that the temperature
150° or even 165°C. The melting tank was only used for remelting TNT
Cardboard fibres were present in the molten TNT because of the dumping of
faulty cartridges into the melt, and contaminants were able to accumulate in
the tank. A similar accident with molten TNT occurred earlier (1940) at Bofors
[76]. Molten TNT was contaminated with cardboard from cartridges of TNT.
The cardboard was impregnated with linseed oil which floated on the surface
of the melt. In the presence of air the oxidation of linseed oil could readily
occur.

The last two accidents show the danger of contaminants on the behaviour of
molten TNT.

The contamination of TNT with various organic substances such as lubricat-
ing oil, linseed oil, asphalt and varnishes lower its ignition temperature [78].

Also contamination of TNT with metals and their oxides can increase the
danger of heating TNT (Vol. I, p. 392). It should be borne in mind that TNT
is an acid which forms salts with metals, very sensitive to impact, friction and
high temperature (Vol. I, p. 364). A patent [79] claims a practical use for TNT
salts of Na, K, Cu (II), Ag (I), Ba, Pb (II), Fe (III), Al for delay compositions.
Unwanted contamination of TNT with metals may lead to danger.

Although the nitration of aromatic compounds should be regarded as a rela-
tively safe operation some unexpected decompositions and even explosions can
occur due to some particular functional groups in the nitrated compounds. It is
of course known that nitration of phenols by a direct reaction (Vol. I, p. 480)
can bring about decomposition through oxidation. The same applies to *o*- and *p*-
xylene (Vol. I, p. 395). Relatively recently attention was drawn to the danger of
nitrating such an apparently 'harmless' compound as phthalic anhydride. The nitra-
tion to 3-nitrophthalic anhydride on a laboratory scale becomes very violent,
after two hours with very little warning, the entire contents of the reactor were
ejected [80]. This fact was rationalized in terms of the formation of phthaloyl
nitrate, di-nitrate and nitrite derivatives [81] unstable substances which
readily explode.

Häuptli [128] carried out extensive experiments on the influence of various
'foreign' substances on the decomposition temperature of TNT. Here are some
of his results while adding 10% of a foreign substance:

	297°C
pure TNT	257°C
with cork	275°C
dry 'red lead'	192°C
fresh red lead	220°C
linseed oil	259°C
asphalt	

graphite	289°C
paraffin oil	260°C
mineral oil (lubricant)	249°C

L. C. Smith [129] pointed out that molten TNT can catch fire when mixed with activated charcoal (Norit). The mixture TNT (Norit 50) 50 begins to decompose at 110°C and at 174°C can produce an explosion.

Environmental Problems of TNT Manufacture (Vol. I, pp. 161, 389)

Two environmental problems are connected with TNT manufacture:

(1) poisoning of the atmosphere with tetranitromethane (TNT);
(2) the disposal of organic products formed during the sellite process.

The material balance shows that 0.4 ton of TNM and 4 tons of isomeric by-products are formed for 100 tons of TNT [98].

With regard to the recovery and use of TNM, its conversion into nitroform was suggested in the U.S.A. [98]. The known method of acting on TNM with aqueous alkali and hydrogen peroxide was recommended (Chapter VIII). Although the demand for nitroform exists and the method was economically justified, the application of the method was discarded as the quantity of nitroform obtainable was insufficient for potential requirements, and the requirement of the Environmental Protection Agency (EPA) can be satisfied by the destruction of TNM with sellite so that the substance will not be vented into the atmosphere.

With regard to solutions from the sellite process ('red waters') the problem of recovery of nitro compounds from the solution has already been discussed (p. 173). None of the suggested methods have received practical application and it appears that the best method of dealing with sellite wastes is evaporation to dryness and burning the residue as in Bofors-Chematur method [72].

Also the purification of TNT by crystallization from the acids (see also Vol. I, p. 378) should be considered. It offers the advantage that acids used for crystallization are recycled and enter the production process. However, the impurities present in the acid after crystallization are introduced into the nitrator which is a drawback of the method.

OTHER NITROAROMATICS

Nitro Derivatives of Hydrocarbons

In recent years very little attention has been given to nitro derivatives of higher homologues of benzene. Some of the homologues (e.g. xylenes) have become important starting substances in the production of valuable intermediates.

The only paper of any significance on the homologues of TNT was given by Desseigne [119]. It referred to 2,4,6-trinitroethylbenzene (Vol. I, p. 414) which was obtained by a three-stage nitration of ethylbenzene. The yield was 77.7% and the setting point of the product 37°C.

Nitro Derivatives of Halogenohydrocarbons

Some halogenonitrohydrocarbons recently achieved importance as intermediates in the formation of important explosives. Such are: 1,3-dichloro- and 1,3,5-trichloro-2,4,6-trinitrobenzene which can serve to obtain high melting explosives: DATB and TATB (Chapter VII).

1,3-Dichlorobenzene can be commercially obtained by chlorination of *m*-dinitrobenzene (Vol. I, p. 193) and nitrated to the trinitroproduct which can be converted to DATB. A description of the industrial method of making 1,3,5-trichloro-3,4,6-trinitrobenzene was given in Vol. I, p. 469.

Nitrophenols (Vol. I, p. 492)

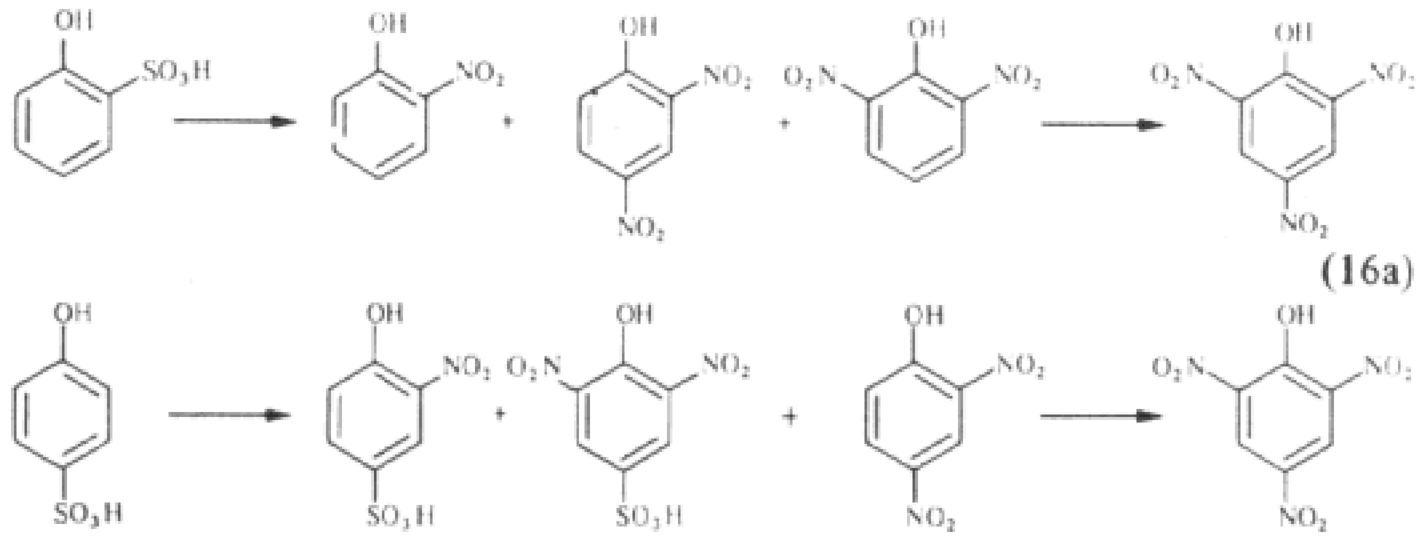
Relatively little attention is paid to high nitrated phenols as explosives, but some of them (e.g. styphnic acid) became important because of the initiating properties of their salts.

Picric Acid

Picric acid remains the best known highly nitrated phenol.

Some characteristics can be found in the monograph by Meyer [1] and attention was paid to chemical properties of picric acid and its substituted derivatives. Thus Pearce and Simkins [86] determined pK_a values (by calculation and experiment) of alkyl homologues of picric acid and its methoxy or halogen derivatives. The pK_a values fit well with data predicted from the Hammett relation. Styphnic acid however shows a deviation.

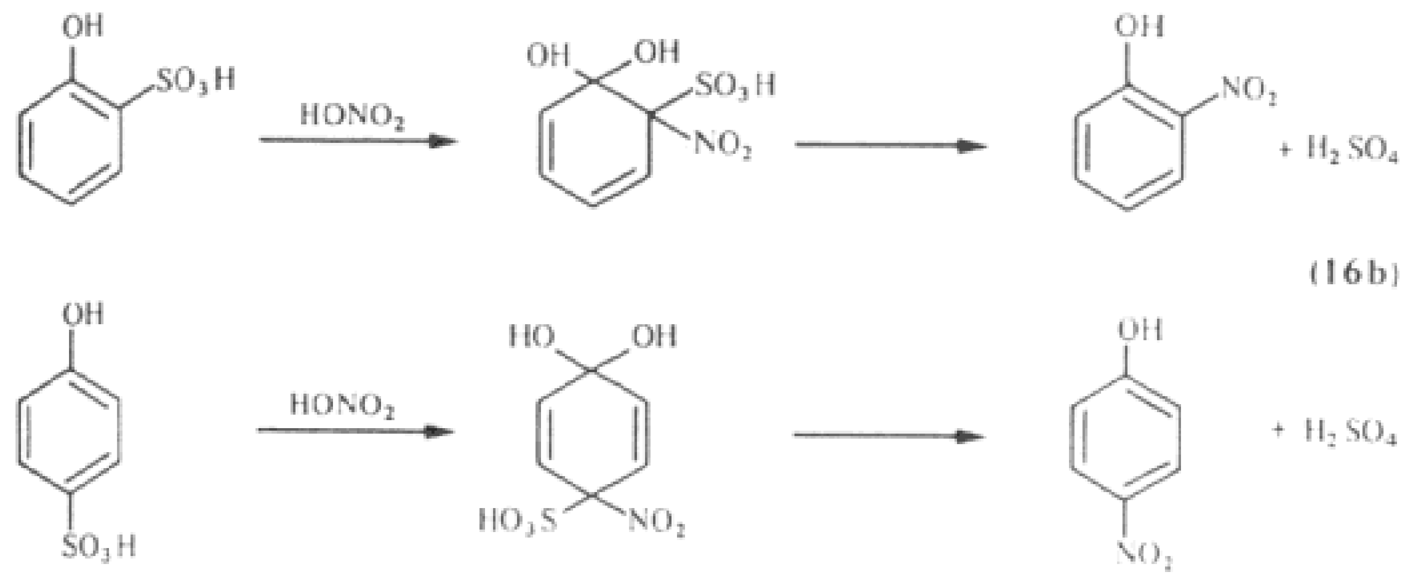
The mechanism of the substitution of sulphonic groups in phenol by nitro groups was extensively studied by Leśniak and T. Urbański [130] and to this purpose the chromato-polarographic method introduced by Kemula and associates [131] was used. The trend of the nitration of *o*- and *p*-phenolsulphonic acids with nitric acid can be depicted by diagram (16a):



(16a)

Thus the diagram on p. 501, Vol. I remains valid particularly as regards the nitration of *p*-phenolsulphonic acid.

The mechanism of the attack of nitric acid upon phenolsulphonic acids was rationalized by T. Urbański and Leśniak as passing through the addition stages forming transient yellow coloured quinoid structures (16b):



(16b)

Salts of Picric Acid

Salts of picric acid are important for two reasons:

(1) for their sensitivity to impact and friction which can be dangerous but can also be of practical importance in initiators and pyrotechnic compositions,

(2) they do not possess the undesirable property of picric acid, which is its acidity.

The salt in practical use is ammonium picrate. Its properties were described in Vol. I, p. 528. During World War II and explosive 'Picratol' composed of 52% ammonium picrate and 48% TNT was in use by the U.S. Army.

2,4-Dinitroresorcinol (Vol. I, p. 536)

A semi-industrial method of making 2,4-dinitroresorcinol was given by Ficheroulle and Soule [133]. It consists of two stages:

(1) Nitrosation

(2) Oxidation.

Nitrosation. The reactor was filled with 280 l. water and 6240 l. sulphuric acid (65.5 Be). 11,200 kg resorcinol were introduced and 100 kg of ice. A solution of 15 kg of sodium nitrite dissolved in 28 l. of water was added. Yellow coloured dinitroso compound was precipitated and immediately the solution was added to 480 g sodium sulphate in 2 l. of water. The precipitate was isolated by filtration, washed with cold water to neutrality (*ca.* 20 l.), finally it was dried and sieved with ethanol (2 l.).

The yield was 16 kg, i.e. 93.5%.

Oxidation. The reactor was filled with 45 l. of toluene and 10 kg of dinitrosoresorcinol. It was cooled to −5°C and over 8 hours 15 l. of nitric acid (d 1.35) diluted with 15 l. water were added. The product was filtered and washed three times with 30 l. water.

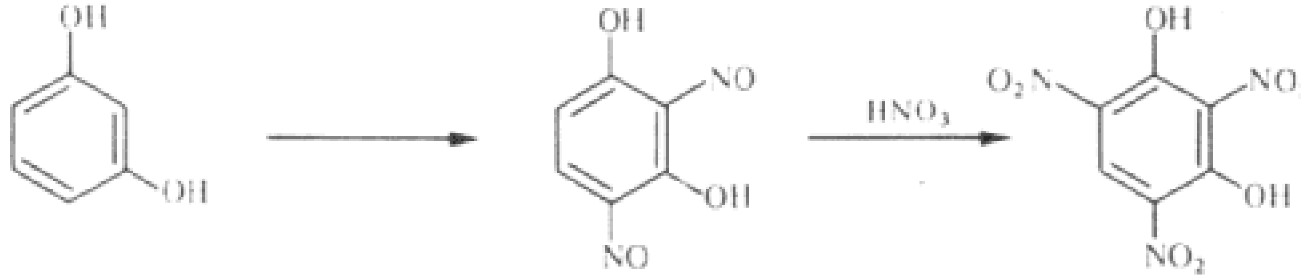
Purification

The dry dinitro compound was dissolved in 80 l. ether, the solution was filtered and ether distilled off. The product was dissolved by boiling with 140 l. water, then cooled and collected on a filter.

From 11,200 kg resorcinol 6500 kg dinitro product was obtained, i.e. the yield was 54–55%.

Styphnic Acid (Vol. I, p. 538)

Two papers [87, 88] have described a novel method of making styphnic acid. Both consist of two steps: (1) nitrosation of resorcinol to dinitroso derivative, (2) oxidation and nitration of the dinitroso compound (17):



(17)

The second step of the reaction can be carried out with nitric acid (d 1.40) at room temperature.

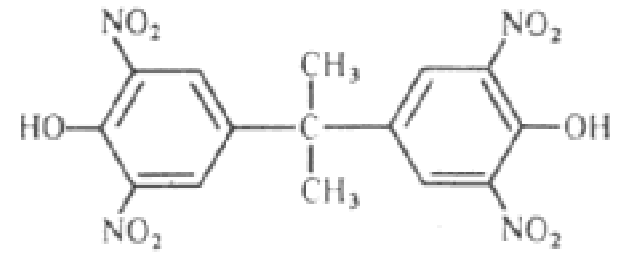
The advantage of this method as compared with the usual one of sulphonation and nitration is that in the usual method excessive foaming occurs.

The disadvantage of the new method is the fact that the dinitroso compound precipitates as a very fine powder, which is difficult to separate by filtration.

The properties of salts of styphnic acid will be given in the chapter dedicated to initiating explosives.

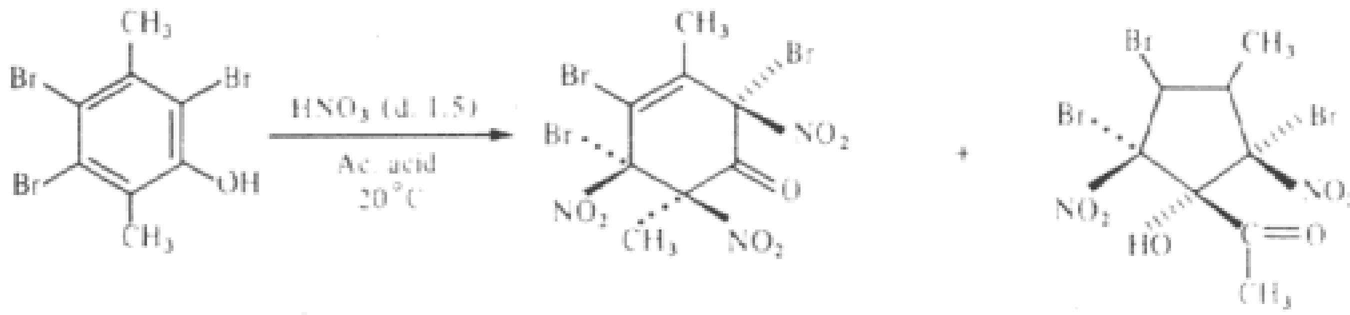
Tetranitrodian

2,6,2′,6′-Tetranitrodian was obtained by Szeky [89]. Its salts can be used as potential ingredients of pyrotechnic compositions.



IX m.p. 230-232°C

Nitro derivatives of a tribromophenol homologue. Zincke and Breitweiser [116] have found that dinitration of a tribromophenol homologue in the presence of acetic acid yielded two isomeric products. It was recently established (due to modern methods) [117] that nitration can also produce an interesting acyloin rearrangement leading to a five-member ring compound according to scheme (18):

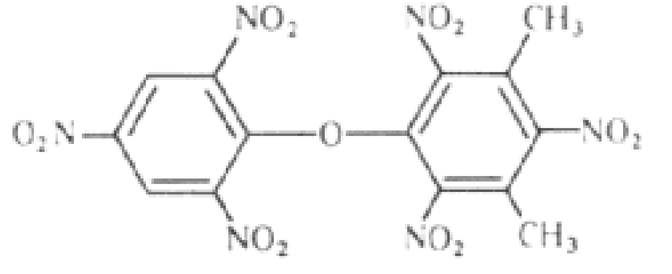


(18)

Picric Acid Ethers

Nitroanisols. Nitration of anisol to *o*- and *p*-nitroanisol was studied by Schofield and co-workers [90]. Mononitration in 54–82% sulphuric acid at 25°C gave the ratio o/p = 1.8–0.7.

Nitro derivatives of diphenyl ether (Vol. I, p. 549). Adamska and Okoń [91] prepared a number of methyl derivatives of penta- and hexadiphenyl ether, for example, 3,5-dimethyl-2,2′,4,4′,6,6′-hexanitrodiphenyl ether.



X m.p. 154-156°C

Nitro derivatives of aniline (Vol. I, p. 556). With the exception of hexanitrodiphenylamine nitro derivatives of aniline are not in use as explosives. Some of them are intermediates of reactions leading to highly nitrated compounds by oxidation $NH_2 \longrightarrow NO_2$ according to the method of Nielsen, Coon *et al*. [10, 16]. See also [38].

Hexanitrodiphenylamine (Hexyl) (Vol. I, p. 562)

The data on explosive properties are also collected in the monograph by Meyer [1]. Some relatively new interest was created by salts of hexyl. They possess properties similar to those of picric acid: they burn readily and some of them show initiating properties.

Due to a very low solubility of its potassium salt, hexyl is used as a reagent for potassium. Also a suggestion was made for using hexyl to extract potassium from sea water [92]. The precipitated potassium salt treated with nitric acid yielded potassium nitrate which on evaporation crystallized out.

A considerable number of papers appeared by J. Hirst and co-workers [111] on the reactions of picryl chloride with substituted anilines. They studied the kinetics of the reaction and the influence of the substituents in aniline on Arrhenius parameters and rate constants.

Among other kinetic studies of picryl chloride and 1-chloro-2,4-dinitrobenzene with bases the works should be mentioned of Parker and Read [112] and Zollinger and co-workers [113] which have shown a much higher reactivity of picryl chloride. The reactions are greatly influenced by solvent and in some instances 1-chloro-2,4-dinitrobenzene is more reactive than picryl chloride [114].

The reactions belong to addition–elimination reactions AE–S_N Ar [115].

Picramic Acid (Vol. I, p. 571)

A detailed description was given [93] for making picramic acid from picric acid and sodium hydrogen sulphide at 50–55°C with a yield of 88–90%.

Other Aromatic Nitro Compounds with Amino Groups

Some other aromatic nitro compounds such as DATB, TATB and DIPAM are of great practical importance and are described in Chapter VII (Heat Resistant Explosives).

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APPENDIX I

DERIVATIVES OF HALOGENO-BENZENE

The nitro derivatives of chlorobenzene were described in Vol. I, pp. 450–471.

More recently nitro derivatives of fluorobenzene have received some attention. Olah, Kuhn and Flood [1] described the nitration of halogeno derivatives of benzene with $NO_2^+ BF_4^-$ (Made of N_2O_5, HF and BF_3) in tetramethylenesulphone as a solvent at 25°C and established different reactivities as compared with benzene (Table AI):

TABLE AI

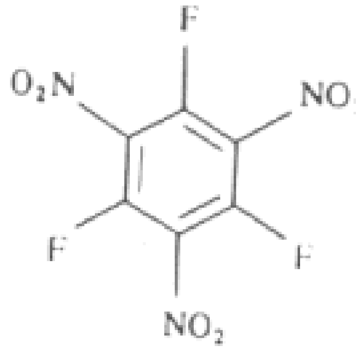
	Relative reactivity	Products %		
		o-	*m-*	*p*
Benzene	1.0			
Fluorobenzene	0.45	8.5	–	91.5
Chlorobenzene	0.14	22.1	0.7	76.6
Bromobenzene	0.12	25.7	1.1	73.2
Iodobenzene	0.28	36.3	–	63.7

Also Kuhn and Olah [2] nitrated 2,4-dinitrofluorobenzene with $NO_2^+ HSO_4^-$ in 100% sulphuric acid at 120°C for 12 hours and obtained picryl fluoride with the yield of 40%.

Fluorine in nitro derivatives of benzene shows a greater reactivity than chlorine in nucleophilic reactions [3]. In view of this attention was paid to 1,3,5-trifluorotrinitrobenzene and its reaction with nucleophiles [3].

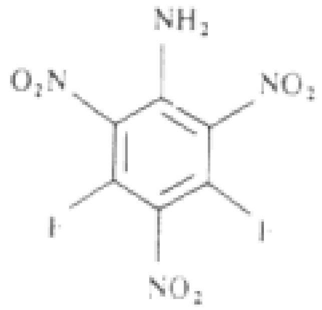
1,3,5-Trifluorotrinitrobenzene

An improved preparation was recently described [4]. High reactivity of fluorine excludes the displacement of nitro groups which was a side-reaction of analogous chloro- and bromo-nitro compounds.



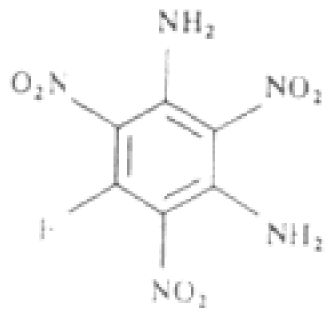
m.p. 80 – 82°C

By reacting 1,3,5-trifluorotrinitrobenzene with gaseous ammonia at −73°C the following compounds were obtained (I–III) by Adolph and co-workers [3]:



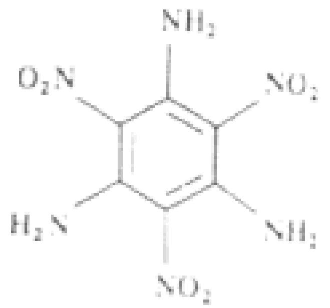
117 – 118.5°C

I



m.p. 222 – 223°C

II

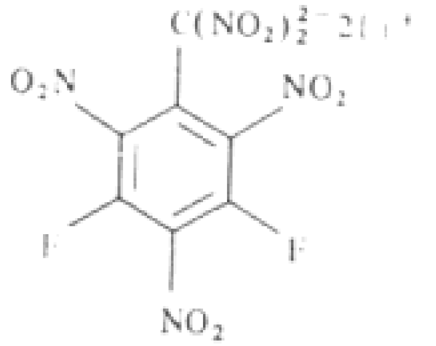


decomp

III

The yields of I, II and III were 42, 12 and 18% respectively.

Trifluorotrinitrobenzene reacted violently with hydrazine. Interesting was the reaction with lithium salt of dinitromethane resulting in formation of IV:



IV

A similar reaction with picryl chloride was described by Eremenko and co-workers [5].

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APPENDIX 2

ANALYSIS OF NITRATING ACIDS

Although analytical problems are outside the scope of the present book, it is advisable to mention the methods of rapid control of nitration. A considerable attention was recently paid to methods of acids analysis.

A brief description and references are given below. The novel methods are:

(1) Injection thermometry of Oehme and Ertl [1],
(2) Automation control of nitration by Belyaev, Kapustina and Peshekhonov [2],
(3) Redox titration of nitric acid in mixed acid [3] (see also Chapter 11).
(4) "In-line" analyser of nitric acid by:
  (a) refractometry
  (b) coulomb-polarography [4]
(5) High-frequency conductometric titration of mixed acid [5]
(6) Polarographic determination of nitric acid [6]
(7) By adding substances which can readily be nitrated by spent acid and the products of nitration can be quickly determined spectroscopically. One of the methods consists in adding salicylic acid which furnished two isomeric nitro compounds: 3- and 5-nitrosalicylic acid [7]. Their yield was determined by UV spectroscopy.

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4. K. Y. GALLAGHER and C. M. JOHNSON, *Sci. Techn. Aerosp. Rep.* 19 (1981).
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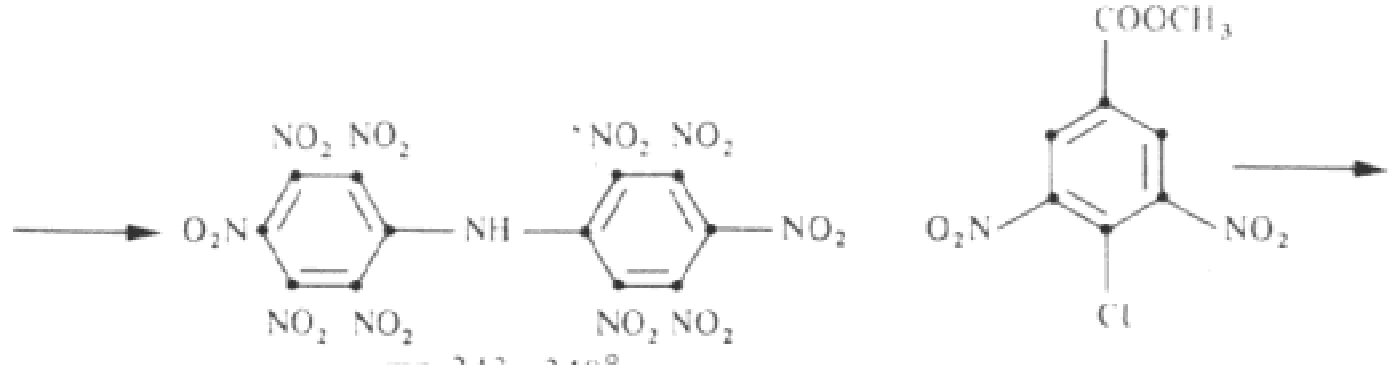
APPENDIX 3

Nielsen and co-workers described recently [1] the preparation of decanitrobiphenyl through a sequence of reactions starting from methyl ester of 4-chloro-3,5-dinitrobenzoic acid:



mp. 243 – 248°

REFERENCE

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CHAPTER 7

HEAT RESISTANT EXPLOSIVES

The last two decades have brought a new line of research in explosives. This is the work on heat resistant explosives.

There was an immense need in industry for an explosive composition which would be safe, reliable and stable at elevated temperatures. For example, it is sometimes necessary to shoot explosive devices in hot wells at temperatures which may reach as high as 200°–300°C. In the steel industry, open hearth furnaces are tapped with explosive shaped charges in tap holes at temperatures above 500°C. Using the explosives available at present, which have the best possible thermal properties, it is necessary to jacket the shaped charges with heavy insulation. Even so, the charge must be initiated within 3–4 min from the time it is set in place or it may fail due to thermal stability. There is also a growing demand in connection with space programmes for explosive compounds which are stable at elevated temperatures and low pressures. The explosive stores carried externally on high speed aircraft at low altitudes are subjected to aerodynamic heating, which may raise the temperature of the filling above 80°C, so that the Torpexes (RDX/TNT/Al) and other conventional explosives are unsuitable for such stores.

Explosives with improved high temperature properties, usually called 'Heat Resistant Explosives' have emerged to meet such requirements. Nitro compounds have been found to be very useful heat resistant explosives. These compounds have received special attention and were reviewed by Dunstan [1], T. Urbański and Vasudeva [2]. They were of special interest [3–7] because of their ability to withstand the high temperatures and low pressures encountered in space applications. No doubt, the manufacture of these explosives is likely to be on kilogram rather than tonne scale, but the application is highly critical. Sometimes, even complex synthetic routes can be adopted, provided the product exhibits the requisite properties, a low vapour pressure and the ability to function satisfactorily after appropriate environmental trials, which may include heating at temperatures as high as 250°C. A few explosives that have these properties are listed in Table 1.

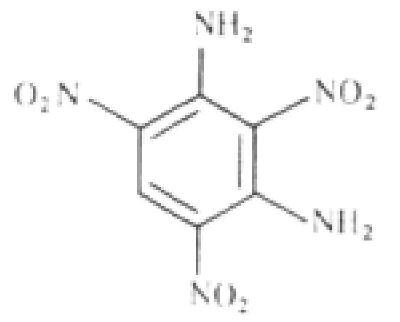
Bicyclic nitroaromatics, hexanitrostilbene (HNS) and diaminohexanitrodiphenyl (DIPAM) are in use for achieving stage separation in space rockets and for seismic experiments on the moon [7]. Single aromatic ring compounds, such as *m*-diaminotrinitrobenzene (TATB) have also been found to be of practical value in various space applications.

There has been speculation about the relationship between the exceptional thermal stability of these compounds and their molecular structure. Thermal decomposition studies show that the stability is associated with high melting point and low vapour pressure and there is evidence that the rates of decomposition are enhanced when substances are in liquid or vapour phase; they reach a higher energy level when molten or vapourized [8].

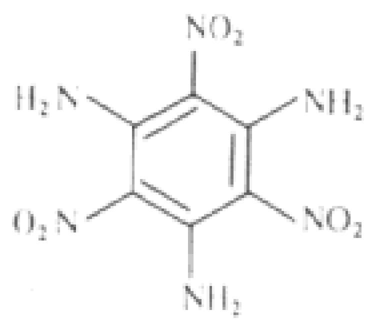
Solid state physical structure appears to be as significant as chemical constitution in determining the stability of explosives, but apart from crystal structure determination on lower molecular weight compounds, such as diaminotrinitrobenzene [9] there is little information available on the magnitude of molecular interactions or crystal lattice effects in these remarkable explosives.

NITRO DERIVATIVES OF BENZENE

1,3-Diamino-2,4,6-trinitrobenzene (DATB) (I) and 1,3,5-trinitro-2,4,6-triaminobenzene (TATB) (II) have qualified as heat resistant explosives among the various nitro derivatives of benzene.

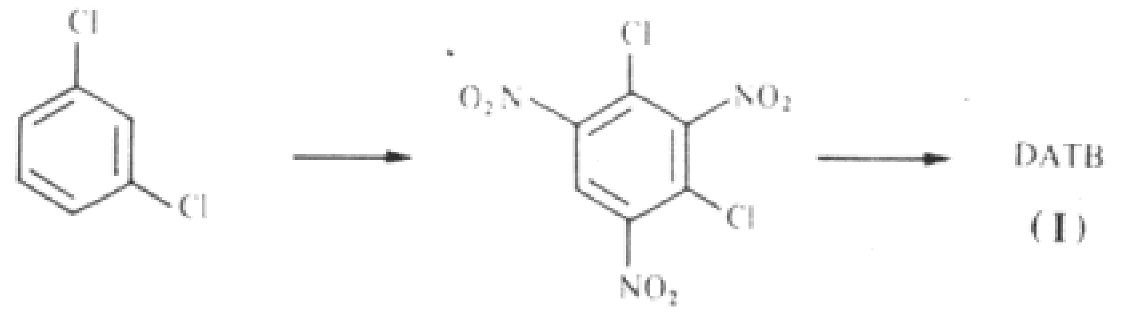


I



II

Several complicated procedures for the syntheses of diaminotrinitro benzene (DATB) have been reported. In one of these, the synthesis is accomplished [10–12] by vigorously nitrating *m*-dichlorobenzene at elevated temperatures. 1,3-Dichloro-2,4,6-trinitrobenzene thus obtained is aminated in methanol to yield DATB [13]. The yield has not been reported.

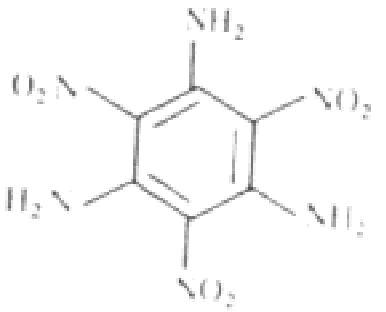


(1)

The second approach comprises the preparation of dipyridinium styphnate from styphnic acid in 94% yield. 1,3-Dichloro-2,4,6-trinitrobenzene can be obtained in 98% yield by allowing phosphorous trichloride and dipyridinium styphnate to react directly at steam-bath temperature. DATB was obtained by the amination reaction (mentioned above) in 97% yield. The overall yield of DATB (I) is considerably better than that obtainable by the existing procedures.

DATB is a lemon-yellow coloured crystalline substance. It is fairly stable when close to its melting point (286°C) decomposing at a rate of less than 1% per hour at 260°C, but it is transformed into crystal form of lower density at 216°C, which temperature, therefore, represents the limit of its utility. The use of DATB in highly explosive compositions has been described in several patents [14, 15].

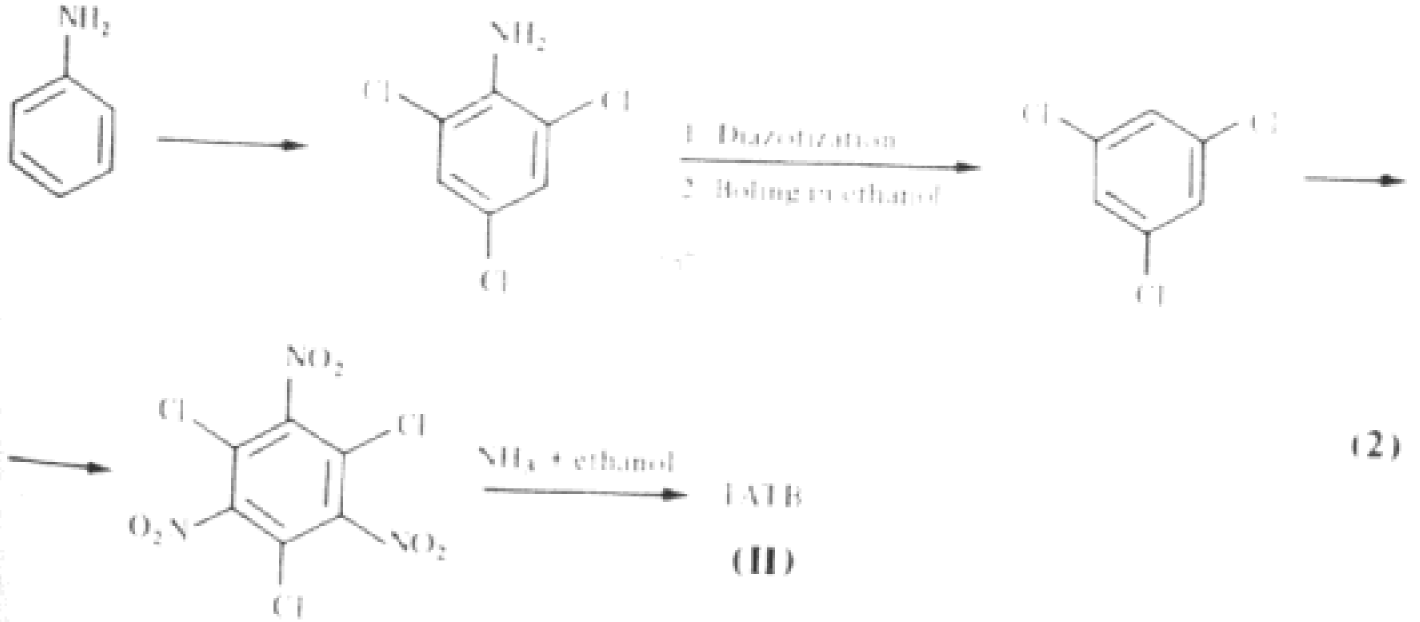
DATB forms charge–transfer complexes with aromatic hydrocarbons, aromatic amines, quinoline and iso-quinoline [37].



TATB

II

1,3,5-Trinitro-2,4,6-triaminobenzene (TATB) (II) was obtained in 1887 by Jackson and Wing [16] by the route shown in (2) which was substantiated later [16a].



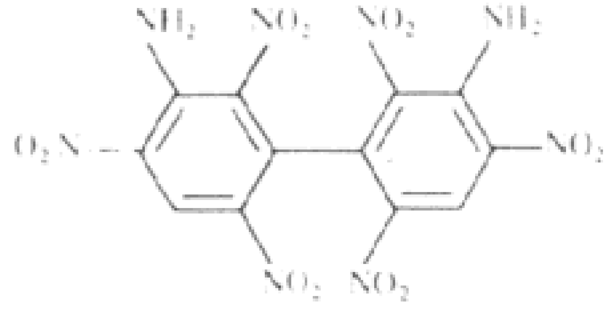
(2)

This is a yellow-brown coloured substance decomposing rapidly just below the m.p. (350°C) but it has excellent thermal stability in the range 260–290°C, which represents the upper temperature limit at which it may be used. The molecular structure of TATB was examined by X-ray analysis [44]. TATB possesses also a low sensitivity. However, the compressed or plastic bonded material tends to expand considerably. Subsequently Kolb and Rizzo [45] examined anisotropic thermal expansion between 214 and 377 K by X-ray analysis and found that the unit cell of TATB is formed by the planar sheets of the molecules whereas an amino group interacts with an *ortho* nitro group of the same benzene ring and with a nearest neighbour molecule. The sheets of TATB are bonded by strong intra- and intermolecular hydrogen bonds. A thermal volume change of 5.1% was found. Expansion was almost exclusively a function of a 4% increase in the axis perpendicular to the sheets of the molecules. The volume coefficient of thermal expansion for crystalline TATB was found to be $30.4 \times 10^{-5}\ K^{-1}$.

According to both groups of authors [44, 45] TATB is in triclinic form. Two other forms: another triclinic and monoclinic should be assigned to a polymorphic and impure substance respectively.

According to references in [45] a pilot plant for TATB exists in the U.S.A.

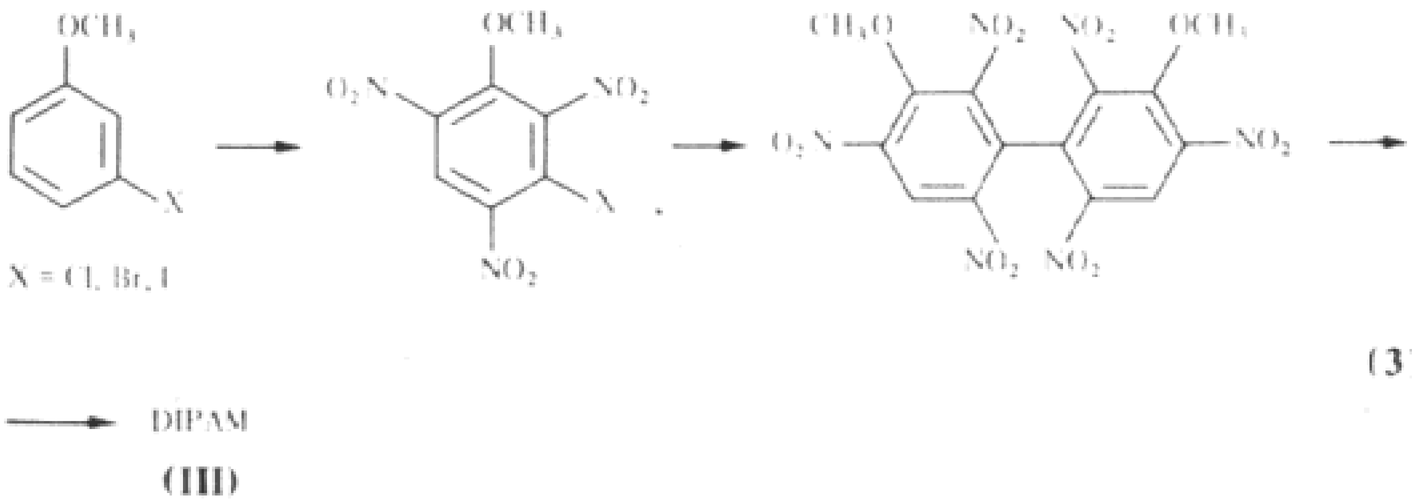
NITRO DERIVATIVES OF DIPHENYL



DIPAM

III

Among the nitro derivatives of diphenyl, 3,3-diamino-2,2′,4,4′,6,6′-hexanitrodiphenyl (DIPAM) (III) has been found to be a thermally stable explosive. Oesterling and co-workers described a method in which the starting material is *m*-haloanisole. The reaction sequence is shown in (3).



(3)

The above method of preparing DIPAM comprises (a) nitration of a *m*-haloanisole with a mixture of nitric acid and oleum to obtain 3-halo-2,4,6-trinitroanisole; (b) condensation of two molecules by reacting with a slurry of copper powder and a diluent to obtain 3,3'-dimethoxy-2,2',4,4',6,6'-hexanitrodiphenyl; and (c) amination to 3,3'-diamino-2,2',4,4'6,6'-hexanitrodiphenyl (III) by introducing ammonia into a solution of hexanitro compound in a diluent which may be methanol, tetrahydrofuran or xylene–methanol–tetrahydrofuran mixture.

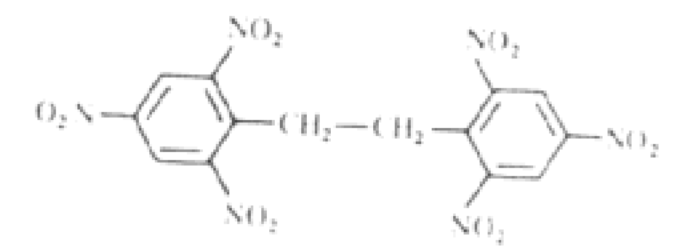
In addition to the ability of this explosive to withstand high temperatures, it is extremely insensitive to electrostatic discharge, requiring more than 32,000 J for initiation.

NITRO DERIVATIVES OF BIBENZYL AND STILBENE

Nitro derivatives of bibenzyl and stilbene are of considerable importance for two reasons: (i) some of them are produced by the nitration of toluene in the course of production of trinitrotoluene (TNT) as a result of the oxidation of CH_3 group; and (ii) some of them show very high melting points and can be regarded as classical examples of explosives resisting high temperatures.

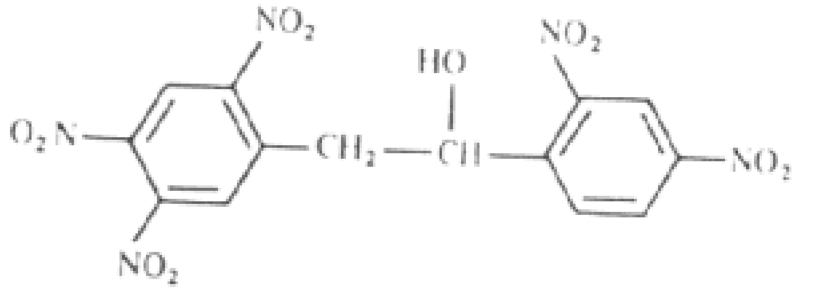
Nitro Derivatives of Bibenzyl

2,2',4,4',6,6'-Hexanitrobibenzyl (IV)



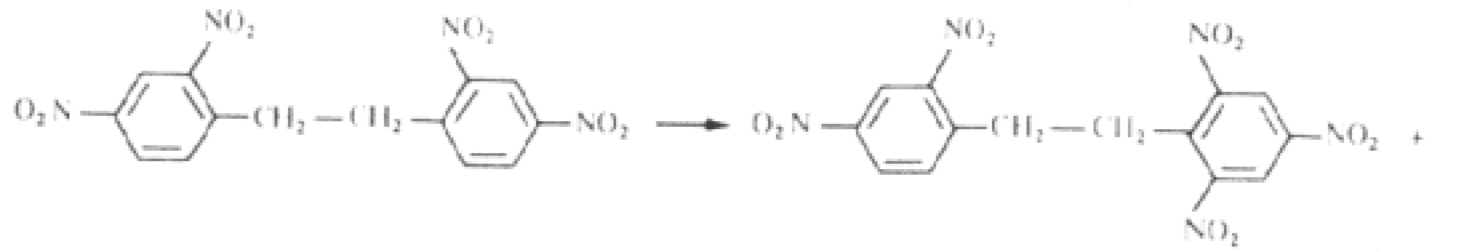
IV

This compound was obtained by Will [17] by nitrating 4,4'-dinitrobibenzyl. He also claimed to have obtained it by the alkaline oxidation of TNT. A substance of the same melting point was obtained by Rinkenbach and Aaronson [18] as a by-product of the nitration of 2,2',4,4'-tetranitrobibenzyl by fuming sulphuric acid and fuming nitric acid at 85°C for a few days. The main product of nitration was claimed to be pentanitrodiphenyl ethanol: α-2,4,5-trinitrophenyl-β-2',4'-dinitrophenyl hydroxyethane (m.p. 187°C) (V).



V

Blatt and Rytina [19] re-examined the findings of earlier workers. They nitrated bibenzyl and 4,4'-dinitrobibenzyl using 100% nitric acid and obtained 2,2',4,4'-tetranitrobibenzyl (m.p. 171–172°C) with 90% yield of the crude product. The product could not be nitrated further unless it was subjected to vigorous nitration conditions, that is heating it with nitrating mixture composed of nitric acid (90% HNO_3) sulphuric acid (95% H_2SO_4) and oleum (15% SO_3) in a steam-bath for 7 hr, resulting in the formation of 2,2',4,4',6-pentanitrobibenzyl (m.p. 187–188°C) (VI) and a relatively small amount (*ca.* 10%) of hexanitrobibenzyl (IV), (4):



VI (4)

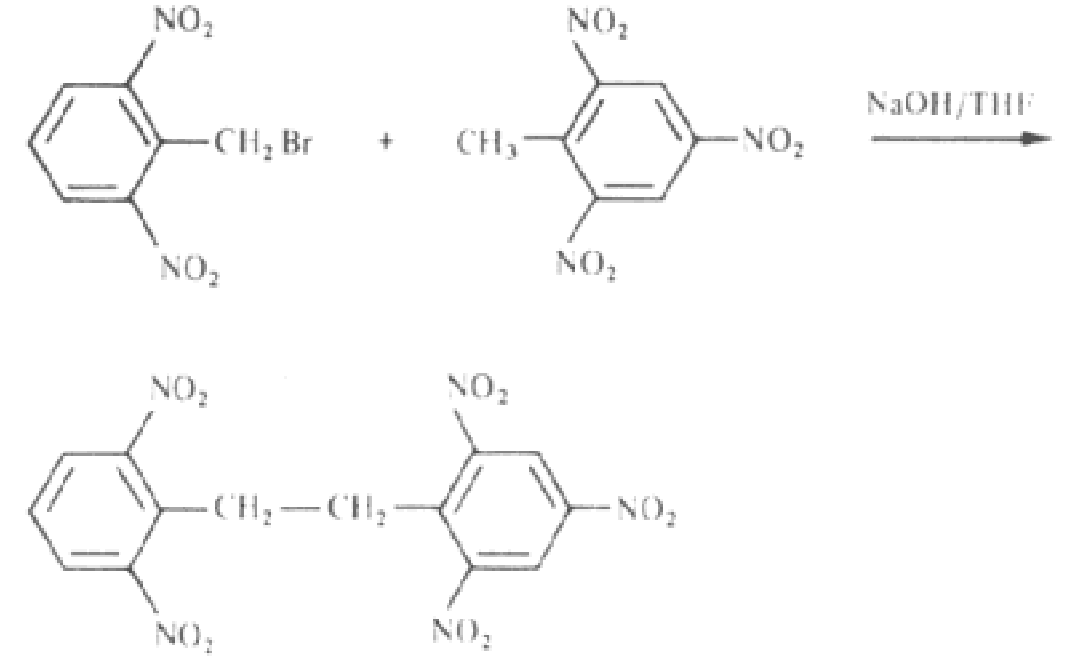
Nitration of pentanitrobibenzyl with the same nitrating mixture for 16 hr yielded 30% of hexanitrobibenzyl and unchanged pentanitrobibenzyl. Compound IV when crystallized from acetic acid, had m.p. 213–215°C. Shipp and L. A. Kaplan [20] nitrated bibenzyl using potassium nitrate in 30% oleum in the temperature range 60–120°C for 30 hr and obtained the product in 46.5% yield. After crystallization from hot acetone and water, IV melted at 218–220°C.

Neither Blatt and Rytina nor Rinkenbach and Aaronson were able to obtain hexanitrobibenzyl by the alkaline oxidation of 2,4,6-trinitrotoluene. However, this was achieved by Shipp and Kaplan [20] who found that TNT could be oxidized to hexanitrobibenzyl or hexanitrostilbene using sodium hypochlorite as the oxidizing agent. Thus, the observation of Will [17] proved to be correct. This was substantiated by Gilbert [51] who used methanol as a solvent at 50°C and a more concentrated hypochlorite solution, the yield was 82%.

Another process [20] consisted in reacting nitro derivatives of benzyl halogenides with trinitrotoluene in sodium hydroxide. In tetrahydrofuran 2,4,4',6-tetranitrobibenzyl (m.p. 179–180°C) and 2,2',4,6,6'-pentanitrobibenzyl (m.p. 155°C) were obtained (5).

Recently an Hungarian patent appeared [46] which consists in oxidative coupling of two moles of TNT in the presence of base, oxygen and a transition metal catalyst, for example, cobalt naphthenate at 50°C (in the presence of DMSO as a solvent) or cupric sulphate.

The method was examined by Golding and Hayes [47]. They tried to oxidize TNT in air in the presence of various catalysts, for example, anhydrous $CuSO_4$/pyridine in the presence of alcoholic KOH and triglyme. A high yield (55.5%) was obtained. Another high yield (53.4%) was given by Rodium (5% on alumin) in alcoholic KOH and triglyme.



(5)

The authors suggest a mechanism for the formation of the anion RCH_2^- [$R = (NO_2)_3C_6H_4CH_2^-$] which would react with the catalyst yielding a free radical according to (6):

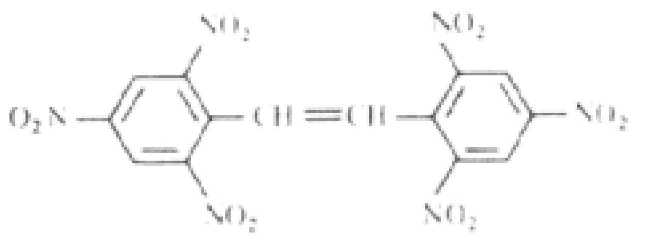
$$
\begin{aligned}
&RCH_3 + OH^- \longrightarrow RCH_2^- + H_2O && \text{(a)}\\
&RCH_2^- + Co(II) \longrightarrow RCH_2^{\cdot} + Co(I) && \text{(b)}\\
&2\,RCH_2^{\cdot} \longrightarrow RCH_2{-}CH_2R && \text{(c)}\\
&Co(I) \xrightarrow{O_2} Co(II) && \text{(d)}
\end{aligned}
\qquad (6)
$$

Oxygen (or air) regenerates divalent cobalt.

Also the radical ion reaction of the type given by Russell (Chapter IV) is possible.

Nitro Derivatives of Stilbene

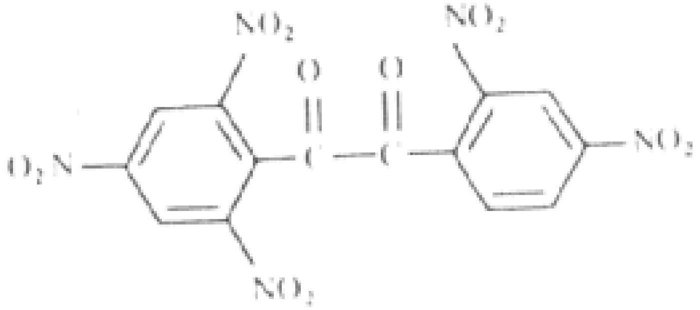
The most important nitro derivative of stilbene is hexanitrostilbene (HNS) (VII)



HNS

VII

The existing description in the older literature is not exact and requires new information. Very likely the product of m.p. 211°C described in Vol. I, p. 416 was not hexanitrostilbene but hexanitrobibenzyl. Also the direct nitration of stilbene does not furnish the required hexanitro derivative, as the double bond is highly vulnerable and oxidation can readily occur to form nitro derivatives of benzil: $C_6H_5CO.COC_6H_5$. Even nitro derivatives of stilbene on vigorous nitration furnish nitrated products of benzil. Thus Challenger and Clapham [21] nitrated 2,4,6-trinitrostilbene with a mixture of nitric acid (d 1.41) and sulphuric acid at 100°C for 2 hr and obtained 2,4,6,2',4'-pentanitrostilbene (m.p. 198°C). When they applied a nitrating mixture composed of anhydrous nitric acid (d 1.5) and sulphuric acid at 100°C they obtained 2,4,6,2',4'-pentanitrobenzil (VIII) (m.p. 260°C). Blatt and Rytina [19] nitrated 2,2',4,4'-tetranitrostilbene by heating it with nitric acid (90% HNO_3), sulphuric acid (95%) and oleum (15% SO_3) in a steam-bath for 7 hr and obtained 2,2',4,4'-tetranitrobenzil (m.p. 222°C).



VIII

A few methods exist to produce nitro derivatives of stilbene. They are:

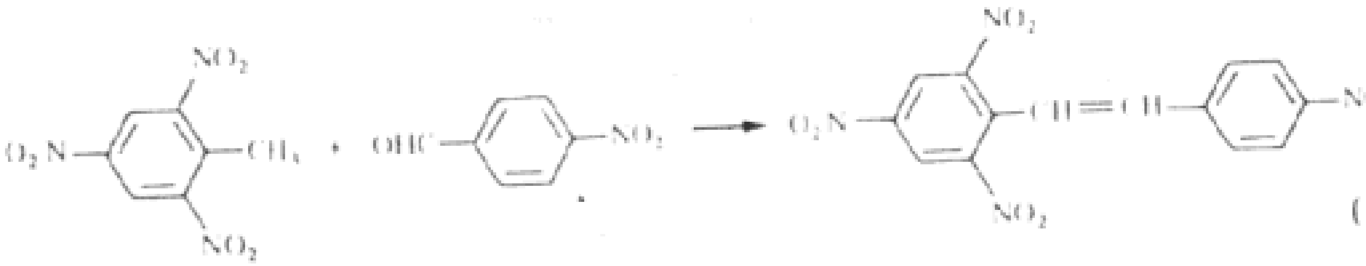
(1) reaction of nitro derivatives of toluene with benzaldehyde,

(2) reaction of nitro derivatives of benzyl halogenides with alkaline agents removing hydrogen halogenide,

(3) oxidation of nitro derivatives of toluene.

1. Reaction of nitro derivatives of toluene with benzaldehyde and its nitro derivatives. This type of reaction was first described by Thiele and Escales [22]. While heating a mixture of 2,4-dinitrotoluene with nitrobenzaldehyde at 160 170°C and allowing the reaction mixture to rest for 2 hr, they obtained all the three possible isomers of 2,4,4'-trinitrostilbene using *o*-, *m*- and *p*-nitrobenzaldehyde.

In a similar way, Ullman and Geschwind [23] obtained 2,4,6,4'-tetranitrostilbene (m.p. 196°C) from trinitrotoluene and *p*-nitrobenzaldehyde.

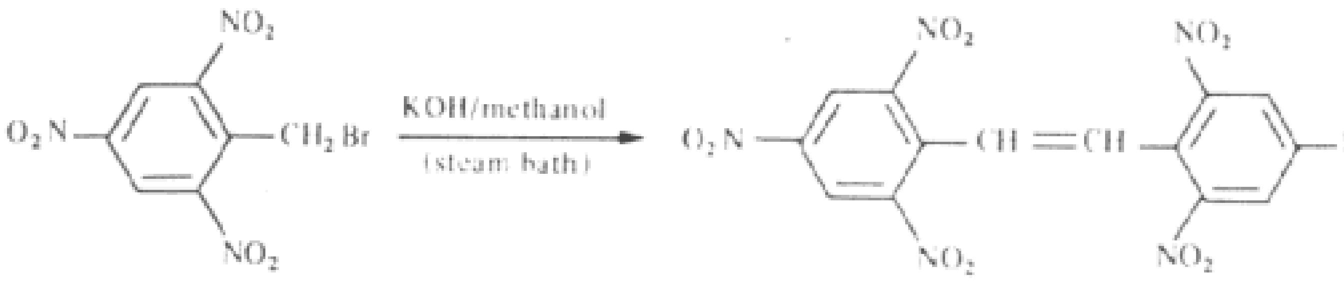


(7)

Shipp [24] tried the same reaction between trinitrotoluene and trinitrobenzaldehyde and obtained hexanitrostilbene in poor yield.

2. Preparation from nitrobenzyl halogenides. This method consists in reacting nitrobenzyl halogenides with alcoholic potassium hydroxide. The reaction was described for the first time by Krassusky [25] who obtained 2,4,2',4'-tetranitrobenzyl (m.p. 266–267°C) by warming 2,4-dinitrobenzyl chloride with potassium hydroxide in ethanol. The reaction did not seem to be successful when 2,4,6-trinitrobenzyl bromide was used as the starting material contrary to the finding of Reich and co-workers (Vol. I, p. 416).

Shipp [24] obtained 2,2',4,4',6,6'-hexanitrostilbene (HNS) in 30% yield by reacting 2,4,6-trinitrobenzyl halogenide with alcoholic potassium hydroxide (8). The product melted at 316°C,



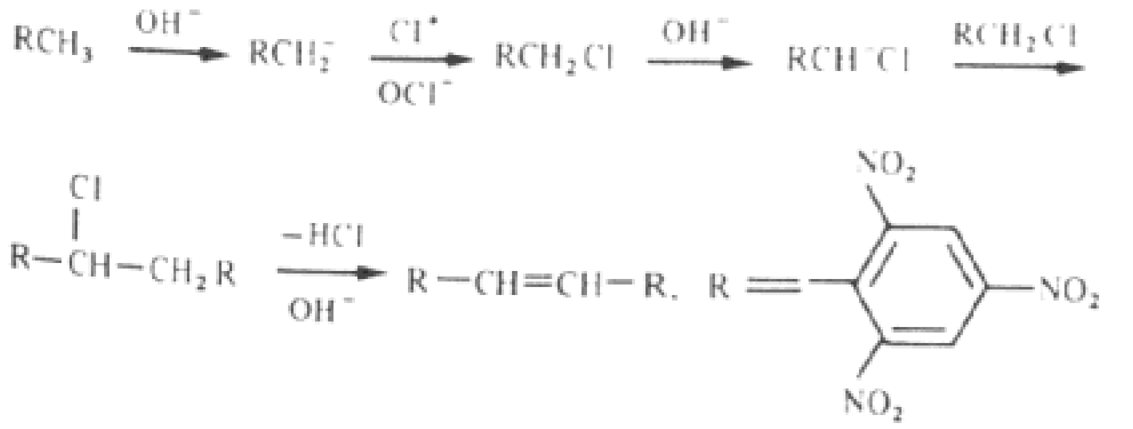
(8)

VII

that is, 105°C above the melting point of the product obtained by Reich. The correct structure of the compound follows from the synthetic route given by Shipp [24].

3. Preparation by oxidation of nitro derivatives of toluene. A number of methods involving this approach have been developed. They can lead to derivatives of both bibenzyl and stilbene. Thus, Green and co-workers [26] obtained 4,4-dinitrobenzyl (m.p. 180–182°C) by oxidizing *p*-nitrotoluene with air in potassium hydroxide solution in methanol at room temperature. When the reaction mixture was warmed 4,4-dinitrostilbene resulted. Green and Baddiley [27] reacted 2,4-dinitrotoluene with diiodine in the presence of pyridine in potassium hydroxide solution in methanol at 40–50°C and obtained 2,2',4,4'-tetranitrostilbene (m.p. 266–267°C).

Shipp and Kaplan [20] obtained 2,2',4,4',6,6'-hexanitrostilbene (HNS) by oxidizing TNT with sodium hydrochlorite. The method consists in adding 10 parts of 5% sodium hypochlorite solution to a chilled solution of 1 part of TNT in 10 parts of methanol. The solution is allowed to stand at ambient temperature until HNS precipitates as a fine crystalline product. The product is crystallized from nitrobenzene to yield pale yellow coloured needles. The mechanism of the reaction is shown in reactions (9).



(9)

It is possible to isolate 2,4,6-trinitrobenzyl chloride or the bimolecular product α-chloro-2,2',4,4',6,6'-hexanitrobibenzyl by stopping the reaction short. This is indeed an excellent preparative reaction for the chloride replacing the tedious series of reactions which had been the only known route for this compound [28].

HNS can form charge–transfer complexes with a number of aromatic amines and phenols [38].

A novel method of producing nitrostilbene derivatives was given by Bethel and Bird [48]. It consists in reacting 4-nitrobenzylhalides with potassium *t*-butoxide. 4,4-Dinitrostilbene resulted.

According to [47] full scale production of HNS exists in the United Kingdom based on the method of Shipp [24].

NITRO DERIVATIVES OF AROMATIC AZA PENTALENES

Tetranitro derivatives of dibenzo-1,3a,4,6a-tetrazapentalene (TACOT) (IX):

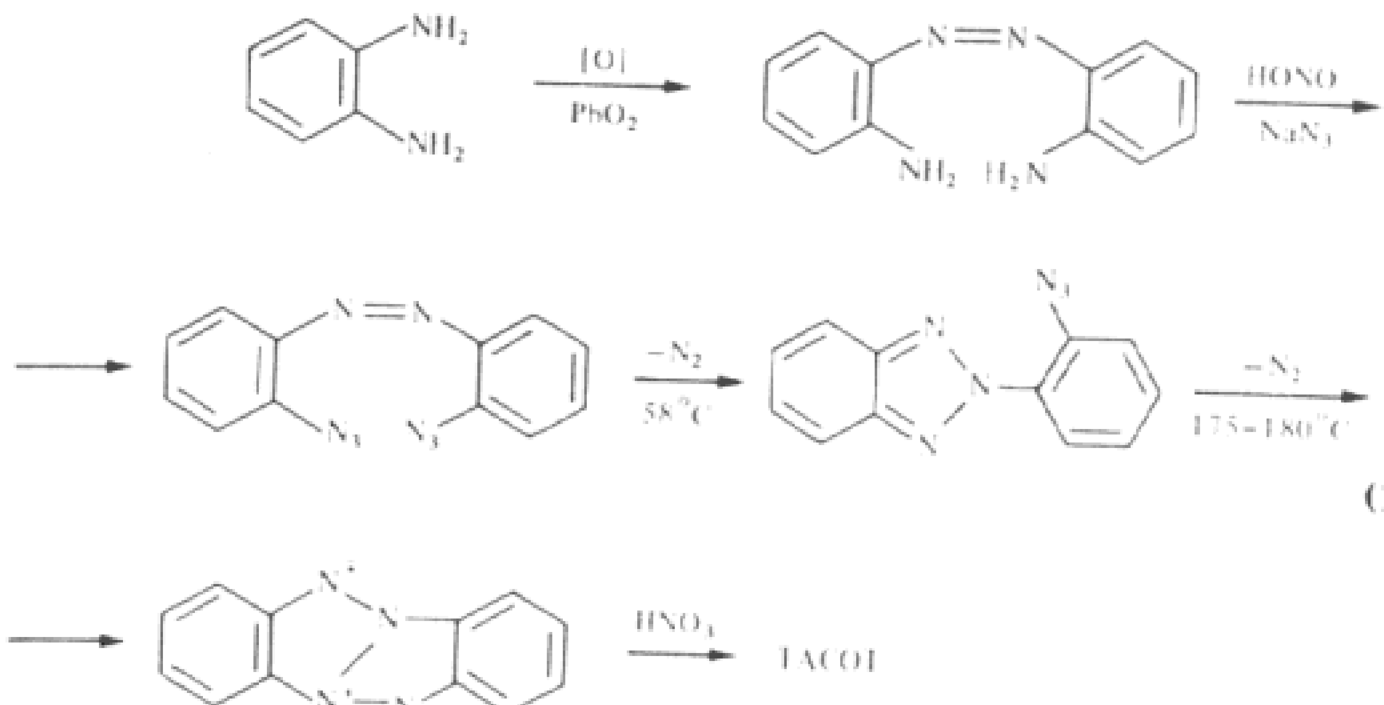
TACOT

IX

This is a mixture of isomers with two nitro groups substituted in different positions in each benzene ring. It is a powerful explosive with unusual and outstandingly high temperature stability [29] TACOT, which is comparable to pentaerhythritol tetranitrate (PETN) in explosive power, has thermal stability greater than that reported for any known organic explosive compound or composition.

TACOT was described for the first time in 1960 in a patent [30] and later in many papers by Carboni and co-workers [31–36] in which the syntheses of this compound and its properties were reported. It can be obtained from *o*-phenylenediamine by the sequence of reactions (10).

Tetranitrodibenzo-1,3a,4,6a-tetraazapentalene is generally prepared from tetraazapentalene by direct nitration. The procedure [29] consists in adding 30 parts of fuming nitric acid to 1 part of dibenzo-1,3a,4,6a-tetraazapentalene in concentrated sulphuric acid. After 15 min, the mixture is heated to 60°C and maintained at this temperature for an additional 15 min period. The orange coloured mixture is poured into ice-water to yield TACOT, which can be recrystallized from dimethyl formamide. The product obtained is composed of numerous isomers of tetranitrodibenzo-1,3a,4,6a-tetraazapentalene, depending on the position of the nitro group (*ortho, meta* or *para*) in each individual



(10)

(IX)

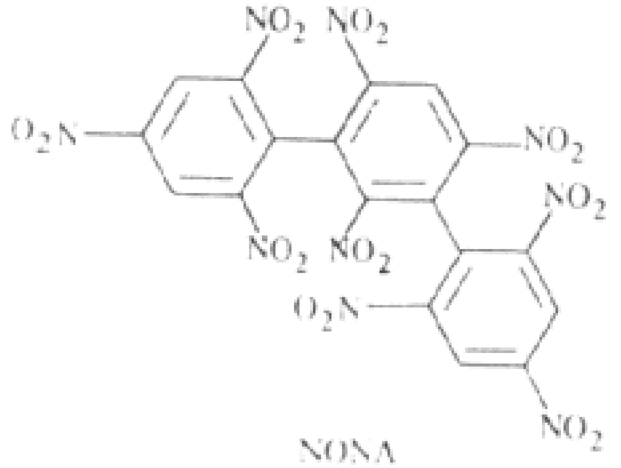
benzene ring. But these isomers have been found to have similar explosive and thermal properties. Therefore TACOT which is a mixture of the three isomers, is used as such in explosive compositions. Its ignition temperature (494°C) is the highest ever registered for explosives. Its explosive power is equal to 96% and 80–85% that of TNT and RDX respectively. It is highly insensitive to impact and compares favourably with dinitrobenzene in that respect. Despite the insensitivity to impact and static charges TACOT can be readily initiated by lead azide primer containing as little as 0.02–0.03 g of lead azide.

TABLE 41. Heat resistant explosives

Explosive	Chemical name	m.p. °C	Crystal density g/cm³	Velocity of detonation m/sec	Detonation pressure (calc.) k bars
DATB	1,3-Diamino-2,4,6-trinitro-benzene	286	1.84	7500	260
TATB	1,3,5-Triamino-2,4,6-trinitro-benzene	350 (decomp.)	1.94	7500	290
HNS	2,2′,4,4′,6,6′-Hexanitrostilbene	318	1.74	7000	215
DIPAM	3,3′-Diamino-2,2′,4,4′,6,6′-hexanitrobiphenyl	304	1.79		
TACOT	Tetranitro-2,3:5,6-dibenzo-1,3a,4,6a-tetra-azapentalene	410	1.85	7200	245

NONA

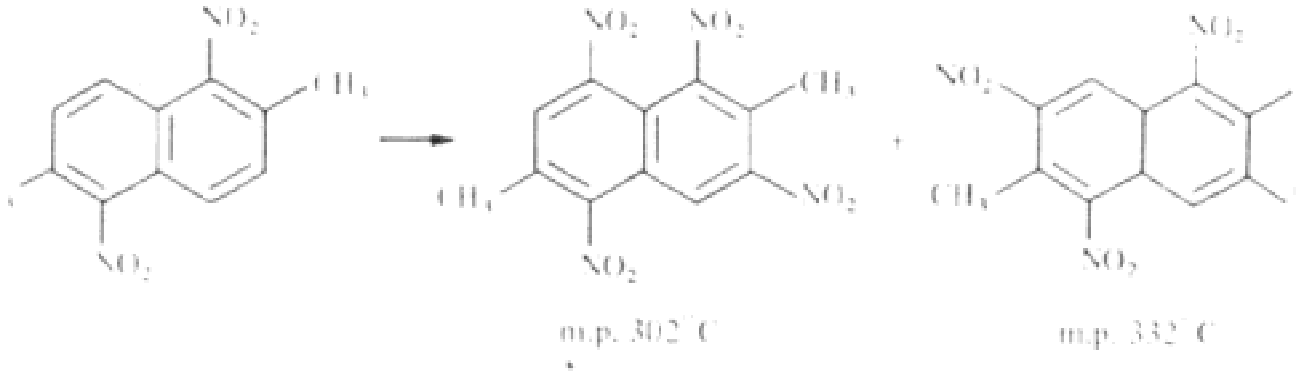
NONA is 2,2′,2″,4,4′,4″,6,6′,6″ – nonaterphenyl obtained by reacting 2 moles of picryl chloride with 1,3-dichloro-2,4,6-trinitrobenzene in the presence of copper dust at 210°C (Ullman reaction) [55]. It has an exceptional heat stability melting with decomposition at 440–450°C. It has a density of 1.78. No more information is available.



NONA

POTENTIAL HEAT RESISTANT EXPLOSIVES

Some work has been done to obtain new heat resistant explosives. A number of potential products were thus obtained, Buckley, Everard and Wells [39]. They nitrated 2,6-dimethyl-1,3-dinitronaphthalene [40] using nitric acid in acetic anhydride and obtained tetranitro derivatives marked by their high melting points in addition to a small amount of a trinitro compound not shown on formula (11).



(11)

It was suggested that the above compounds should be used to produce analogues to hexanitrostilbene by their oxidation.

Buckley and co-workers [56] continued their work on high nitrated naphthalene derivatives. They nitrated 1-methylnaphthalene with dilute nitric acid (d 1.42) in Cl CH₂CH₂Cl at 40°C and obtained 4,8- and 4,5-dinitro-1-methylnaphthalene (I and II respectively).

On further nitration below 2°C with nitric acid (d 1.5) and sulphuric acid (d 1.84) they obtained trinitro- and tetranitro derivatives, of relatively low melting points:

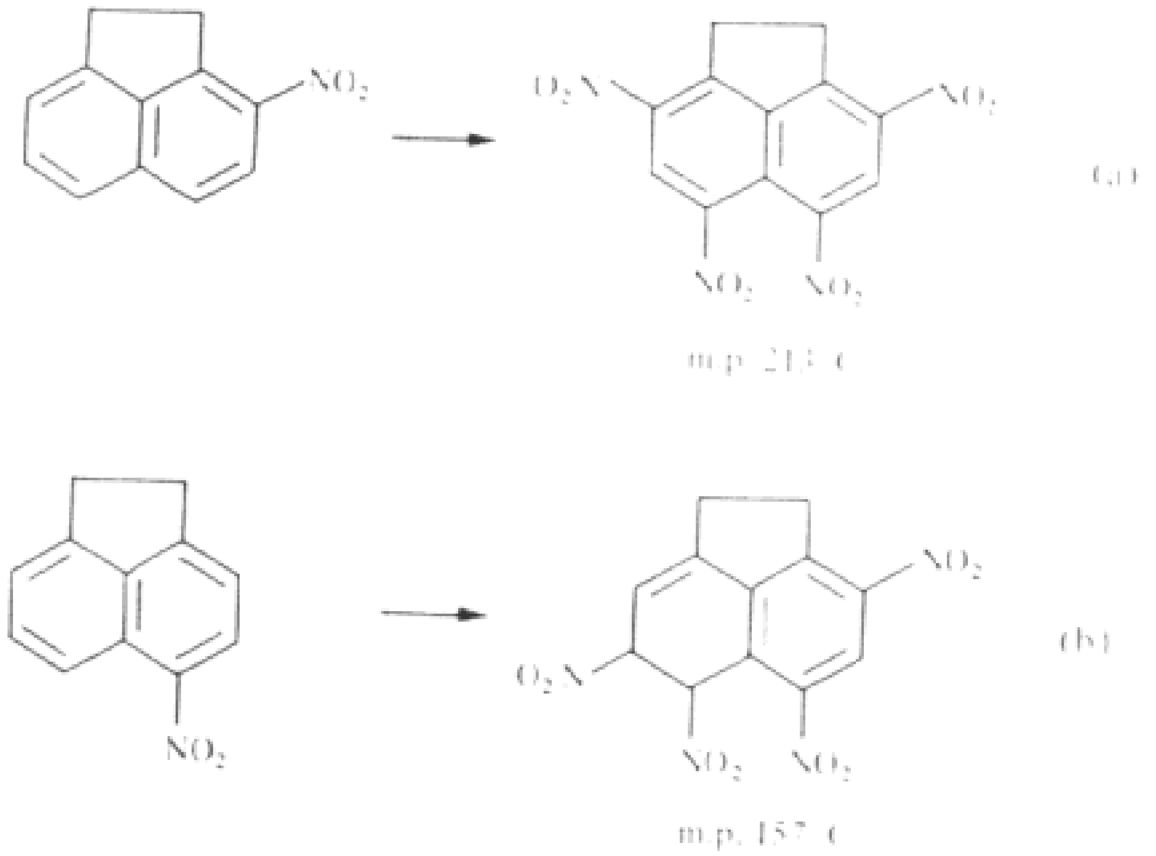
I → 2,4,8-trinitro-, 4,5,8-trinitro- and 2,4,5,8-tetranitro-1-methyl naphthalene
m.p. 135 138°C m.p. 218°d m.p. 220°C

II → 2,4,5-trinitro-1-methyl naphthalene (m.p. 190°d)

The yields of tetranitro derivatives were low (6%).

Another line of research consisted in producing polynitroacenaphthene [41]: 3-, 4- and 5-nitroacenaphthene were nitrated and yielded di, tri- and tetranitroacenaphthenes. Also pentanitroacenaphthene was obtained. None of the substances has shown a very high m.p., the highest was that of 3,7-dinitroacenaphthene (m.p. 276°C).

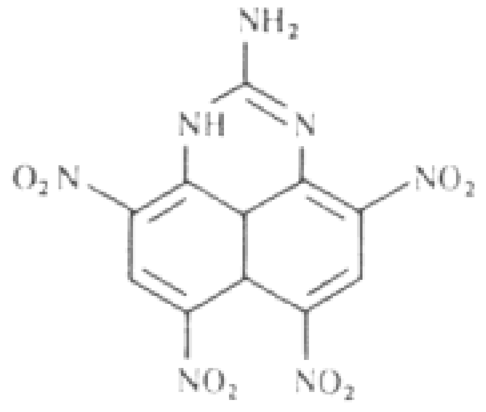
However, tetranitro derivatives obtained by nitration of 3- and 4-nitroacenaphthenes, 3,5,6,8- and 3,5,6,7-tetranitroacenaphthenes (12a) and (12b) respectively can be of some interest as explosives.



(12)

Another potential heat resistant nitro compound is 2-amino-4,6,7,9-tetranitroperimidine (X) [42]. The mother substance: 2-aminoperimidine can be obtained from perinaphthylene diamine and ammonium cyanate with a good yield [43]. The substance is used in analytical chemistry as a reagent for sulphate ion because of the very low solubility of the sulphate.

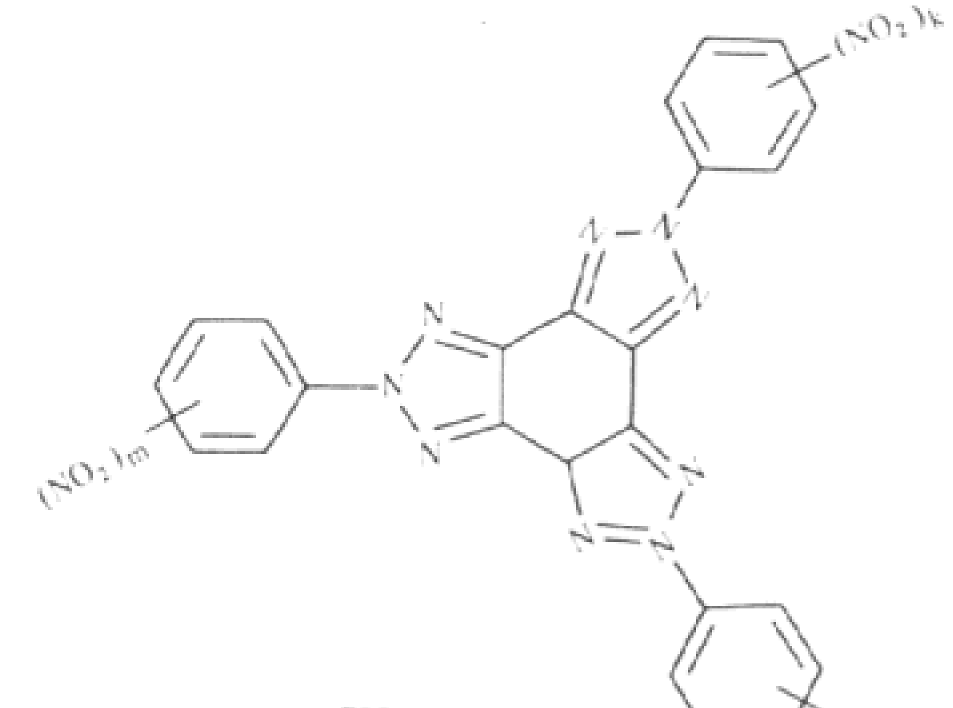
It was recently announced [50] that 1,3,5,7-tetranitroadamantane (TNA) possesses properties which are likely to be of value as a heat resistant explosive. Its m.p. is above 350°C. It is also very insensitive to impact.



X

In some countries Octogene (HMX) is considered as a heat resistant explosive [50, 51]. Its m.p. was found to be between 276–277°C (Vol. III, p. 117) and 280°C [51].

Nitro derivatives of 2,5,8-triphenyl-tris-triazolobenzene (XI) are very interesting heat resistant compounds [52]. The substances were obtained by coupling diazotized nitroanilines with 1,3,5-triaminobenzene, followed by oxidation with $CuSO_4$. Compounds from *p*-nitroaniline and 2,4-dinitroaniline had m.ps of 369–370°C and 400°C respectively.



XI

Resistance to Irradiation

The heat resistant explosives: TACOT, DATB and TATB are remarkably stable towards various irradiations such as gamma radiation from Co^{60} according to Avrami [49].

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APPENDIX

Kuboszek and co-workers used phase-transfer catalysis and catalytic two phase system to obtain some heat resistant explosives such as: HNS [1, 2], HNBB [3], Hexanitrodiphenylmethane [4], Hexanitrodiphenylamine [5] and polynitro derivatives of polyphenylethers [6].

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CHAPTER 8

ALIPHATIC NITRO COMPOUNDS

(Vol. I, p. 579)

In the course of the last two decades the chemistry of aliphatic nitro compounds – both nitroalkanes and nitroalkenes has received particular attention. A variety of compounds have been obtained and their properties examined.

Between 1950 and 1960 increased interest in the use of nitroalkanes as potential explosives and propellants has been a major factor in expanding the chemistry of this relatively ignored field.

Evidence of the increasing interest in the field were Symposia on Nitro Aliphatic Chemistry in 1961 [1] on Nitro Compounds in 1963 [2], and in 1968 [3]. Then a few excellent review articles appeared by: Doležel [4], Noble, Borgardt and Reed [5], Shechter [6a], Shechter and R. B. Kaplan [6b], a review on nucleophilic substitution $S_{RN}1$ of aliphatic nitro compounds by Beletskaya and Drozd [245], collective volumes edited by H. Feuer [7], monographs by: Perekalin and Sopova [8], Novikov and co-workers [9]. See also [120]. Some books exist where the chemistry of nitroalkanes form important chapters, viz.: by Asinger [10], Matasă and Matasă [11], Sosnovsky [12].

Nitroalkanes have also opened some new fields in organic synthesis. The problems were tackled in a number of monographs and review articles [13–19] – however, most of them are outside the scope of the present book. Such is also the monograph by Krein and Shekhter [233] describing the nitration of lubricating oils to produce anti-corrosion materials.

There are some natural nitroalkane derivatives existing, such as β-nitropropionic acid present in some plants.

MONONITRO ALKANES

As is known (Vol. I), alkanes can be nitrated in vapour phase by nitric acid or nitrogen dioxide. Nitration with nitric acid at temperatures of 400–435°C (method of Hass, Vol. I, p. 86) became a well established commercial method of making nitroalkanes. A considerable number of papers mainly by Hass and co-workers (Vol. I) and Titov (Vol. I) gave both theoretical and practical foundations for this remarkable process and subsequently less theoretical work has appeared. Less attention was paid to the nitration of alkanes with nitrogen dioxide (method of T. Urbański and Słoń, Vol. I, p. 94) which has not been put to industrial use.

The author of this book continued some of his work, for example, nitrating *n*-heptane with a great excess of nitrogen dioxide [20]. It was found that equal distribution of the nitro groups occurred along the chain: *ca.* 40% were found for positions 2 and 6, 3 and 5, and *ca.* 20% for position 4. This confirmed the view expressed by Hass (Vol. I, p. 95) and Asinger (Vol. I, p. 95), [10, 21, 22] that the nitration of CH_2 groups of longer chain alkanes proceeds according to the statistical rule. This finding was contrary to some views that position 2 in long chain alkanes is the preferred position [23].

Ślebodziński, T. Urbański and Łukasiewicz [24] nitrated *n*-hexane with nitrogen dioxide at temperatures varying from 120° to 300°C with molar ratios *n*-hexane:NO_2 varying from 1:10 to 5:1. The highest yield and safest conditions were obtained with the ratio 3:1 at 300°C. The yield of nitro compounds was *ca.* 42% in relation to *n*-hexane converted. The composition of the nitro alkane fraction was as given in Vol. I, pp. 94–95.

The identification of nitroalkanes was carried out by coupling nitroalkanes with diazonium salts [25]. The method was based on the work of V. Meyer *et al.* [26] and used by some authors for the identification of nitroalkanes [27, 28].

With the advent of chromatography the method of gas chromatography was used for the separation and identification of nitroalkanes. This was described in papers by Bethea and Wheelcock [29]. The gas–liquid chromatography of C_1–C_4 nitroalkanes was used by Biernacki and T. Urbański [30].

Minc, T. Urbański and Falęcki [96] examined the action of ionizing radiation from Cobalt source (Gamma Cell 220) upon *n*-hexane dissolved in N_2O_4 in sealed tubes. The reaction was carried out for 200 hr at room temperatures, and the yield of 1-nitrohexane was 1%. The experiments were discontinued when a violent explosion occurred in one of the tubes.

Albright *et al.* [97] examined the influence of gamma radiation upon the vapour phase nitration of propane with nitric acid at 400–450°C. There was a slight effect of irradiation on the yield of nitro products, in agreement with the above finding [96]. The increase of the yield of nitro alkanes was of the order of only 10–15%.

OTHER METHODS OF INTRODUCING THE NITRO GROUP INTO SATURATED COMPOUNDS

The other methods of introducing the nitro group into saturated compounds have been reviewed by Larson [31].

Here are the main outlines for the conversion of oximes to nitro compounds.

Emmons and Pagano [32] used peroxytrifluoroacetic acid to oxidize oximes to nitro compounds with a yield of up to 76%. The reaction is carried out in acetonitrile as a solvent in the presence of a buffer to neutralize trifluoroacetic acid formed in the reaction. This is a simple and convenient method of obtaining nitro aliphatic and alicyclic compounds. Thus, nitrocyclohexane and 1-nitroheptane were obtained with yields of 62 and 72% respectively. See also [33].

Another method of oxidation of ketoximes to nitro compounds consists in the bromination of ketoximes with *N*-bromosuccinimide to obtain bromonitroso compounds which were oxidized with nitric acid and hydrogen peroxide to bromonitro compounds. The latter were debrominated by sodium borohydride to yield secondary nitro compounds [34] (1):


$$R_2C{=}NOH \xrightarrow{NBS} R_2C(Br)(NO) \xrightarrow{HNO_3+H_2O_2} R_2C(Br)(NO_2) \xrightarrow{NaBH_4} R_2CHNO_2 \qquad (1)$$

The method has found an application to the preparation of nitro steroids [35].

Oximes can be oxidized to nitro compounds with ozone [227], and recently an excellent yield was obtained by oxidation of ketoximes with hypochlorous acid to form chloronitroso compounds which on further oxidation with tetra-*n*-butylammonium hypochlorite yielded secondary nitroalkanes [228].

Oxidation of Amines

The reaction of the oxidation of aromatic amines to nitro compounds examined by Emmons and co-workers (Vol. I, p. 132) gave a high yield of nitro derivatives. Emmons [36] tried to use peracetic acid to obtain tertiary nitroalkanes. The reaction gave a high yield (e.g. nitrooctane was obtained with a yield as high as 87%). The use of peroxytrifluoroacetic acid, successful in the oxidation of oximes, did not give favourable results with amines. To obtain nitrosteroids from the amines, *m*-chloroperbenzoic acid was successfully used (the yield was 50–79%) [37].

Potassium permanganate can also be used to oxidize tertiary amines otherwise resistant to oxidation [38].

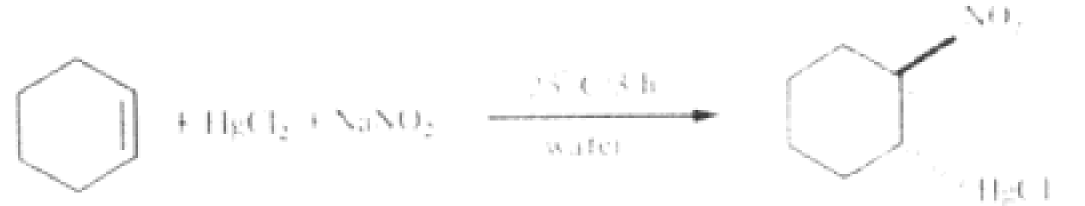
Reaction of Alkyl Halides with Sodium Nitrite

The method of Kornblum (Vol. I, p. 127) received a wide application, for example, for the synthesis of α-nitro esters [39] and β-nitroketones [40]. However, this method has some limitations. Thus *t*-butyl halide does not furnish the expected nitro compounds. Also cyclohexyl bromide does not react with sodium nitrite. On the contrary, cyclohexyl iodide reacts with sodium nitrite but the product is cyclohexane in 57% yield.

Similar to the reaction of V. Meyer, nitrous esters are also formed during the Kornblum reaction, for example, bromocyclopentane is converted to both nitrocyclopentane and nitrous ester [41]. For more information see [31].

Nitromercuration of Alkenes

An interesting reaction of nitromercuration was found by Bachman and Whitehouse [107]. It consists in acting with sodium nitrite and mercuric chloride on alkenes, for example, on cyclohexene (2):



(2)

β-Nitromercurial chloride results with the yield of 80%. The products were used to obtain nitroalkenes (28a).

Formation of Nitroalkanes from Nitrate Esters

Thermal decomposition of nitrate esters has been shown to result in the formation of small amounts of nitroalkanes [237]. Bachman and Connon [238] described the method of converting nitrate esters into nitroalkanes by reacting nitrate esters with metal nitrites in suitable solvents. More detailed information is given in Chapter X on nitrate esters.

CHEMICAL PROPERTIES OF NITROALKANES

Nitronic Acids

One of the most important properties of primary and secondary nitro alkanes is their ability to form aci-nitro compounds, also referred to as nitronic acids:


$$R^1R^2CHNO_2 \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} R^1R^2C{=}N(O)OH \qquad (3)$$

Polar Solvents Favour the Aci-form

Nitronic acids are relatively weak (pK_a = 2–6) resembling carboxylic acids with regard to their strength. The nitronic acids can form esters. They can be prepared in three ways:

(1) by the alkylation of sodium or potassium nitronate salts, for example,


$$R^1R^2C{=}NO_2^-Na^+ + CH_2RCH_2X \longrightarrow R^1R^2C{=}NO_2CH_2CH_2R \qquad (4)$$

X = halogen

(2) by the alkylation of silver nitronate salts,
(3) by the reaction of nitro alkenes and nitronic acids with diazomethane.

Method (1) has considerable limitations, as the nitronic ester decomposes readily to yield oximes and aldehydes and ketones.

Nitronic esters are able to enter the 1,3-addition reaction (Chapter IV, formula 30).

Salts of nitronic acid can decompose readily in a dangerous manner. Particularly dangerous are salts of nitromethane (Vol. I, p. 586; Vol. III, p. 136). Dry sodium salt of nitromethane can explode when touched with a spatula.

The chemistry of nitronic acid and derivatives is a very wide field and the reader should consult an excellent monographic review by Nielsen [42].

Activating Influence of the Nitro Group

The nitro group activates aliphatic systems and makes possible a number of addition reactions such as: aldolic addition of aldehydes (Henry reaction), Mannich reaction, Michael addition, Diels–Alder reaction, for example [155].

The reader should be advised to consult an excellent monographic review given by Baer and Urbas [43].

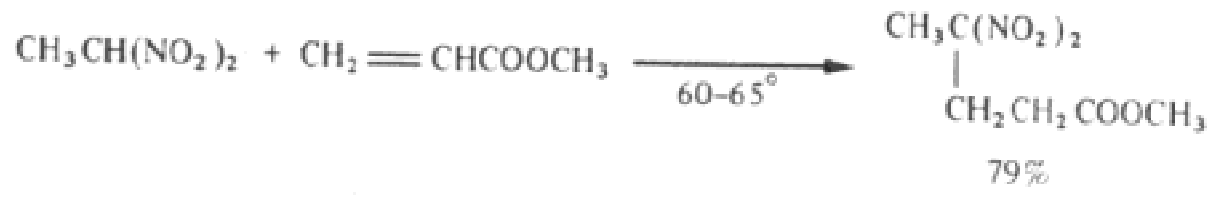
Here are a few data based on more recent publications.

1. Aldolic addition and the Mannich reaction (Vol. I, p. 186). The aldolic addition reaction of nitroalkanes with carbohydrates (specifically aldoses) continues to be an important reaction in sugar chemistry which according to Baer [43] in some respects surpasses in versatility Emil Fischer's classical cyanohydrin synthesis. Particularly noteworthy are publications by Baer and Kovář [44, 45], Funubaski, Yoshimura and co-workers [46–51] and other Japanese workers [52], Russian workers [53, 54] and Bilik [55].

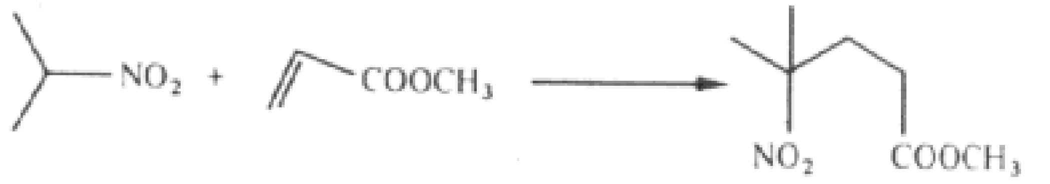
A different method of preparing glucosinolates through nitroalkanes was given by MacLeod and Gil [56].

With regard to the Mannich reaction the monographs, for example, that of Reichert [57] should be consulted.

2. Michael addition. Ostaszyński and Wielgat [58] used potassium fluoride as a catalyst for the Michael addition of nitromethane to a double bond. (Alkali fluorides were originally suggested by Yasuda *et al.* [59] as catalysts for the Michael addition reactions.) The work of addition of nitroalkanes was continued [60]. Various acceptors, for example, methylacrylate and acrylonitrile, were used. Among nitroalkanes gem-dinitroalkanes were applied as donors. Nitroalkanes readily formed double salts with KHF_2, $RbHF_2$ and $CsHF_2$. The yield of the adducts of such salts with compounds containing a double bond varied between 60 and 90%, viz. (5):

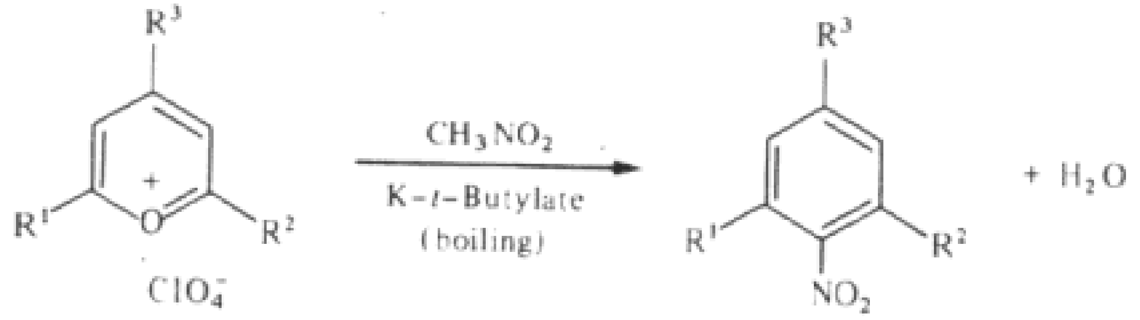

$$CH_3CH(NO_2)_2 + CH_2{=}CHCOOCH_3 \xrightarrow[60\text{–}65^\circ]{} \underset{79\%}{\overset{CH_3C(NO_2)_2}{\underset{CH_2CH_2COOCH_3}{|}}} \quad (5)$$

Alternatively, nitroalkanes can be added to an activated double bond, (6) [61]:



(6)

3. Reaction of nitromethane with pyrilium salts. Dimroth [62] in a number of papers since 1956 [63] has described an interesting reaction in the formation of aromatic nitrocompounds by reacting nitromethane with pyrilium salts (e.g. perchlorate) substituted in positions 2,4,6 in basic medium (7) with a yield varying from 25 to 60%:

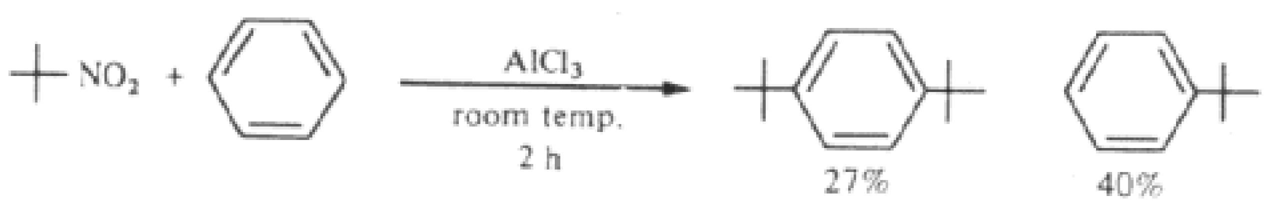


(7)

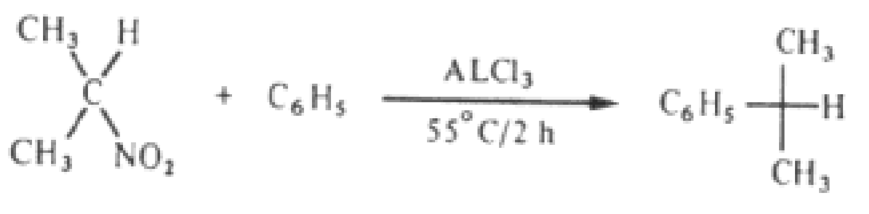
By-products of the reaction are cyclohexylinden derivatives.

4. Nitroalkanes as alkylating agents in Friedel-Crafts reactions. An interesting reaction was recently reported by Casini and co-workers [64]. They found that Friedel-Crafts reaction of benzylic or tertiary nitro compounds with benzene gave normal alkylation products (8) and (9) respectively. 2-Nitropropane gave cumene (10) subject to further transformations.

$$C_6H_5CH_2NO_2 + C_6H_6 \xrightarrow[\substack{\text{room temp.}\\ 24\text{ h}}]{AlCl_3} \underset{10\%}{C_6H_5CH_2C_6H_5} \quad (8)$$



(9)


$$\begin{matrix} CH_3 & H \\ & C \\ CH_3 & NO_2 \end{matrix} + C_6H_5 \xrightarrow[55^\circ C/2\text{ h}]{ALCl_3} C_6H_5\!-\!\overset{CH_3}{\underset{CH_3}{C}}\!-\!H \quad (10)$$

5. *Oxidation of nitroalkanes to aldehydes and ketones* (Vol. I, p. 186). The Nef reaction (Vol. I, p. 186) for the formation of aldehydes and ketones from primary and secondary aliphatic nitro compounds was modified by Nametkin and Pozdnyakowa [90] and Grundman [91] who improved the yield of ketones (from secondary nitroalkanes) by using an oxidizing medium of potassium permanganate and hydrogen peroxide respectively. The reaction with permanganate was extensively used by Asinger *et al.* [20b, 22], Ślebodziński, T. Urbański *et al.* [24] in the analysis of the products of nitration of long chain alkanes.

McMurrey and co-workers modified the reaction by carrying it out in a reductive medium of $TiCl_3$ followed by hydrolysis and an oxidizing medium of O_3 [92a] and [92b] respectively. See also Bartlett *et al.* [93]. They used *t*-butyl hydroperoxide in the presence of pentavalent vanadium salt as a catalyst. Kornblum and Wade [94a] gave an unusual method of oxidation of secondary nitroalkanes to ketones with nitrous esters and sodium nitrite at room temperature:

$$R_2CHNO_2 + NaNO_2 + n\text{-}C_3H_7ONO \longrightarrow R_2CO + n\text{-}C_3H_7OH + NaNO_3 + N_2O. \quad (11)$$

The yield was up to 88% depending on nitroalkane.

6. *Nucleophilic displacement of the nitro group from nitroalkanes*. Such reactions were described by Kornblum [94b], Benn and Meesters [95]. The reactions consist in the substitution of the nitro group with aryls. The reaction of Kornblum will be described in the paragraph dedicated to arylnitroalkanes.

NITROMETHANE (Vol. I, p. 579)

Shaw [65] presented new data referring to the physico-chemical properties of nitromethane (as compared with those of methyl nitrite).

Shaw's data are as follows:

Density at 15°C	1.140
Boiling point	101°C
Melting point	−29°C
Heat of formation	−27 kcal/mol
Heat of vaporization	9,1 kcal/mol
Specific heat C_p^o	13.7 cal/mol deg
Activation energy of thermal decomposition	59.0 kcal/mol
Detonation velocity	
experimental	6300 m/s
calculated	6890 m/s

Some figures given by Meyer [66] are slightly different:

Density	1.1385
Boiling point	101.2°C.

He also gives vapour pressures:

1.3 millibar	at −29°C
10 millibar	0°C
32 millibar	20°C
140 millibar	50°C
283 millibar	80°C

A considerable amount of work has been dedicated to the problem of decomposition of nitromethane in gas-phase. They were reported in Vol. I (p. 579) and in the review article by Makovky and Lenji [67].

A few papers referring to flash photolysis should be mentioned: those by Norrish and co-workers [68], Pimentel and co-workers [69], Nicholson [70], McGarvey and McGrath [71].

Crawforth and Waddington [72] examined pyrolysis of nitromethane between 305° and 440°C. They found the reaction to be pressure dependent. Above 150 mm it is approximately of the first order

$$k = 10^{14.1} \text{ exp. } (-55 \text{ kcal/RT}) \text{ sec}^{-1}.$$

The main products are: methane, CO, N_2, NO, HCN and water. The authors suggested the mechanism through the initially formed methyl radical:

$$\begin{array}{lll} \cdot CH_3 + CH_3NO_2 & \longrightarrow & CH_4 + \cdot CH_2NO_2 \\ \cdot CH_3 + NO_2 & \longrightarrow & CH_3NO_2 \\ \cdot CH_3 + NO_2 & \longrightarrow & CH_3O\cdot + NO \\ \cdot CH_3 + NO & \longrightarrow & CH_3NO \end{array} \quad (12)$$

A few papers were dedicated to the decomposition of nitromethane in shock-tubes: Bradley [73], Hiraoka and Hardwick [74], Borisov and co-workers [75]. Glänzer and Troe [76] examined the decomposition of nitromethane highly diluted with argon in shock waves between 900 and 1500 I, and concentration of argon 1.5×10^{-6} and 3.5×10^{-4} mol/cm³. A unimolecular reaction occurred:

$$CH_3NO_2 \longrightarrow \cdot CH_3 + \cdot NO_2 \quad (13)$$

The rate constant *k* is expressed by the equation:

$$K = 10^{17.1} \text{ exp } (-42 \text{ kcal/RT}) \text{ sec}^{-1}.$$

A subsequent reaction occurred between free radicals:

$$\cdot CH_3 + \cdot NO_2 \longrightarrow CH_2O + NO + \cdot OH \quad (14)$$

Shock initiation of liquid nitromethane (as compared with that of methyl nitrite) was given by Shaw [65].

Practical use of nitromethane as an explosive. The use of nitromethane is limited owing to its high volatility. According to Meyer [66] nitromethane was used in the U.S.A. for underground model explosion ('Pre-Gondola') in preparation for the nuclear charge technique, and for stimulation blasting in oil and gas wells.

Nitromethane can also be used as monergolic liquid fuel for rockets.

NITROETHANE, 1-NITROPROPANE AND 2-NITROPROPANE

Glänzer and Troe studied a shock wave thermal decomposition in argon of nitroethane [77], 1- and 2-nitropropanes [78].

The following are data obtained (Table 42).

TABLE 42. Characteristics of shock wave thermal decomposition of nitroalkanes

	Nitroethane	1-Nitropropane	2-Nitropropane
Temperatures (K)	900–1350	915–1200	915–1200
Rate constant k sec^{-1}	$10^{15.9}$ exp (–57 kcal/RT)	2.3×10^{15} (–55 kcal/RT)	2.4×10^{15} (–54 kcal/RT)
Primary reaction step of C–N bond fission	$C_2H_5^{\bullet} + {}^{\bullet}NO_2$	n-$C_3H_7^{\bullet} + {}^{\bullet}NO_2$	i-$C_3H_7^{\bullet} + {}^{\bullet}NO_2$

2-Nitropropane can be subjected to dimerization under the action of alkali metals in carbon tetrachloride, DMSO in the atmosphere of nitrogen (15) [79]:

(15)

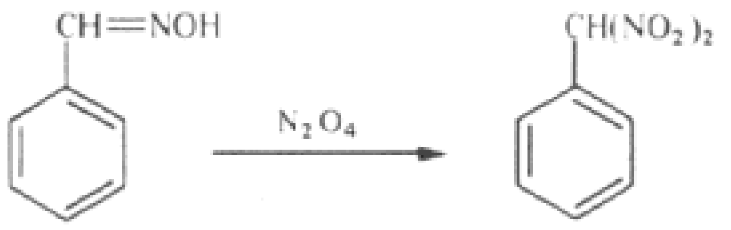
2-Nitropropane is widely used in the U.S.A. as a solvent, however its carcinogenic action has been reported [80].

ARYLNITROALKANES

Arylnitroalkanes form an interesting group of compounds: they combine the properties of the aromatic ring with those of nitroalkanes. The simplest is of course phenylnitromethane (Vol. I, pp. 96, 123, 275, 598). The chemistry of arylnitromethane was reviewed by Novikov and Khmelnitskii [81].

As has already been pointed out (Vol. I, p. 275) phenylnitromethane can be formed during the nitration of toluene, while using nitrogen dioxide as a nitrating agent.

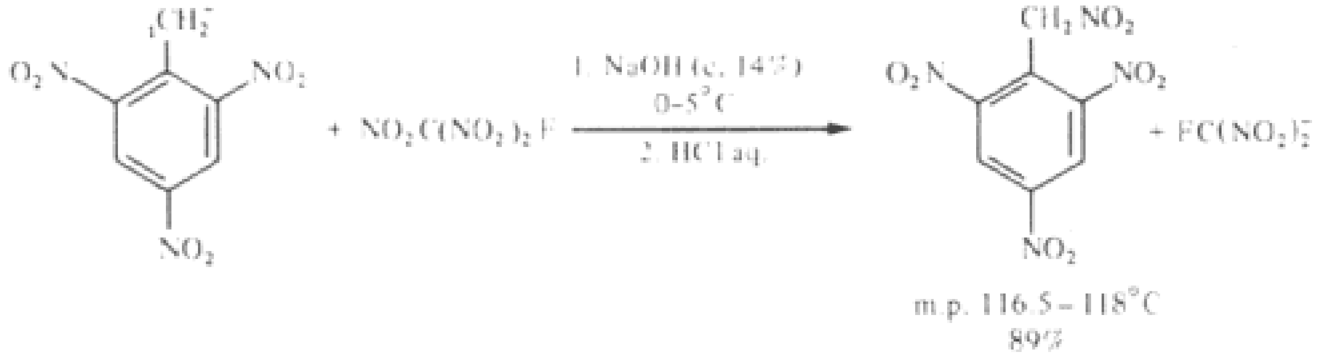
Higher nitrated derivatives of phenylnitromethane, among them those of derivatives of dinitro- and trinitromethane (Vol. I, p. 399) are important. The reaction of Ponzio [82] consists of acting with N_2O_4 on benzaldoxime: phenyldinitromethane results (16):



(16)

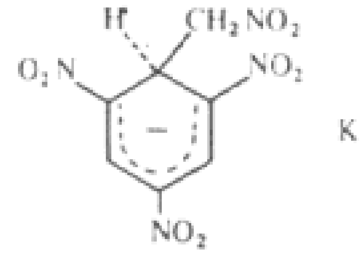
According to Fieser and Doering [83] the reaction should be carried out by gradually mixing solutions of benzaldoxime and N_2O_4 in dry ether at the temperature of boiling ether. The yield of the reaction produced in such a way was 38% lower than in the Ponzio original method (50%), but violent reaction is avoided.

Derivatives of phenylnitromethane nitrated in the aromatic ring have again received (Vol. I, p. 598) attention, particularly in relation to the properties of TNT. Sitzmann, L. A. Kaplan and Angres [84] acted on 2,4,6-trinitrotoluene in alkaline medium with fluorotrinitromethane which is an alkaline nitrating agent and was prepared by Kamlet and Adolph [85]. The reaction (17) brought about the formation of 2,4,6-trinitrophenyl-nitromethane through the intermediate 2,4,6-trinitrotoluene anion (Chapter VI, reaction 5, and [86]):



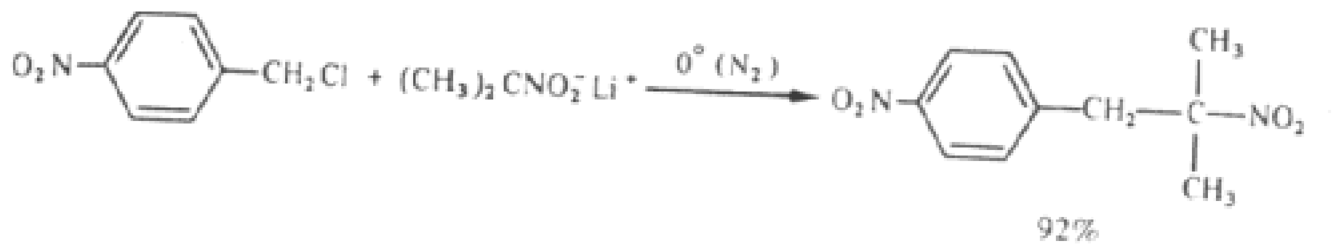
(17)

The same compound was obtained earlier by Russian workers [87] through the action of chloranil (as an oxidizing agent) on the σ-complex (I) of 2,4,6-trinitrotoluene with potassium salt of nitromethane.

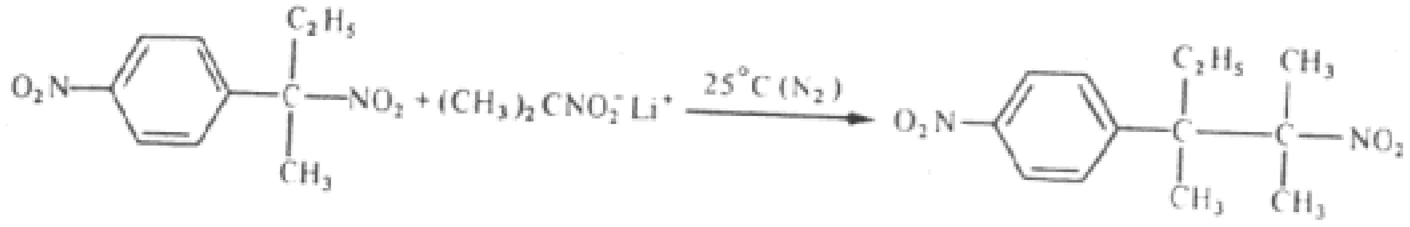


I

A considerable amount of work was done by Kornblum and co-workers on the chemistry of arylnitroalkanes, particularly the p-nitrocumyl system with a side chain of branched nitroalkane in the *para* position to the nitro group [17, 88]. Two interesting reactions are given here as examples:



(18)



(19)

In both types of reaction lithium salts of nitroalkane were used and the reactions appeared to proceed via a chain mechanism in which radical anions and free radicals are intermediates.

A remarkable feature of reaction (19) is the substitution of the nitro group attached at tertiary carbon of the *p*-nitrocumenyl system. The reaction of the displacement of a nitro group from a saturated carbon atom through an anion has been described for the first time [88c].

In the same system of cumene a replacement of the nitro group by hydrogen was described by Kornblum and co-workers [88d]. The agent replacing the nitro group was sodium salt of methanethiol in an aprotic solvent:

$$R_3CNO_2 \xrightarrow[\text{room temp}]{CH_3S^-} R_3CH \qquad (20)$$

Łytko-Krasuska, Piotrowska and T. Urbański [89] reported the reaction of replacement of a secondary aliphatic nitro group by hydrogen while treating the nitro compound with potassium hydroxide in ethylene glycol at 120–140°C. The reaction proceeded by a radical anion mechanism. Ono and co-workers [121] described new methods of replacing the nitro group in aliphatic compounds by hydrogen. One of the methods consists in acting with *N*-benzyl-1,4-dihydronicotinamide [121a], and another [121b] by acting on tertiary and secondary nitro compounds with tin hydrides (or deuterides) of the type Bu_3SnH (or Bu_3Sn D). The treatment of nitro compounds with tin hydrides occurred by refluxing in benzene in the presence of azobisisobutyronitrile. Bu_3Sn H was converted to the nitrite Bu_3Sn ONO.

Denitration of tetranitromethane and 1,1,1-trinitroethane by electrochemical reduction was reported by Petrosyan and co-workers [248, 249].

NITROCYCLOALKANES

Cycloalkanes, for example, cyclohexane can be nitrated with dilute nitric acid at a higher temperature (Vol. I, p. 84) or with nitrogen dioxide (Vol. I, p. 96).

Reich [98] reported that the best yield of nitrocyclohexane can be obtained with nitric acid of 30–50% HNO_3 at 120–140°C under 10–15 atm. The yield of nitrocyclohexane was up to 80%.

Nitrocyclohexane can be reduced to cyclohexane oxime to further transform into caprolactam. Several patents cover this method, but no practical application seems to have been found for it.

Nitro derivatives of cyclohexane can be obtained by the method of Severin (Chapter IV, formula 16) while reducing some nitroaromatic hydrocarbons with Grignard reagent or with sodium borohydride. Sodium borohydride reduced 1,3,5-trinitrobenzene to 1,3,5-trinitrocyclohexane (Vol. I, p. 252).

ESTERS OF NITROALCOHOLS AND UNSATURATED ACIDS

Nitroalcohols composed of nitroalkanes and formaldehyde have been esterified with acrylic and methacrylic acids in order to obtain products which could be subjected to polymerization. This is a part of the big programme on searching for solid propellants. The work on the above line was initiated by British Thomson-Houston Co. [235] described in a number of patents reviewed by Marans and Zelinski [236] who also gave an account of their own experiments. Nitroalcohols from nitromethane, nitroethane, 1-nitropropane and formaldehyde reacted with methyl esters of acrylic and methacrylic acids in the presence of concentrated sulphuric acid and cuprous chloride or toluene sulphonic acid and hydroquinone. Acrylic and methacrylic acid esters of nitroalkyls were formed through transestrification. They were polymerized at 100°C with benzoyl peroxide in an atmosphere of nitrogen. Only 2-methyl-2-2-nitropropyl ester gave a hard resin, whereas the other nitroalcohols gave viscous resins. The presence of the nitro group in the molecule seems to inhibit the polymerization in agreement with the findings described in Chapter IV.

INDUSTRIAL METHODS OF NITRATING ALKANES

Commercial Solvents Corporation, Inc., Terre Haute, Indiana, U.S.A. has a factory producing nitroalkanes by the method of Hess and co-workers (Vol. I, p. 86). In 1956 the annual production was in the order of 4400 tons. Also in Germany during World War II Badische Anilin – und Sodafabrik A.G., Ludwigshafen had a pilot plant for the daily production of 300 kg of nitroalkanes. It was working for three years (1939–1942) and in 1942 a larger plant capable of producing 1 ton daily was under construction, but was destroyed by bombing (according to Doležel [4]).

The industrial method for the nitration of propane is based mainly on the description by Doležel [4] in the German edition of the book by the author of the present monograph. Some details can also be found in the review article by Shechter and R. B. Kaplan [6b].

German Method of Nitration of Lower Alkanes

The method used in Germany at BASF (Ludwigshafen) was established by Schickh. It consisted of a stainless steel (V2A) nitrator in the form of a coil (1) (Fig. 29) submerged in a heating bath of molten sodium and potassium nitrate keeping the temperature at 400–450°C. A higher temperature was used for the nitration of methane and lower for higher hydrocarbons. Vapours of nitric acid (concentration 48% HNO_3) together with the hydrocarbon entered the coil from container (2). Molar ratio hydrocarbon:HNO_3 8–10 was maintained. The reaction products entered the cooling coil (3) and condenser (4). Liquid products were collected in the separator (5). Lower acid layer entered (6) and the upper layer was distilled off and collected in a condenser (7). The cyclon (8) retained the liquefied product and the gaseous hydrocarbons entered scrubbers (9) and (10) where they were washed with water, and then with sodium hydroxide solution in (11) to free them of traces of acids. The residual higher boiling products were retained in (12) and gaseous hydrocarbons returned to the nitrator. The gaseous oxidation and decomposition products were released through a valve (13).

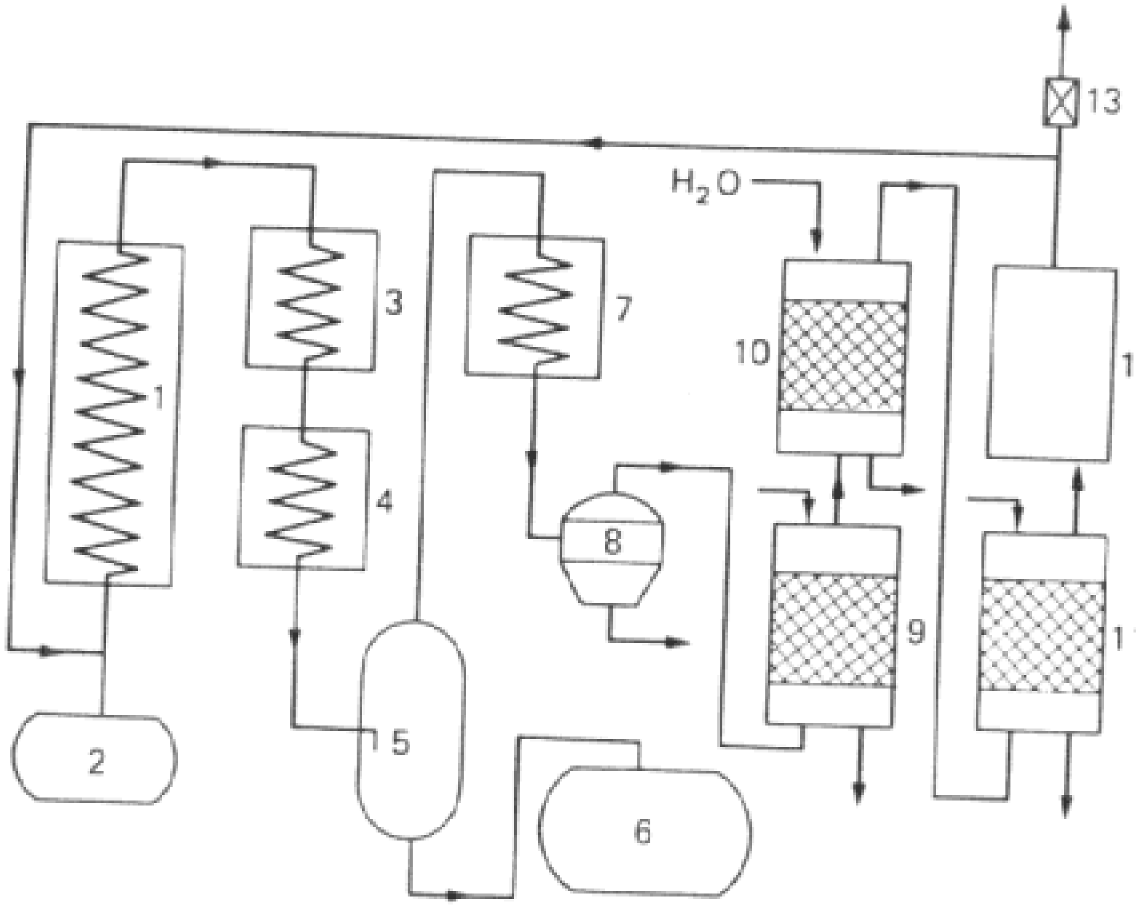


FIG. 29. Nitration scheme of Schickh used in Germany at BASF to nitrate alkanes according to Doležel [4].

The conversion of methane, ethane and higher hydrocarbons were 13%, 30% and 40–50% respectively. Methane was also nitrated under pressure of 10 atm., which increased the conversion to 20%.

Method of Commercial Solvents Corporation, Inc.

The nitration of hydrocarbons is carried out in a Stengel–Eagli [99] multisegment reactor (Fig. 30). It is usually composed of five segments.

The warmed alkane enters through (1) to the upper part of the nitrator. Nitric acid is injected through (2) and (3) to various segments of the nitrator. Electric heaters (4) maintain the correct temperature inside the apparatus. The constant temperature in the nitrator is maintained owing to the balance between the endothermic vaporization of nitric acid and exothermic heat of the reaction. Any deviations from the correct temperature are immediately avoided by valves (5) introducing air (or water). The products are evacuated through (6).

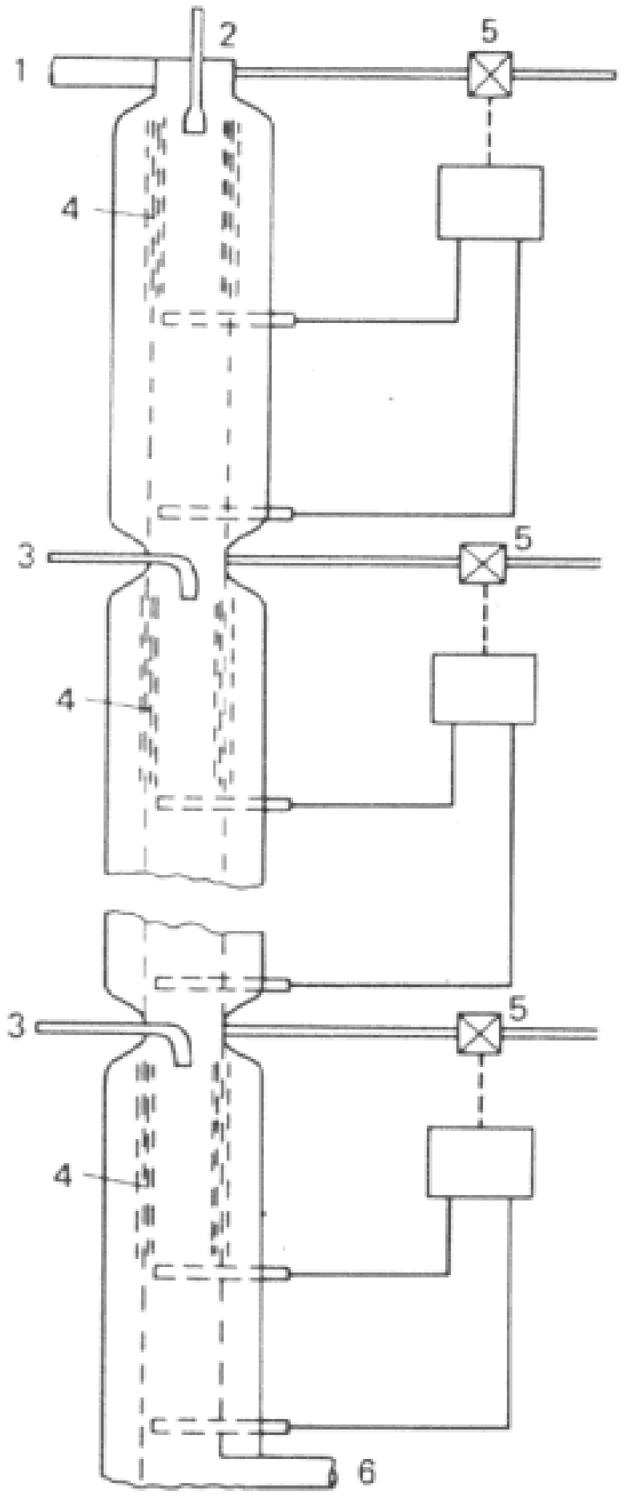


FIG. 30. Stengel–Eagli nitrator of alkanes used by Commercial Solvents Corp., Inc. according to Doležel [4].

The diagram of the method of nitration of propane is given in Fig. 31. Propane is supplied by pump (1) through a control valve (2), heater (3) and valve (4) to the upper part of the nitrator (5). Nitric acid (75–78% HNO_3) enters each segment of the reactor where the temperature of 400–435°C is kept constant. The temperature is maintained through a balance between the heat of nitration and the heat of evaporation of nitric acid, as previously mentioned. Heat regulators (6) and valves (7) can maintain the correct temperature in every segment. The temperature in every segment is measured by thermoelements.

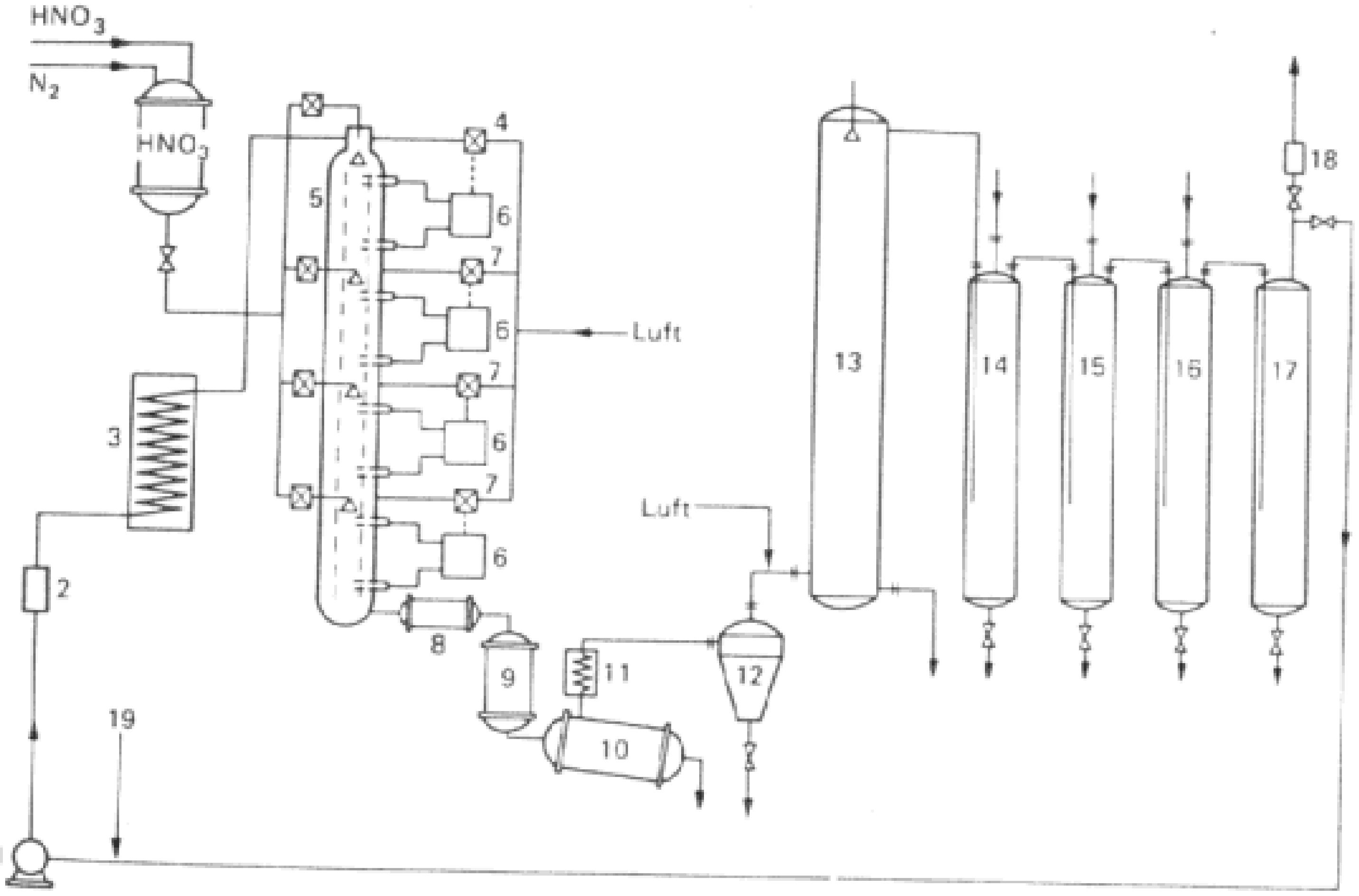


FIG. 31. Diagram of nitration of propane by Commercial Solvents Corp., Inc. according to Doležel [4].

The ratio propane:HNO_3 in the upper segment is of the order of 24.2:1 and the average ratio in the nitrator is 4.81:1. The pressure inside the nitrator is 8.75 kG/cm^2. If the temperature rises above 435°C, some water vapour is injected into the nitrator (higher concentrations of nitric acid tend to increase the temperature above the permitted limit).

The reaction gases are cooled intensely in (8) and condensed in (9). In (10) gaseous products enter (11) where they are cooled and in the cyclone (12) additional liquid fraction is obtained. The gaseous products containing nitrogen oxide enter the scrubber (13) together with air and NO is oxidized to NO_2. The scrubber is irrigated with water and thus nitric acid is recovered. Further washing of gases with water is achieved with scrubbers (14–17). In the last one (17) the flow rate of gases is lowered to free them from traces of water droplets. The gases leaving the last scrubber are rich with unreacted alkanes and return (through 19) to the nitrator. The gaseous by-products (e.g. N_2, CO, CO_2) leave the system through valve (18).

The conversion of propane to nitro compounds is in the order of 30–38%. The nitrated product is composed of 25% nitromethane, 10% nitroethane, 40% 2-nitropropane and 25% 1-nitropropane.

Distillation

The fractionation of nitro compounds is not a complicated problem, provided sufficiently efficient distillation columns are used. More difficult is the removal of acids (nitric acid, nitrogen oxides, organic acids), aldehydes and ketones, with water. The insoluble nitro compounds are subjected to azeotropic distillation. Water is separated as an upper layer and nitro compounds (with a small proportion of water on the bottom) are sent to distillation in order to separate the nitroalkanes. The flow-sheet is given in Fig. 32. The mixture of nitro compounds from an intermediate container (1) enters through a rotameter (2), pre-heater (3) into the upper part of column (4). The azeotropic mixtures go through condenser (5) to separator (6). The separated water returns to column (4) and the nitroalkanes through rotameter (7) enter column (8) where washing by a counter-current method with sodium bisulphite to free them from traces of nitric and nitrous acid. Nitro alkanes having a lower density pass through the column upwards to enter column (9) where the products are washed with water. Water is pumped back to column (4) to recover the dissolved nitro alkanes. The separated oil passes to the intermediate vessel (10). From here it goes through rotameter (11) and pre-heater (12) into the distillation column (13). An azeotrop which is composed of nitro alkanes and water distils. From the bottom part of column (13) and sent to an intermediate vessel (14), rotameter (15) and eventually to column (16) where nitromethane distils out. The bottom part of column (16) contains nitromethane, and nitropropanes. The mixture of nitro alkanes enters through intermediate (17) and rotameter (18) to column (19). Nitroethane distils out from the latter. In the bottom of column (19) both nitropropanes remain. They are sent through a pump to the intermediate vessel (20) and from there to rotameter (21) into column (22) where 2-nitropropane distils out. The lower part of column (22) passes through (23) and rotameter (24) to column (25) where 1-nitropropane distils out.

Hazards of the Nitration of Alkanes

Matasă [100] discussed the problem of the hazards of the nitration of alkanes. In his remarkably important paper he considered:

1. Explosibility of gaseous mixtures,

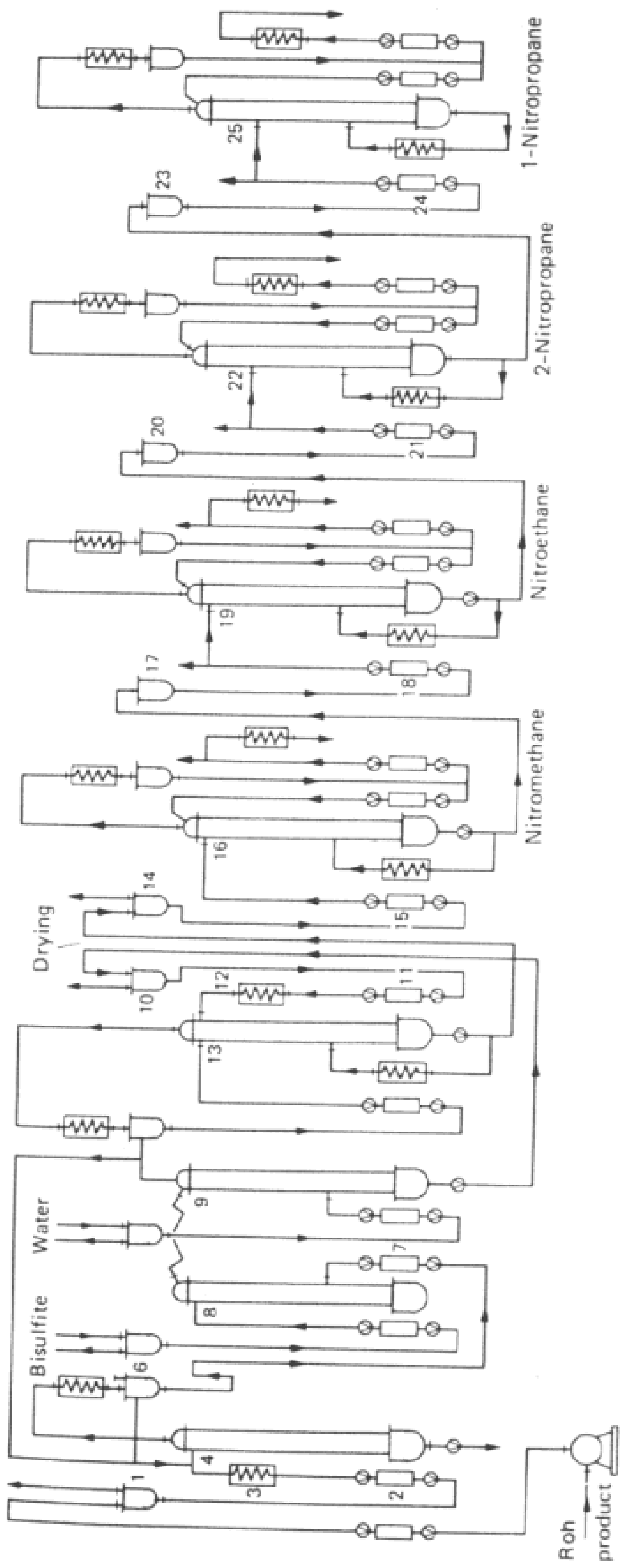


FIG. 32. Fractional distillation of nitroalkanes by Commercial Solvents Corp., Inc. according to Doležel [4].

2. Exothermic reactions of nitration and oxidation,
3. Reactivity of the liquefied product,
4. Explosive properties of nitro compounds.

Oxidation can be suppressed by adding molten salts to the reacting compounds, according to Albright [101]. Sodium nitrate is the most suitable salt probably breaking the reaction chain. Matasă summarized his work in a diagram – Fig. 33 based on the nitration of cyclohexane with nitric acid in a vapour phase. It gives the zone of nitration against the time of contact, molar ratio and reaction temperature.

The dangerous zone is divided into two parts: upper (1) in which pyrolysis mainly occurs and is manifested by rapid variations of pressure and explosions, and lower (2) where the reaction proceeds quietly, but the products are liable to react further. He also indicated a practical criterion of the reaction: the colour of the products. Yellow colour characterized the normal course of the reaction,

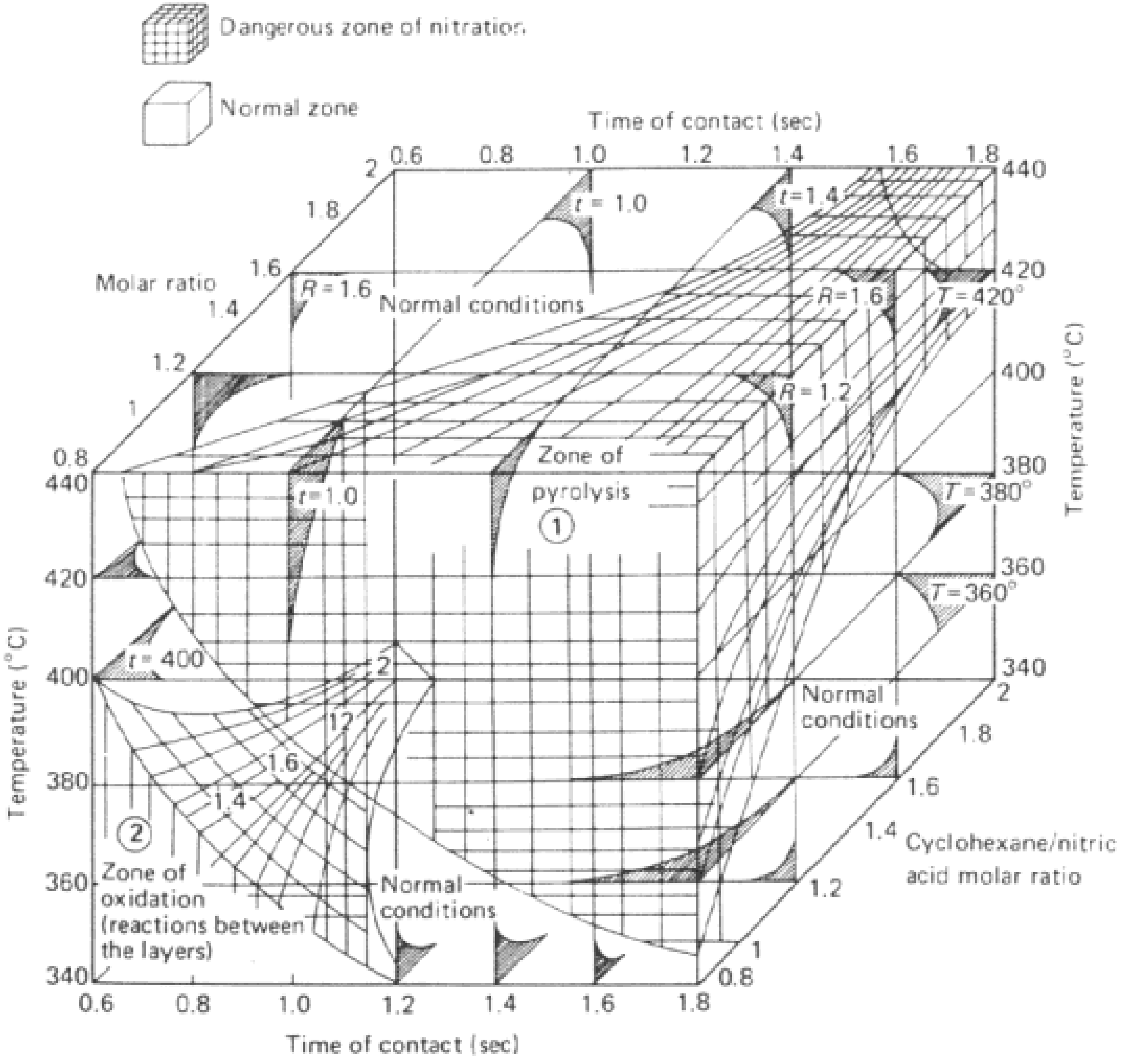


FIG. 33. Variation of the zone of nitration of cyclohexane according to Matasă [98].

whereas green and brown indicate a reaction between liquid products and too high temperature of the reaction or a too long contact time.

The molar ratio hydrocarbon–nitric acid was of the order of 10:1 and if oxygen was added it was up to 4 moles in quantity.

To reduce the cost of nitration (and probably to increase safety) hydrocarbon and nitrogen were used instead of pure hydrocarbon [6b]. The addition of oxygen to the system may offer the advantage of increasing the amount of heat evolved during nitration and thus helping to keep the reaction in adiabatical conditions. The oxygen helps in obtaining valuable oxidation products such as alcohols, aldehydes, ketones and carboxylic acid [6b].

According to the same source, at 395°C conversion of propane increased from 20% to 76% based on nitric acid used while the ratios of oxygen, propane and nitric acid changes from 0:11:1 to 3.8:11.4:1.

1,2-DINITROETHANE (Vol. I, p. 594)

Very little attention has been paid to this compound owing to its low stability. However, one paper can be mentioned which deals with the problem of conformation through the measurement of dipole moment [230]. The conclusion was that free rotation of NO_2 is most probable around the C–C axis. 1,2-Dinitroethane can be used as a source of hydroxylamine [231] and caprolactam from cyclohexanone [232].

2,2-DINITROPROPANE

This compound created a certain interest due to the presence of geminal nitro groups. The symmetry of the compound was examined by Buczkowski and Urbański [248] by infra-red and Raman spectra. The authors came to the conclusion that the compound belongs to C_{2v} symmetry (according to Herzberg classification).

NITROALKENES (Vol. I, pp. 81, 95, 99, 107)

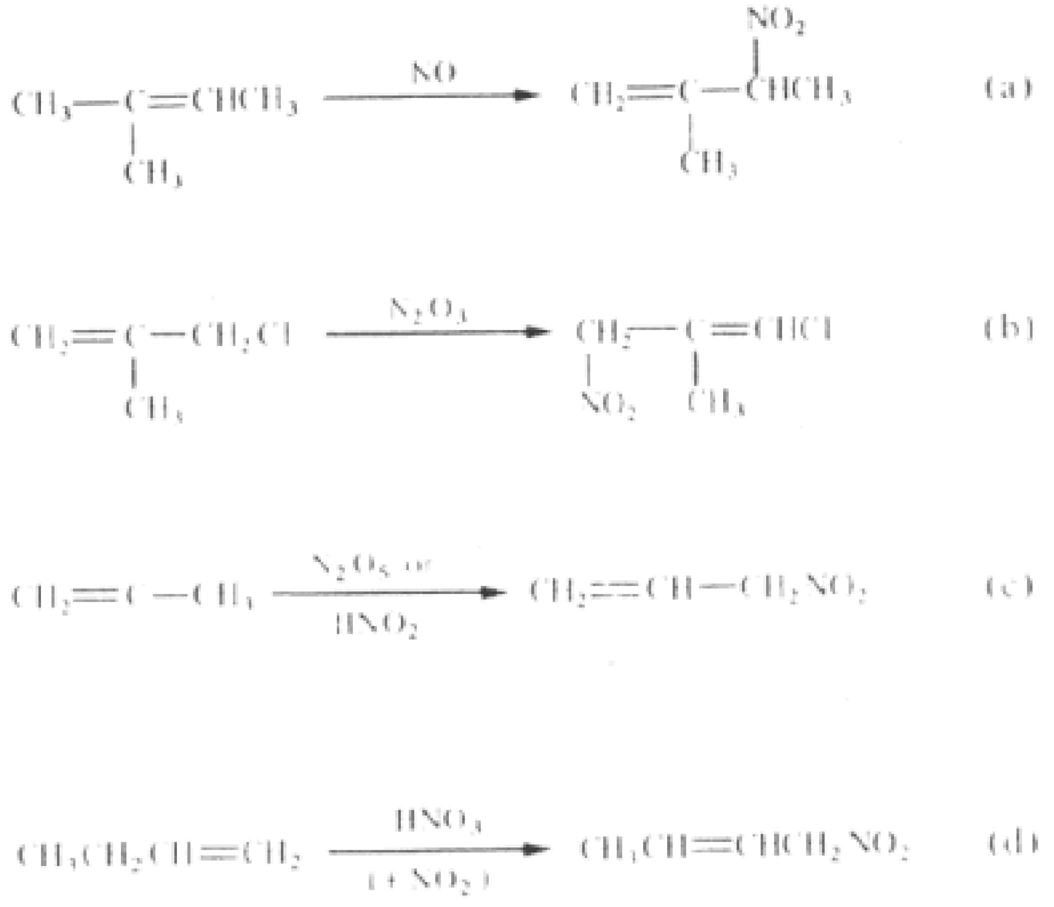
Nitroalkenes form an interesting group of compounds: they contain a strongly activating nitro group and a double bond which, under the influence of the nitro group, shows a particular activity.

The increasing interest in nitroalkenes is manifested by two monographs: those of Perekalin [8] and Novikov [9]. Some review papers dealing with the properties of nitroalkenes have also appeared [102].

Methods of Preparation of Nitroalkenes

The methods of preparation of nitroalkenes can be divided into several groups [6, 8, 9].

1. Action of nitrogen oxides and nitric acid on unsaturated hydrocarbons viz. NO (in the presence of catalytic amounts of NO_2), N_2O_3, N_2O_4, N_2O_5, HNO_3. Nitroalkenes are accompanied here by vicinal dinitro compounds, nitronitrites, nitronitrates, nitro–nitroso compounds, nitrosonitrites, nitrosonitrates, dinitrites and nitronitrates [6, 8, 9] (also Vol. I, pp. 96, 594). Some mononitro alkenes can also be formed. Here are a few examples taken from the above monographs and [12]:



$$CH_3{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CHCH_3 \xrightarrow{NO} CH_2{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}\overset{\displaystyle NO_2}{\overset{|}{C}}HCH_3 \qquad (a)$$

$$CH_2{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}CH_2Cl \xrightarrow{N_2O_3} \underset{\displaystyle NO_2}{\underset{|}{CH_2}}{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CHCl \qquad (b)$$

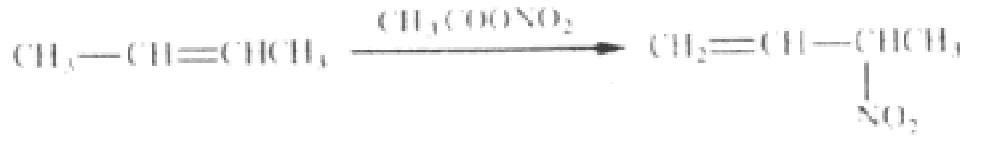
(21)

$$CH_2{=}C{-}CH_3 \xrightarrow[HNO_2]{N_2O_5\ or} CH_2{=}CH{-}CH_2NO_2 \qquad (c)$$

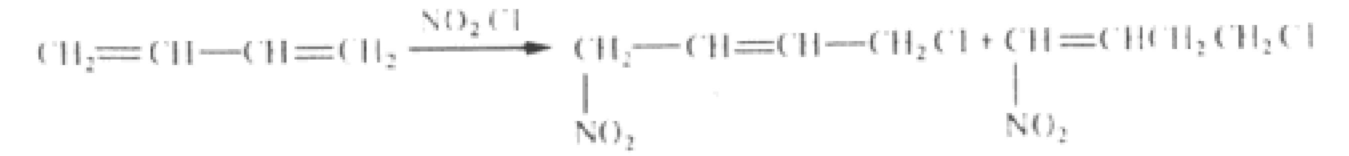
$$CH_3CH_2CH{=}CH_2 \xrightarrow[(+NO_2)]{HNO_3} CH_3CH{=}CHCH_2NO_2 \qquad (d)$$

Reaction (21a) needs some explanation as regards its mechanism. Nitrogen oxide is disproportionated into nitrogen and nitrogen dioxide and the latter acts as the nitrating agent.

Acetylnitrate and nitronium chloride can also produce nitroalkenes while acting on alkenes:



$$CH_3{-}CH{=}CHCH_3 \xrightarrow{CH_3COONO_2} CH_2{=}CH{-}\underset{\displaystyle NO_2}{\underset{|}{C}}HCH_3 \qquad (22)$$



$$CH_2{=}CH{-}CH{=}CH_2 \xrightarrow{NO_2Cl} \underset{\displaystyle NO_2}{\underset{|}{CH_2}}{-}CH{=}CH{-}CH_2Cl + \underset{\displaystyle NO_2}{\underset{|}{CH}}{=}CHCH_2CH_2Cl \qquad (23)$$

The reaction of V. Meyer can also be used: for example, allyl bromide reacts with silver nitrite to yield 3-nitropropenel: $CH_2 = CH{-}CH_2NO_2$.

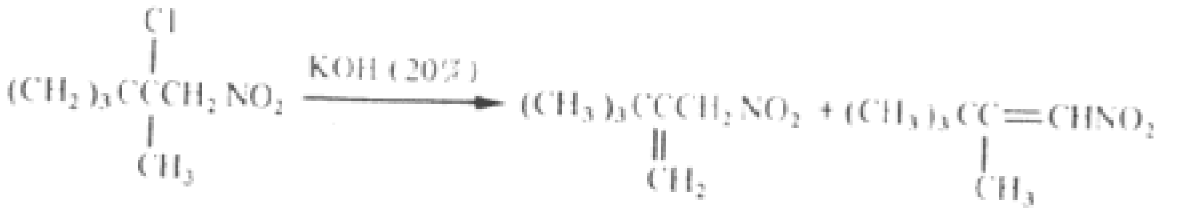
2. Dehydration of nitroalcohols and their esters. Nitroalcohols obtained by the Henry method can be readily dehydrated with phthalic anhydride (Vol. I, p. 596).

In some instances it has been found that esters can give purer substances [103]. According to Gold [104a] nitroalkenes can be obtained in good yield (up to 85%) by vapour phase catalytic cleavage of esters of nitroalcohols, for example:

$$CH_3COOCH_2CH_2NO_2 \xrightarrow[(300-400^\circ C)]{\Delta} CH_2{=}CHNO_2 + CH_3COOH \qquad \textbf{(24)}$$

As a catalyst calcium–magnesium phosphate appeared to be the best.

Dehydrohalogenation of halogenonitro alkanes, for example (25):

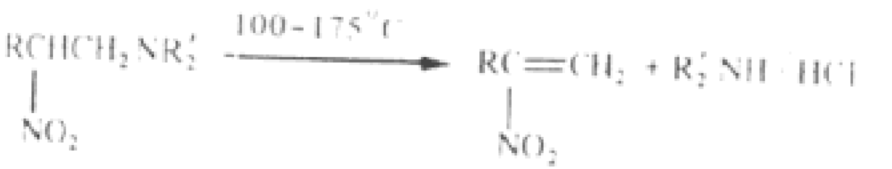


$$(CH_2)_3\overset{Cl}{\underset{CH_3}{C}}CH_2NO_2 \xrightarrow{KOH\ (20\%)} (CH_3)_3C\underset{CH_2}{C}CH_2NO_2 + (CH_3)_3C\underset{CH_3}{C}{=}CHNO_2 \qquad \textbf{(25)}$$

Vinyl product (I) was mainly formed.

Denitration of polynitroalkanes with potassium hydroxide can also produce nitroalkenes (Vol. I, p. 98, IX–X).

Deamination of Mannich bases hydrochlorides can also furnish nitroalkenes [9] through pyrolysis (26):



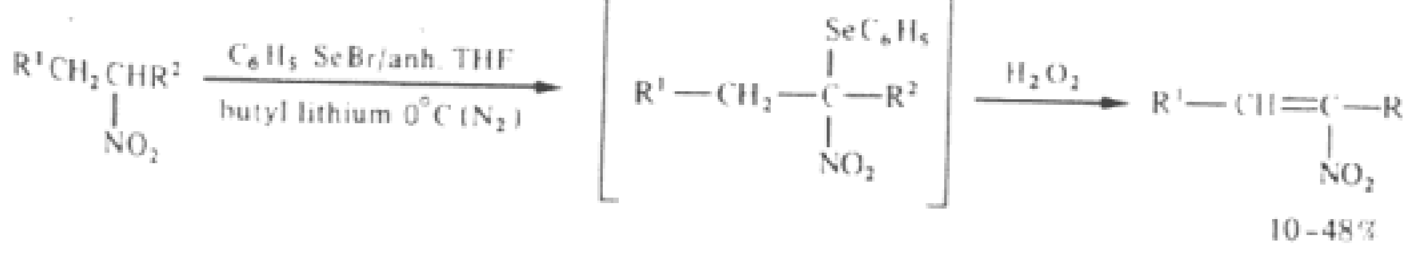
$$R\underset{NO_2}{CH}CH_2NR'_2 \xrightarrow{100-175^\circ C} R\underset{NO_2}{C}{=}CH_2 + R'_2NH \cdot HCl \qquad \textbf{(26)}$$

For more information about the variety of reactions leading to nitroalkenes see [8, 9].

Recent Reactions of Formation of Nitroalkenes

Dehydrogenation of nitroalkenes was recently reported by Japanese workers: Sakakibara *et al.* [105]. The reaction consists in acting with phenylselenenyl bromide on nitroalkanes in the presence of butyl-lithium. Nitrophenylselenoalkanes are formed in the first instance, and decompose under the action of hydrogen peroxide (27):

(27)

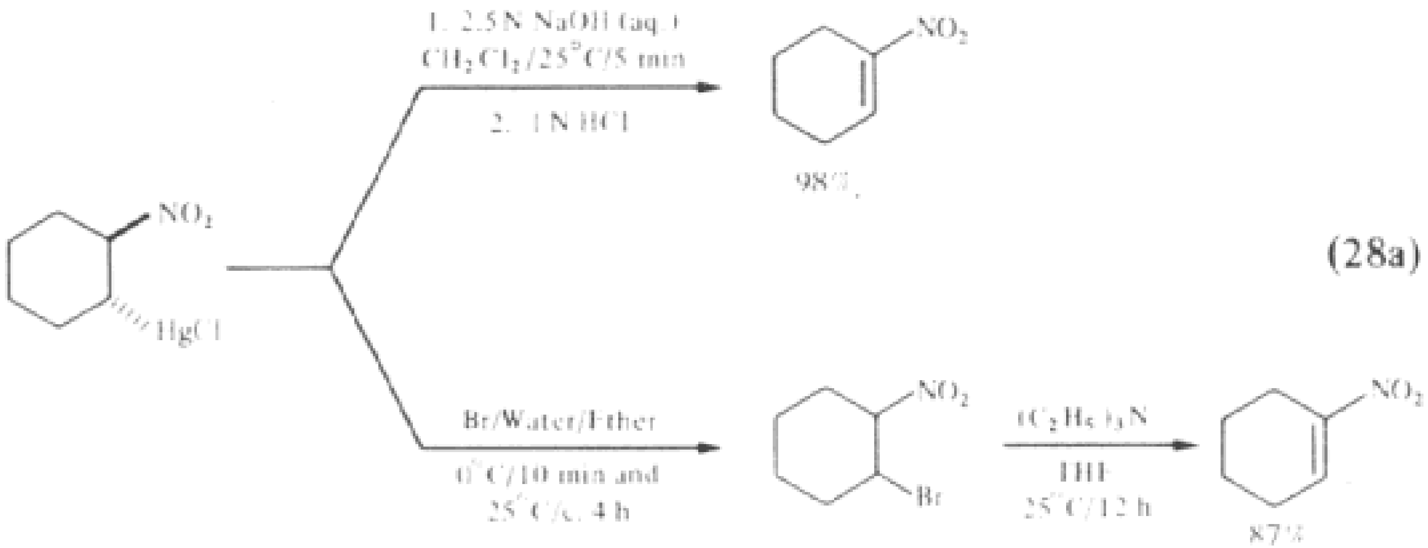


$$R^1CH_2\underset{NO_2}{CH}R^2 \xrightarrow[\text{butyl lithium } 0^\circ C\ (N_2)]{C_6H_5\ SeBr/\text{anh. THF}} \left[R^1-CH_2-\overset{SeC_6H_5}{\underset{NO_2}{C}}-R^2\right] \xrightarrow{H_2O_2} R^1-CH{=}\underset{NO_2}{C}-R^2$$

10–48%

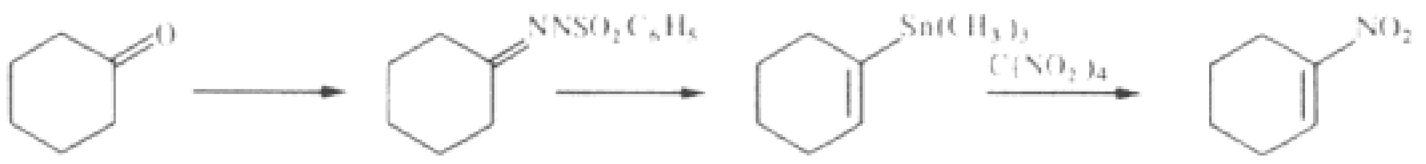
Nitroalkenes resulted with yields of 50–83%.

Corey and Estreicher [106] developed new methods for the preparation of conjugated 1-nitrocycloalkenes (28). They used nitromercurial chlorides (28a) obtained by Bachman and Whitehouse [107] or vinyl stannanes. The latter were transformed into conjugated nitroalkenes by the action of tetranitromethane (28b):

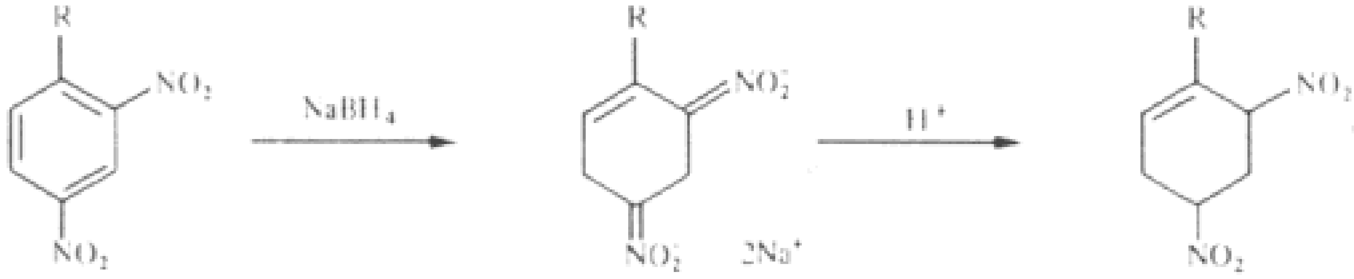


(28a)

(28b)



Severin and co-workers [108] gave an original method for the preparation of dinitrocyclohexene derivatives by acting with sodium borohydride on aromatic dinitro compounds (29)



(29)

R = Cl, Br, CH₃

Chemical Properties of Nitroalkenes

Nitroalkenes are pale yellow coloured liquids with boiling points slightly lower than those of corresponding nitroalkanes. They are lacrimatory substances with a pungent odour. They produce irritation of the mucous membranes, respiratory tract and skin.

They are susceptible to many addition reactions and anionic polymerization.

Addition Reactions

Addition of water and hydrogen sulphide yield alcohols and mercaptans respectively. Addition of alcohols and mercaptans yields nitroethers and nitrothioethers respectively. Halonitroalkanes are formed by the addition of halogens or hydrohalogenides. Nitrogen oxides yield dinitroalkanes. Nitronium chloride and nitrosyl chloride furnish nitrochloroalkanes. The addition of cyanohydride yields nitrocyanoalkanes. Amino nitroalkanes were obtained by adding ammonia or amines. Grignard reagent with a subsequent hydrolysis yielded dialkylhydroxylamine or nitroalkanes. Michael addition to nitroalkenes was also recorded. Nitroalkenes are important philodienes in the Diels-Alder reaction [104b].

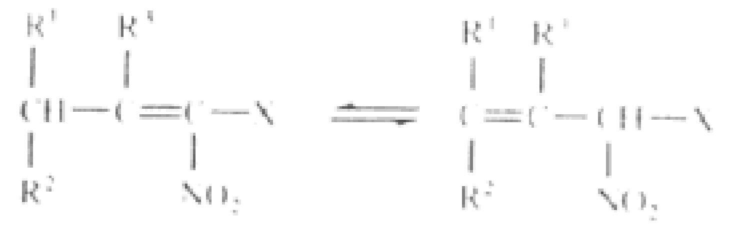
A more detailed description of these reactions is outside the scope of this book but can be found in [1], in monographs [8, 9] and they are mentioned in a review article by Jagur-Grodzinski [109].

Among the recent papers an addition of allilesilan to α-nitroalkenes [110] was described.

A particular kind of addition is the polymerization of nitroalkenes – this will be discussed in a separate paragraph.

Isomerization

The isomerization of nitroalkenes is one of the most interesting properties of these compounds. The isomerization can be depicted by a diagram [102a] (30):

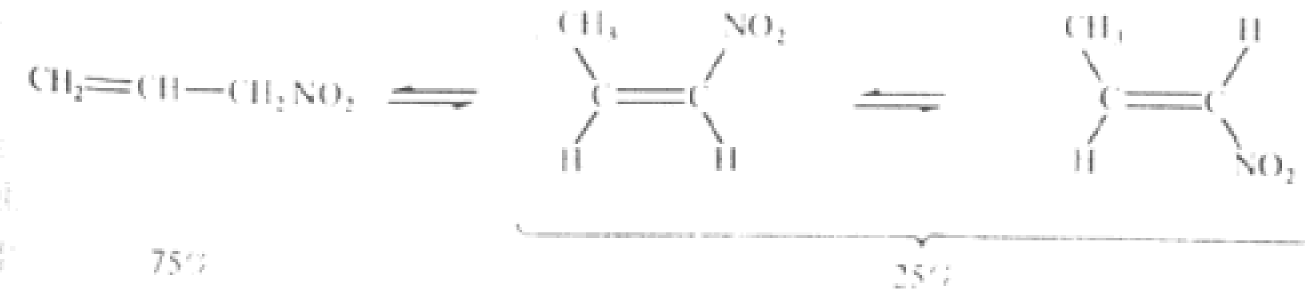


$$CHR^1R^2-CR^3=C(NO_2)-X \rightleftharpoons CR^1R^2=CR^3-CH(NO_2)-X \qquad (30)$$

X can be H, halogen, COOH, CN etc.

Isomerization occurs under the action of catalytic amounts of bases (KOH, $(C_2H_5)_3N$).

Such isomerizations were described by Shechter and Shephard [111], Bordwell and Gerbich [112]. Witanowski, T. Urbański and co-workers [113] examined the isomerization of 3-nitropropene by catalytic amounts of sodium methoxide. By using the NMR technique they established the existence of the equilibrium (31):



(31)

A number of papers by Hesse have appeared on isomerization under the action of bases [114] and on the mechanism of isomerization by Leseticky and Prochazka [115], Piotrowska and Kochany [116], Werkhoff [117].

Reduction of the Double Bond

Reduction of the double bonds in nitroalkenes without the reduction of the nitro group can be carried out with sodium borohydride: when applied to nitroalkenes the nitroalkanes can be obtained (the method of Severin [108b]).

Polymerization

The ease of polymerization of nitroalkenes has attracted the attention of chemists for a long time. In particular the polymerization of nitroethylene has been extensively studied. An excellent critical description has been given by Jagur-Grodzinski [109]. Nitroethylene polymerizes readily in the presence of alkalis. Polymerization is exothermic (21.78 kcal/mol at 20°C) and in the presence of strong alkalis can be explosive.

Secondary and tertiary amines and phosphines have been found to be effective but not very strong catalysts. By polymerizing at −75°C in dimethylformamide high molecular weight linear polymer was obtained. Polymerization has an ionic character.

Poly(nitroethylene) prepared at low temperature is a white fibrous material soluble in dimethylformamide. When polymerization is carried out at room temperature it is a yellowish coloured powder of low molecular weight. Lauenberger [103] found that poly(nitroethylene) obtained by anionic polymerization is of relatively low molecular weight (M = *ca.* 500). He also obtained co-polymers with acrolein or acrylonitrile using tri-*n*-amyloamine as a catalyst at 0°C. The co-polymers were in the form of grains or flakes. He established that nitroethylene cannot be subjected to radical polymerization under the action of benzoylperoxide or 2-azodiisobutylnitrile.

Polymerization of 2-nitro-1-propene is less vigorous (the heat of polymerization is 13.0 kcal/mol at 20°C). The polymer is a viscous liquid or a brittle solid.

The chemical stability of the polymers of both nitroethylene and 2-nitro-1-propene is low. This is partly due to the traces of catalysts present in the polymers which can act as decomposition catalysts. Poly(nitroethylene) turns yellow and then dark brown coloured after a few hours at room temperature and at 60°C respectively. In the latter case it becomes insoluble in organic solvents. According to Farmer [118] poly (nitroethylene) gives a negative 'vacuum stability test' (Vol. II, p. 25) – an explosion occurs at 120°C. Nevertheless the polymer freed from the polymerization catalyst (by boiling in tetrahydrofurane acidified with acetic acid) shows good stability, comparable to that of nitrocellulose.

So far polynitroethylene (and propylene) do not seem to have a practical application [119].

Characteristics of the main nitroalkenes are given in Table 43.

TABLE 43. Physical constants of some nitroalkenes

Compound	Formula	Boiling point (°C)	Specific gravity	UV absorption nm
1-Nitroethylene	$CH_2{=}CH{-}NO_2$	98.5°	1.073	227
2-Nitro-1-propene	$CH_2{=}\underset{\underset{CH_3}{\mid}}{C}{-}NO_2$	57° (100 m kg)	1.0643	225
1-Nitro-1-propene	$CH_3{-}CH{=}CH{-}NO_2$	54° (28 mmHg)	1.0661	229 235

NITROACETYLENES

A few representatives of this group of compounds were recently obtained by Russell *et al.* [122] by acting with lithium acetylides on 2-chloro-2-nitropropane or 2,2-dinitropropane in tetrahydrofurane:

$$\underset{X=Cl,\ NO_2}{RC\equiv CLi + X{-}C(CH_3)_2NO_2} \longrightarrow \underset{20\text{–}53\%}{RC\equiv C{-}C(CH_3)_2NO_2} + LiX \qquad (32)$$

POLYNITRO ALIPHATIC COMPOUNDS (Vol. I, p. 587)

Over the last three decades considerable attention has been given to the search for energy rich propellants and explosives among polynitro aliphatic compounds. An excellent review has been given by Noble, Borgardt and Reed [5] on such compounds.

However, most of the polynitro aliphatic compounds show relatively low stability and high sensitivity and these facts have limited their practical usefulness [119]. The author of the present book will describe only:

(1) general methods of formation of polynitro compounds,
(2) physico-chemical, chemical and explosive properties of the most important compounds for which a practical application can be found or have already become commercial products.

NITRATION OF HYDROCARBONS

The problem of whether the nitration of hydrocarbons can yield dinitro compounds became controversial. According to T. Urbański and Słoń (Vol. I, p. 95) the nitration of hydrocarbons from propane to *n*-heptane at 220–230°C with a great excess of NO_2 can yield viscous oil containing dinitro products (10–22% of the total quantity of products). Grundman and Haldenwanger (Vol. I, p. 84) obtained gem-dinitrocyclohexane when cyclohexane was nitrated at 122°C under pressure of 4 atm. Asigner and Oltay [123] nitrated 1-nitrooctane and obtained a mixture of dinitro products with various positions of the nitro groups. Statistical distribution equal to all positions from $C_{(2)}$ to $C_{(7)}$ (*ca.* 15%) was found.

It seems that the high temperature of nitration applied by Hess and coworkers (Vol. I, p. 86) 410–430°C was too high for dinitro compounds and they decomposed.

The nitration of olefins can sometimes give polynitro compounds [124] (33)

$$CH_3CH{=}C(NO_2)CH_3 \xrightarrow{70\%\ HNO_3} CH_3CH(NO_2)C(NO_2)_2CH_3. \qquad (33)$$

Nitration through the addition of nitric acid or nitrogen oxides to alkenes forms a special chapter. This was described in Vol. I, pp. 96–99 and reviewed [5–9].

Only a few typical reactions will be given here leading to a higher number of nitro groups. Such is the reaction of Novikov and co-workers [124] (34)

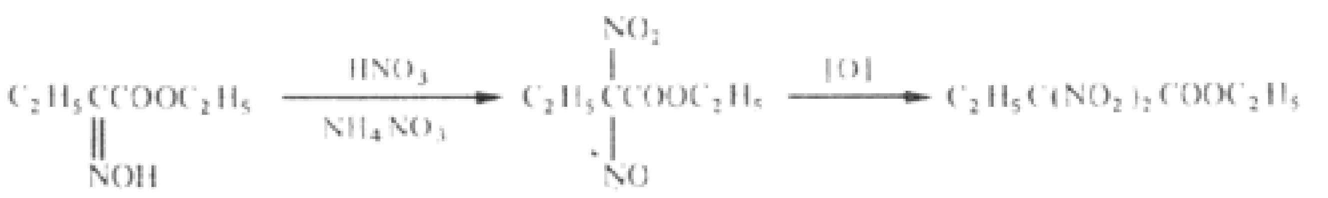
(34)

o-, *m*- and *p*-nitro

Parker, Emmons and co-workers [125] described the method of preparation of trinitroacetonitrile

$$NC{-}CH_2COOH + 3HNO_3 + 3SO_3 \xrightarrow{CCl_4} NC{-}C(NO_2)_3 + CO_2 + 3H_2SO_4. \qquad (35)$$

The oxidation of oximes and other hydroxylamine derivatives followed by the action of nitric acid has also been described [126] (36)



$$\underset{\underset{NOH}{\|}}{C_2H_5CCOOC_2H_5} \xrightarrow[NH_4NO_3]{HNO_3} \overset{\overset{NO_2}{|}}{\underset{\underset{NO}{|}}{C_2H_5CCOOC_2H_5}} \xrightarrow{[O]} C_2H_5C(NO_2)_2COOC_2H_5 \qquad (36)$$

Substitution of Halogen

A modification of the Victor Meyer reaction for long chain hydrocarbons (over C_8) was given by Kornblum (Vol. I, p. 127) [127] and reviewed by the same author. Another modification of the V. Meyer reaction was given as early as 1870 by ter Meer [128]. It applies to 1-nitro-1-haloalkanes. By acting with sodium nitrite on the sodium salt of 1-nitro-1-haloalkanes *gem*-dinitroalkanes are formed. The reaction was reviewed and studied by Hawthorne [129]. The reaction has a number of limitations, more universal is the ingenious method by R. B. Kaplan and Shechter [130] for preparing *gem*-dinitro alkanes from nitroalkanes. It gives positive results where the method of ter Meer fails.

The reaction consists of an oxidation–reduction process of 1-nitroalkanes and can be depicted by scheme (37)

$$R_2C{=}NO_2^- + AgNO_3 + NaNO_2 \xrightarrow[0-30^\circ C]{H_2O} \underset{90\%}{R_2C(NO_2)_2} + 2\,Ag \tag{37}$$

The reaction proceeds smoothly in alkaline aqueous media with silver nitrate and inorganic nitrites. Because of this method Feuer and colleagues [131] were able to obtain α, α, ω, ω-tetranitro alkanes. With four carbon atoms of chain of the nitroalkane, the yield of tetranitro compound could reach 84%.

Electrolytic Methods

The electrolytic coupling of primary and secondary nitroalkanes in basic medium has been reported by Bahner [132]. Another reaction yielding gem-dinitroalkanes was carried out with silver anode [133]. There is a similarity between this reaction and the Kaplan–Shechter method as silver is generated at the anode.

ADDITION REACTIONS

Two addition reactions were applied to produce polynitro aliphatic compounds:

(1) Michael addition.
(2) Diels–Alder addition.

Michael Addition

One of the first papers was by Lambert and Piggott [134] who studied the reaction of α-nitroalkenes (i.e. conjugated nitro compounds) with nitroalkanes:

(38)

Shechter and Cates [135] studied the addition of nitroform to α, β-unsaturated ethers to produce α-trinitromethyl ethers in good yield. Hamel [136] tried Michael addition and Mannich reaction and obtained a number of polynitro compounds.

Diels–Alder Addition

Relatively less attention has been paid to the Diels–Alder reaction producing polynitro compounds. Gold and co-workers [137] successfully used 2,2-dinitromethanol which in the course of refluxing lost water to produce 1,1-dinitroethylene, a very strong dienophile:

$$CH(NO_2)_2CH_2OH \xrightarrow{\Delta} CH_2{=}C(NO_2)_2 + H_2O. \tag{39}$$

OXIDATIVE DIMERIZATION

Shechter and R. B. Kaplan [138] obtained *vic*-dinitroalkanes by the oxidation of primary and secondary alkanes (in alkaline medium) with sodium persulphate (40):

$$R_2C{=}NO_2 \xrightarrow{Na_2S_2O_8} R_2C(NO_2){-}C(NO_2)R_2 \tag{40}$$

α, ω-DINITROALKANES

α, ω-Dinitroalkanes were prepared in a classical way by the V. Meyer method of reacting diiodides and bromides with silver nitrite [5]. The modification of the method by Kornblum (Vol. I, p. 127) [127] using sodium nitrite in dimethylformamide made the compounds more accessible. Feuer, Nielsen and Colwell [139] used α, ω-dinitroalkanes for the Henry reaction with formaldehyde to obtain diols which can be nitrated to obtain compounds with two *O*-nitro groups.

gem-Dinitroalkanes (1,1-Dinitroalkanes)

A considerable number of papers have been published on the properties of gem-dinitroalkanes and their fluorine derivatives by Nazin, Manelis and Dubovitskii [252] and kinetics of their thermal decomposition. The energy of dissociation of the bond C—N was found to be 47–48 kcal/mol.

TRINITROMETHANE (NITROFORM) DERIVATIVES (Vol. I, p. 587)

The last two decades of searching for high energy compounds were dedicated to products with the trinitromethyl group. The growing interest in these compounds is reflected in two symposia [1] and [2] and in an excellent review by L. A. Kaplan [140].

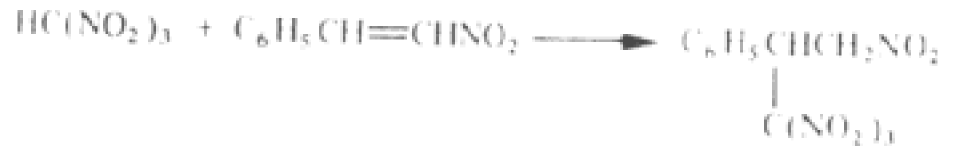
The method of manufacture of nitroform from acetylene found as early as 1900 by Baschieri (Vol. I, p. 587) was described by Orton and McKie [141]. It became possible to convert one of the carbons of acetylene to nitroform through a mercury catalysed oxidation–nitration process with nitric acid. Nitroform is an intermediate product of nitration and yields tetranitromethane under the action of excess nitric acid (Vol. I, p. 594). The method was developed during World War II by Schultheiss [142] and Schimmelschmidt [143] on a large laboratory scale with the aim of producing tetranitromethane. Later the industrial scale method for the manufacture of nitroform was created by Wetterholm [144] (and is described below).

Properties of Nitroform

Trinitroalkanes deriving from nitroform have a low intensity absorption band at *ca.* 280 nm and with hydrazine give a strong absorption at 350 nm. This fact can serve to spectrophotometric analysis [145, 146].

Three electron accepting groups in nitroform produce very strong acid properties. Its pK_a is 0.1 [146].

Nitroform is a nucleophile and can be added to nitroalkenes at low temperature (*ca.* 0°C) in methanol with a good yield. This was done by the pioneering work of Novikov and co-workers [246, 247] and L. A. Kaplan and Hine [147], for example (41):



$$HC(NO_2)_3 + C_6H_5CH{=}CHNO_2 \longrightarrow \underset{\displaystyle C(NO_2)_3}{\underset{|}{C_6H_5CHCH_2NO_2}} \qquad (41)$$

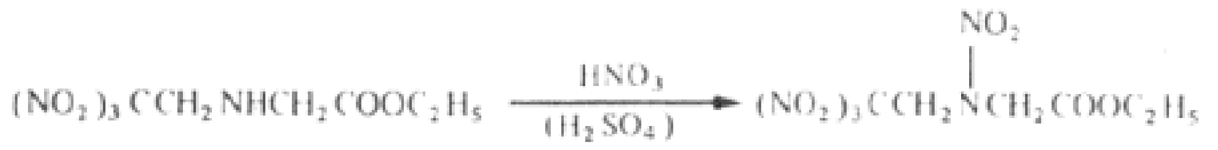
Addition to carbonyl compounds is an important reaction, for example, nitroform with formaldehyde yields 2,2,2-trinitroethanol (Vol. I, p. 588) [148]. As previously mentioned (Vol. I, p. 588) the reaction is strongly exothermic. According to Wetterholm [153] it evolves 8.56 kcal/mol. The next step is the Mannich reaction which offers synthetically valuable trinitromethyl amines and their derivatives. The simplest Mannich base is made of nitroform, formaldehyde and ammonia:

$$(NO_2)_3CCH_2NHCH_2C(NO_2)_3 \qquad \textbf{II}$$

$$(NO_2)_3CCH_2\underset{\displaystyle NO_2}{\underset{|}{N}}CH_2C(NO_2)_3 \qquad \textbf{III}$$

Product II is unstable and can decompose on standing but after nitration, III shows a much better stability [149]. This observation is in agreement with that of Feuer and Swarts [150] and in the work of Feuer, Bachman and co-workers [151] who described reactions of nitroform with formaldehyde and amino acid esters to form *N*-trinitroethylamino acid esters.

The products were unstable, but after nitration stable *N*-nitro compounds resulted (42):



$$(NO_2)_3CCH_2NHCH_2COOC_2H_5 \xrightarrow[(H_2SO_4)]{HNO_3} (NO_2)_3CCH_2\overset{\displaystyle NO_2}{\overset{|}{N}}CH_2COOC_2H_5 \qquad (42)$$

Wetterholm [153] reacted 2,2,2-trinitroethanol with urea to obtain *N,N'*-bis (trinitroethyl) urea ('DiTeU') (IV) a new strong explosive, near to Cyclonite with regard to its power.

$$(NO_2)_3CCH_2NHCONHCH_2C(NO_2)_3$$

m.p. 191°C

IV

It is described on – p. 259, reaction (56) [250].

Another interesting and new approach to using 2,2,2,-trinitroethanol as an explosive was given by Japanese authors: Shiino, Fujiwara and Kusakabe [214].

Frankel [152] described a number of Michael type additions of nitroform to unsaturated compounds. The most interesting was that of addition to nitroethylene.

Ville [234] also described some Mannich bases, their *N*-nitro derivatives and acrylic ester of trinitroethanol. He also obtained the product of addition of nitroform to acrylic esters.

The interesting properties of mercuric salt of nitroform were extensively studied by Novikov and co-workers [9a].

They described (among other reactions) the use of it for the mercuration of aromatic and heterocyclic compounds and the addition of mercuric salt to alkenes and their derivatives.

The thermal decomposition of nitroform and some of its fluorine derivatives were extensively studied by Mazin, Manelis and Dubovitskii [252, 253].

They obtained ortho-esters of 2,2,2-trinitroethanol: such as the orthoformate (TNEOF) (V) and orthocarbonate (TNEOC) VI by reacting 2,2,2-trinitroethanol with chloroform and carbontetrachloride respectively in the presence of anhydrous ferric chloride. The yields were 74% and 89% respectively.

$HC[OCH_2C(NO_2)_3]_3$	$C[OCH_2C(NO_2)_3]_4$
V	**VI**
m.p. 128°C	m.p. 161°C

The substances appear to be of good stability. They are soluble in polar solvents. The saturated solutions of V and VI in nitromethane are 1.53 and 1.48 respectively. Their oxygen balance is +0.10% and +0.13% respectively.

The substances show very low sensitivity to impact (they do not explode when 5 kg weight was dropped from 50 cm).

Data on the explosive properties of solutions of both substances in nitromethane and nitroethane are given in Table 44.

TABLE 44. Explosive properties of TNEOF and TNEOC with nitroalkanes

Composition		Density g/cm^3	Detonation velocity m/s
TNEOF Nitromethane	50 50	1.356	7075
TNEOF Nitromethane	77.1 22.9	1.533	7575
TNEOC Nitromethane	69.7 30.3	1.480	7350
TNEOF Nitromethane	77.0 23.0	1.496	7440

Manufacture of Nitroform

The manufacture of nitroform from acetylene was described by Wetterholm [144]. The flow-sheets of the process are given in Figs 34 and 35.

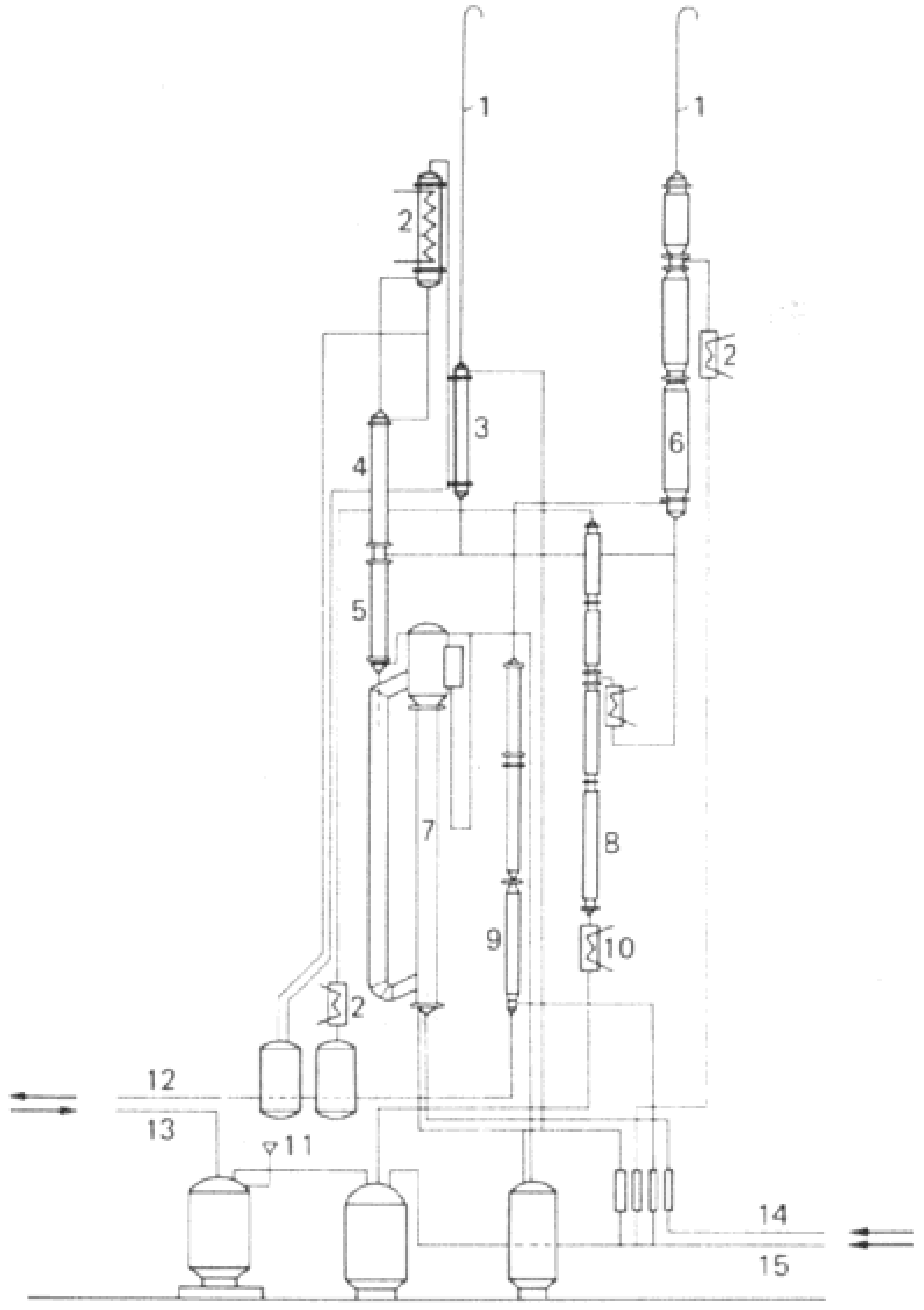
Figure 34 depicts a nitrator where the oxidation–nitration takes place combined with a recovery system for the large amount of nitrogen oxides evolved.

Figure 35 presents a distillation system consisting of fractionating towers and an evaporator.

The equipment includes a concentration of dilute nitric acid formed in the course of the reaction. This is a standard procedure and is not included in the figures.

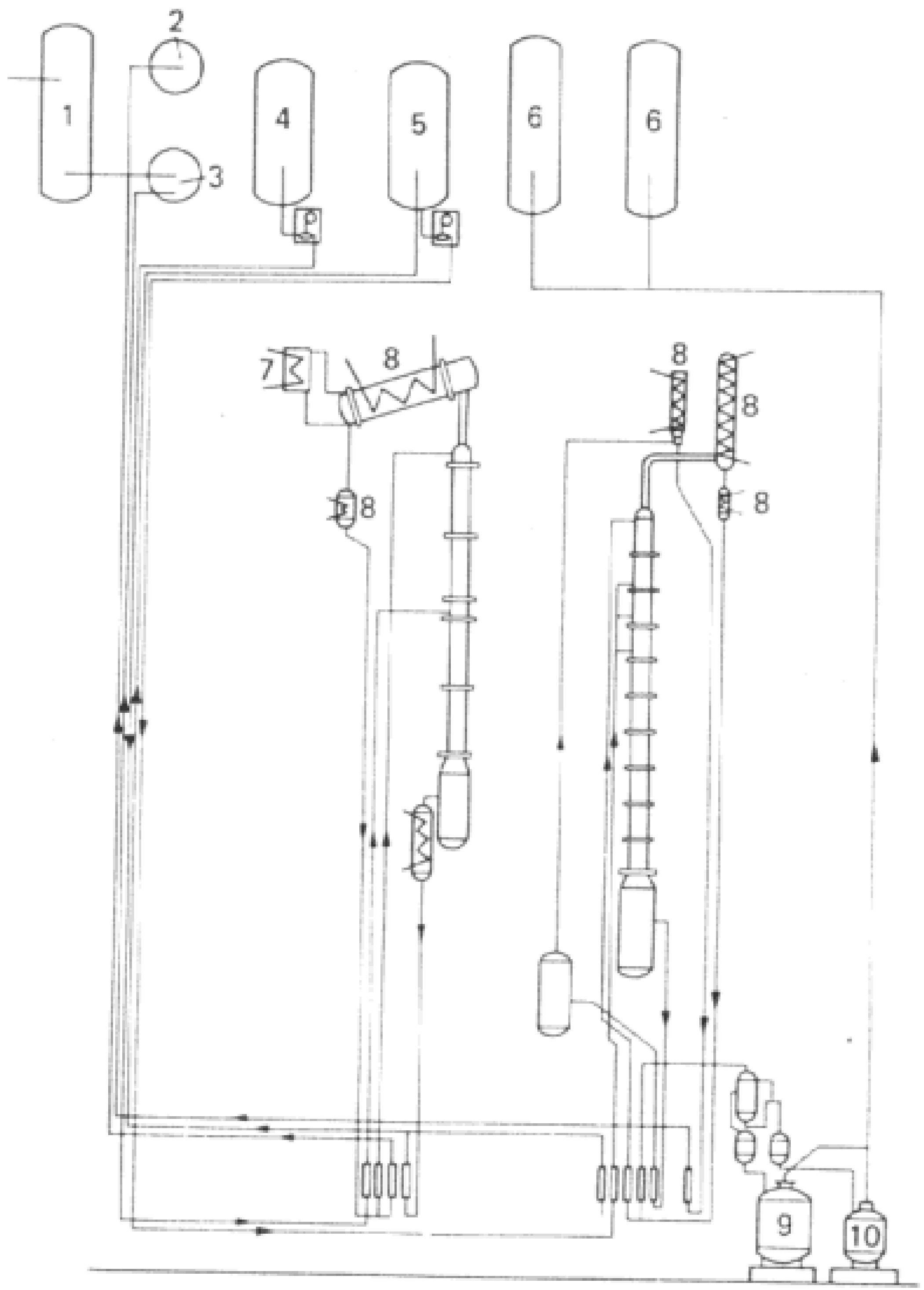
The reaction of nitration is carried out at 45–48°C. From the overflow the products of the reaction go to a stripper where they are freed from nitrogen oxides with air in a countercurrent with cold nitric acid at −15°C. The scrubbing acid is used as part of the acid feed. The gases generated during nitration consist of CO_2, CO, nitrogen oxides and some nitroform. The gases pass through a hot scrubber which retains nitroform. Next is a packed tower where pure N_2O_4 is condensed in a cooler. The waste gases are composed of 76% CO_2, 12% CO, 6% N_2, 6% HNO_3.

The extraction of nitroform from a strong nitric acid consists of two steps:



1 Waste gases
2 Cooling liquid
3 Cold scrubber
4 N_2O_4 distillation
5 Warm scrubber and stripper (N_2O_4)
6 N_2O_4 scrubber
7 Nitrator
8 Bleaching tower
9 Nitrogen oxide stripper
10 Water
11 Catalyst
12 Nitration solution out
13 Nitric acid in
14 Acetylene
15 Air in

FIG. 34. Production of nitroform. Nitration system according to Wetterholm [138].



1 Dilute HNO_3
2 Conc. HNO_3
3 Dilute HNO_3 from dist. III
4 Nitrating solution
5 Residue from dist. I
6 Nif-solution from dist. II
7 Cooling liquid
8 Water
9 Dist. II Nif in water
10 Dist. II Water in Nif

FIG. 35. Production of nitroform (Nif). Distillation system according to Wetterholm [138].

(1) Distillation of the acid until the composition reaches the minimum azeotrop. Nitroform does not distil during this period.
(2) Addition of water and distillation of nitroform with water.

The overall yield of transformation of acetylene to nitroform is *ca.* 74%.

TETRANITROMETHANE (TNM) (Vol. I, p. 588)

There is an increasing interest in tetranitromethane as a source of energy rich explosives and this is manifested by a number of papers related to the physical and chemical properties of the compounds. An excellent review on TNM was given by Altukhov and Perekalin [156].

Physical and Physico-chemical Properties of TNM

The setting point is +13.75 [157a], +14.2 [157b] (an incorrect figure was given in Vol. I, p. 588); boiling point 126°C [157]; specific gravity d_4^{15} = 1.6484, d_4^{30} = 1.6218, mol. refraction MR_D = 31.39 (calculated 29.30) [158].

The ultraviolet spectrum is manifested by the main band at 280 nm, the infrared spectrum has two strong bands 1618 and 1266 cm^{-1} corresponding to asymmetric and symmetric vibrations respectively, and a number of less prominent bands at 1645, 1439, 1370, 990 and 973 cm^{-1} [159]. Examination of the infrared spectra of TNM at different temperatures (−40° to −126°C) [160] indicated that TNM exists in two crystalline forms with their transition point at −99.8°C.

The mobility of one nitro group of TNM suggested originally that one nitro group possesses a different structure from the others, for example, the nitrite or peroxy structure. This proved to be wrong and it has now been firmly established by X-ray analysis that TNM possesses a perfectly symmetrical structure [161] – Fig. 34. This was substantiated by dipole moment measurement which has been found to be equal to 0 within the experimental error. Electron diffraction also confirmed the symmetrical structure of TNM [162].

Quantum chemical calculation was carried out by Shlyapochnikov and Gagarin [163]. It was shown that the electron increased at the oxygen atoms of the nitro groups of TNM and was reduced at the nitrogen and carbon atoms. This is marked in Fig. 36.

The energy of formation of TNM is according to different authors 4.7–8.9 kcal/mol and enthalpy of formation −18.5 kcal/mol. [156]. Heat of decomposition – equation (43)

$$C(NO_2)_4 \longrightarrow CO_2 + 3O_2 + 2\,N_2, \tag{43}$$

is according to various sources 89.6–102.9 kcal/mol [156]. The energy of the C – N bond was calculated: 38.2–39.3 kcal/mol [164, 165].

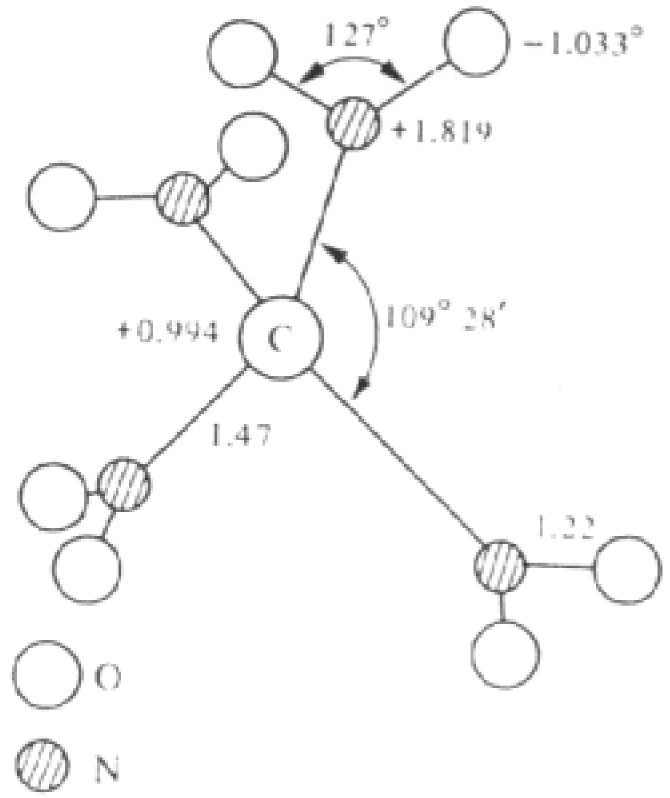


FIG. 36. Structure of tetranitromethane [156].

Chemical Properties (Vol. I, p. 589)

The most important and unique property of TNM is the perfect symmetry of the compound, absence of polarity and identical properties of all four nitro groups. In spite of it TNM can yield the nitronium cation NO_2^+ and trinitromethyl anion $C(NO_2)_3^-$ under certain conditions. Also the existence of corresponding ionic pairs is possible as well as the formation of radicals $NO_2^{\cdot}$ and $C(NO_2)_3^{\cdot}$.

As a rich compound of NO_2 groups, TNM shows strong electron accepting properties and several complexes of charge-transfer character are known which can further react to yield nitroaryls, arylnitroalkenes, α-nitroketones, tetranitroalkanes and dinitroisoxazolidines.

Perekalin and co-workers [156, 166, 167] subjected a number of charge transfer complexes formed by TNM to a systematic study using electronic spectroscopy.

Charge-transfer complexes of TNM with unsaturated compounds are particularly characteristic: an intense colour (from yellow to dark red) can detect the presence of double bonds, for example in tautomeric forms (reaction of Ostromyslenskii [168] and Werner [169]). The reaction however, has a limited application, for example, no colour is given by maleic and fumaric acids. Also some compounds without double bonds give the colour. Such are compounds with divalent sulphur. TNM can be applied successfully to detect components in chromatograms.

Most complexes of TNM with unsaturated compounds are weak [170], their enthalpy of formation is of the order of 1.0 kcal/mol.

Perekalin, Altukhov and co-workers carried out an extensive research on addition of tetranitromethane to double bond [255–258].

Altukhov and Perekalin [156] suggested the scheme for the formation of CT complexes between TNM and a donor D:

$$D + C(NO_2)_4 \rightleftharpoons \underset{\text{Transition form}}{D^{+\delta} \cdots {}^{-\delta}C(NO_2)_4} \rightleftharpoons \underset{\text{Complex}}{[D \cdots NO_2]^{+\delta} \cdots {}^{-\delta}C(NO_2)_3} \qquad \textbf{(44)}$$

Nucleophilic Substitution

Hantzsch and Rinkenberger [171] established that TNM can quantitatively be hydrolysed to trinitromethane by potassium hydroxide or potassium ethoxide. However, aqueous concentrated KOH can produce a deeper hydrolysis with the formation of KNO_3, KNO_2 and K_2CO_3 [172]. The reaction of the formation of trinitromethane ('nitroform') from TNM became a standard method of making nitroform used for synthesis of polynitro aliphatic compounds.

TNM reacts with 3–5% aqueous Na_2SO_3 solution [173] (Vol. I, p. 589) and the reaction became the standard method of removing TNM from TNT.

An important reaction is that of halogenides of potassium, rubidium and caesium in dimethyl formamide yielding halogenotrinitromethane [174, 175]:

$$C(NO_2)_4 \xrightarrow[-KNO_2]{KX} XC(NO_2)_3 \qquad \textbf{(45}$$

$$X = Cl, Br, F$$

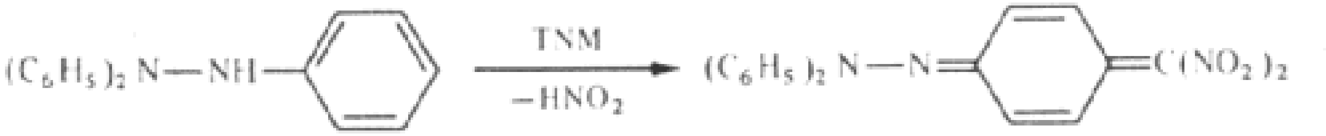
A similar chlorination can be carried out by chloramines [176].

Nitrosation of Tertiary Amines

Schmidt and co-workers [172, 177] obtained *N*-nitroso derivatives of tertiar amines by acting with TNM on the amines in pyridine or in acetic acid.

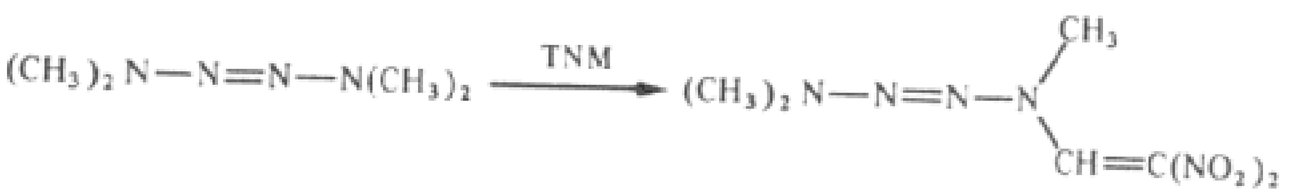
gem-Dinitromethylation

TNM in the presence of oxidizing agents can introduce gem-dinitrometh group, for example, triphenylhydrazine and diphenylhydrazine can react accor ing to scheme (46) [178] and (47) [179]:


(4

$$(C_6H_5)_2N{-}NH_2 \xrightarrow[-HNO_2]{TNM} (C_6H_5)_2N{-}N{=}C(NO_2)_2 \qquad \textbf{(4}$$

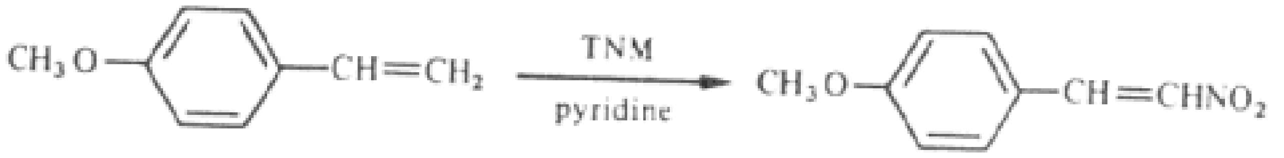
An interesting reaction was reported on the action of TNM on tetramethyltetrazen [180] (48):



(48)

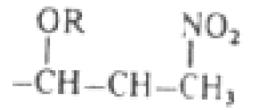
Nitration

TNM is a nitrating agent in alkaline medium. Schmidt and co-workers [181] succeeded in nitrating compounds such as arylalkanes with the double bond conjugated with those of the aromatic ring (49)



(49)

In the presence of methanol and ethanol the reaction leads to the formation of α-methoxy- and ethoxy β-nitro compounds:



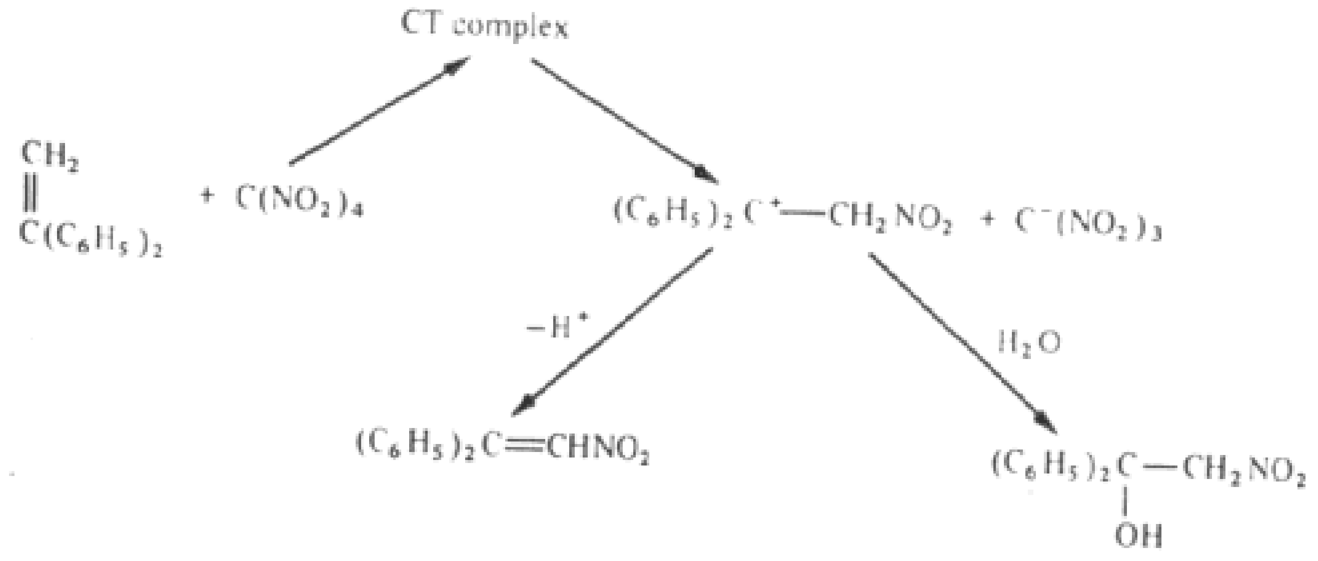
$$-\underset{\text{OR}}{\text{CH}}-\underset{\text{NO}_2}{\text{CH}}-\text{CH}_3$$

(R = CH_3 and C_2H_5 respectively).

It is important to note that non-conjugated aralkenes are not nitrated with TNM.

An important contribution to the reaction of TNM with alkenes, aralkenes and dienes was given by Altukhov and Perekalin [156]. As an example the reaction of 1,1-diphenylethylene with TNM is given.

Here originally a CT complex was formed, TNM being an acceptor and the alkene a donor, next an ionic pair and the cation can react forming nitroalkene or nitroalcohol. The anion yielded nitroform (50).



(50)

Nitroalkenes react in a different way owing to the presence of a strong acceptor:

(51

Recently thebain was nitrated with TNM in methanol [182].

Radical Reactions

A number of papers have been dedicated to homolytic degradation of TN under the action of ultraviolet or γ-rays. The reaction of TNM with bases (e. benzidine) beings with the formation of CT complexes [183] yielding radical anions which in turn are split into radicals (NO_2) and anions (e.g. nitroformanion

Irradiation with γ-rays at 77K yielded radicals: $\cdot NO_2$ and $\cdot C(NO_2)_3$ [184].

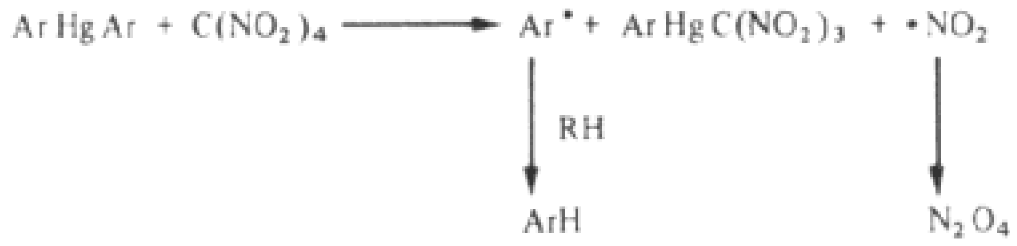
As most nitro compounds TNT inhibits polymerization induced by radiati [185, 186] and free radical polymerization [180–191]. This is rationalized b the fact that TNM is a radicals acceptor. The higher the number of nitro grou in nitro alkanes the stronger the inhibition of polymerization [189].

Ionic Polymerization

TNM is a strong acceptor of electrons and subsequently can initiate ion polymerization. As an example it can serve the polymerization of vinylcarbaz in the presence of methyl methacrylate [192].

Metalorganic Compounds

The reaction of TNM with aryl mercury or tin compounds yielded hydr carbons [193], for example (52):



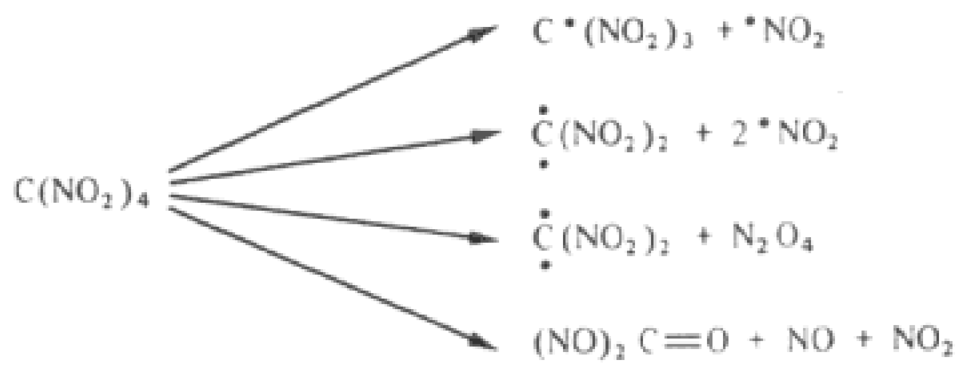
(5

TNM reacts with copper to yield free radicals $\cdot C(NO_2)_3$ and $\cdot NO_2$ [194].

Explosive Properties

According to Roth (Vol. 1, p. 590) TNM can be detonated [195] by usin strong booster of 10.5 g PETN. In a steel tube 21/27 mm diameter it gave 64 m/s. The heat of detonation was found to be 540 kcal/kg [157]. As in m explosives with a high positive oxygen balance the addition of a small amount of organic substances to TNM considerably increases the ease of detonation.

Thermal decomposition of TNM was studied by Nazin and co-workers [196], and is depicted by scheme (53):



(53)

Toxicity (Vol. I, p. 593)

TNM is highly toxic affecting respiratory organs and the nervous system. According to the American Industrial Hygiene Association [197] the permitted concentration in air is 0.001 mg/l. A considerable number of papers have been published on the toxicity and pharmacology of TNM [198–203].

In connection with the health problem a number of physico-chemical methods for the determination of TNM in air and in solutions have been described, such as spectrophotometry, colorimetry of solutions and polarography. They are reviewed by Altukhov and Perekalin [156].

Preparation of TNM (Vol. I, p. 594)

Nitration of acetylene in the presence of mercuric nitrate seems to be the most common method of preparation of TNM. It means that the reaction is not stopped at the stage of the formation of nitroform [144] but the latter is further nitrated under the action of the excess of nitric acid.

According to Meyer [157] the best method of making TNM consists of the nitration of ketene by introducing a stream of it into cold 100% nitric acid. After the reaction is completed the resulting solution is poured into water and ice, and TNM is separated. This method was described by Darzens and G. Levy [204].

HEXANITROETHANE (HNE) (Vol. I, p. 596)

Interest has recently been revived in hexanitroethane and some data on the properties of the substance have been collected by Meyer [66], viz.:

m.p. 147°C
density 1.85 g/cm³, ignition point 175°C

heat of explosion 743 kcal/kg
volume of detonation gases 672 l/kg
Vapour pressure: at 20°C 0.5 millibar
50°C 1.5 millibar
70°C 5.0 millibar
85°C 28.0 millibar

Physico-chemical properties were given by P. Noble and co-workers [239], the oxidizer properties by Frankel and co-workers [240], and heat of formation by Apin, Pepekin and co-workers [241]. The standard enthalpy of formation was found to be 20.0 ± 1.0 kcal/mol, and in the gas phase 36.9 ± 1.4 kcal/mol. The enthalpy of sublimation is 16.9 ± 0.4 kcal/mol.

An important finding has been described by Krien, Licht and Trimborn [242], who discovered that HNE changes its crystalline structure at around 16 +16°C. The low temperature modification is stable in the range from −83° to 19°C. The low temperature form is rhombic and has density 2.21 g/cm³ whereas that of ambient temperature is cubic and possesses the density given above (1.85). The transition is reversible and the heat of transition ΔH is 9.87 cal/kg. Specific heat at 16°C is 0.26 kcal/kg.

It was found [242] on a differential scanning calorimeter that the endothermic crystal change begins at +17°C, sublimation at +127°C followed by exothermic decomposition (142°C) and endothermic melting at 147°C.

The substance has a waxy appearance and can be readily pressed but at 0°C and below that temperature some cracks can appear due to the change of the crystal habit.

Thermal decomposition of HNE was studied by H. P. Marshall and co-worker [243], Nazin, Manelis and Dubovitskii [244]. They gave the following value for the energy of activation: $E = 37.8$ kcal/mol and log B = 18.5 [243] an 35.8 kcal/mol and log B = 17.3 (for the interval of temperatures 90–135°C [244].

NITROCARBOXYLIC ACIDS

Nitrocarboxylic acids were reviewed by Novikov and co-workers in their ri monograph [9]. Although not possessing explosive properties they may be value for the synthesis of amino acids, surface active agents and ingredients rocket propellants.

Only a brief outline will be given here, the reader should otherwise cons the monograph [9].

Nitration of fatty acids was first effected by Bous in 1855 [205] who nitrat caprylic acid with nitric acid. Claus and Pfeiffer [206] nitrated stearic acid w nitric acid (d 1.48) in glacial acetic at the solutions boiling temperature. In search for an industrial application for the nitrated saponifiable oils, Radcl and Polychronis [207] nitrated stearic, hydroxystearic, oleic and ricinoleic acids. They found that cold nitric acid had no effect on stearic acid, whereas oleic acid (as should be expected from its unsaturated character) yields nitro-oleic acid along with oleic acid nitrate. Ricinoleic acid in turn gave on nitration nitro-nitrate and nitrate derivatives.

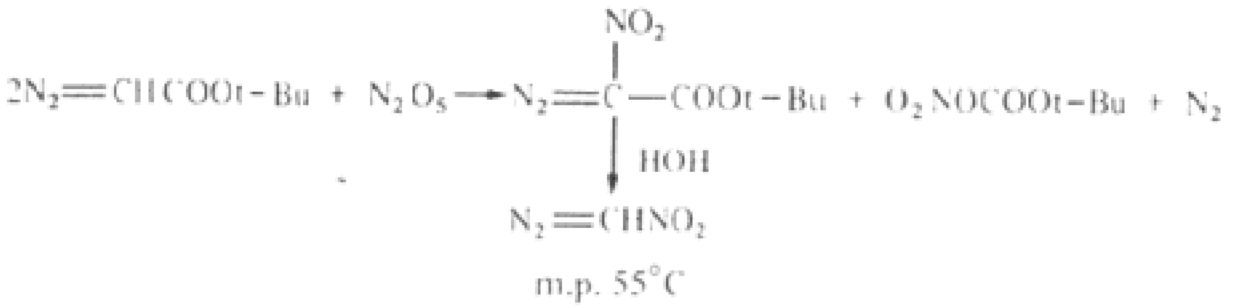
T. Urbański and Biernacki [208] nitrated ethyl *n*-valerate with nitric acid in glacial acetic acid–acetic anhydride at 23 ± 2°C and found that a mixture of 2-, 3- and 4-nitrovalerates was formed in the ratio 0.5:0.7:1. At 63 ± 2°C a certain amount of 1-nitrobutane was formed due to the decarboxylation of the 2-nitrovalerate.

Valeric acid was not nitrated at 23°C and required a minimum temperature of 33 ± 2°C.

The nitration of propionic acid with nitric acid in the vapour phase gave a small yield (5%) of 3-nitropropionic acid according to Hass and Hudgin [209].

NITRODIAZOMETHANES

Interesting nitro derivatives of diazomethane were obtained by Schöllkopf and co-workers. Thus Schöllkopf and Markusch [210] described nitrodiazomethane which was obtained from *t*-butyl diazoacetic ester by nitration with N_2O_5 followed by hydrolysis (54) *see* also Chapter I, p. 30:



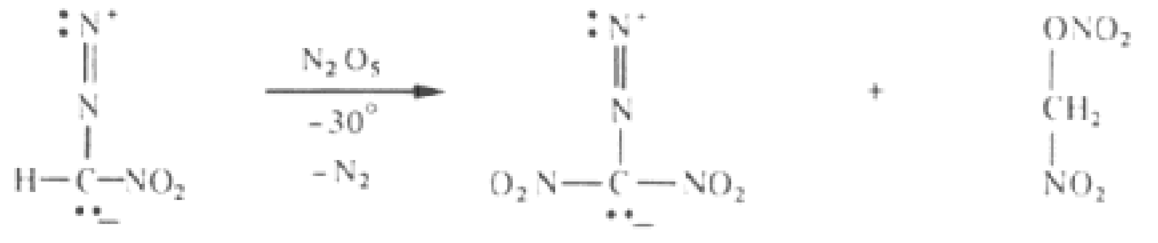
$$2N_2{=}CHCOOt\text{-}Bu + N_2O_5 \longrightarrow N_2{=}\overset{\displaystyle NO_2}{\overset{|}{C}}{-}COOt\text{-}Bu + O_2NOCOOt\text{-}Bu + N_2 \qquad (54)$$

$$\xrightarrow{HOH} N_2{=}CHNO_2$$

m.p. 55°C

Nitrodiazomethane decomposes with HCl in moist ether yielding $ClCH_2NO_2$.

Dinitrodiazomethane was prepared by the action of nitric anhydride on mononitrodiazomethane [211] (55):



(55)

Dinitrodiazomethane
m.p. 65°C d.
42%

No data on explosive properties are available. It appears that the low decomposition temperature renders the compounds of no practical use, but they are certainly of great theoretical interest.

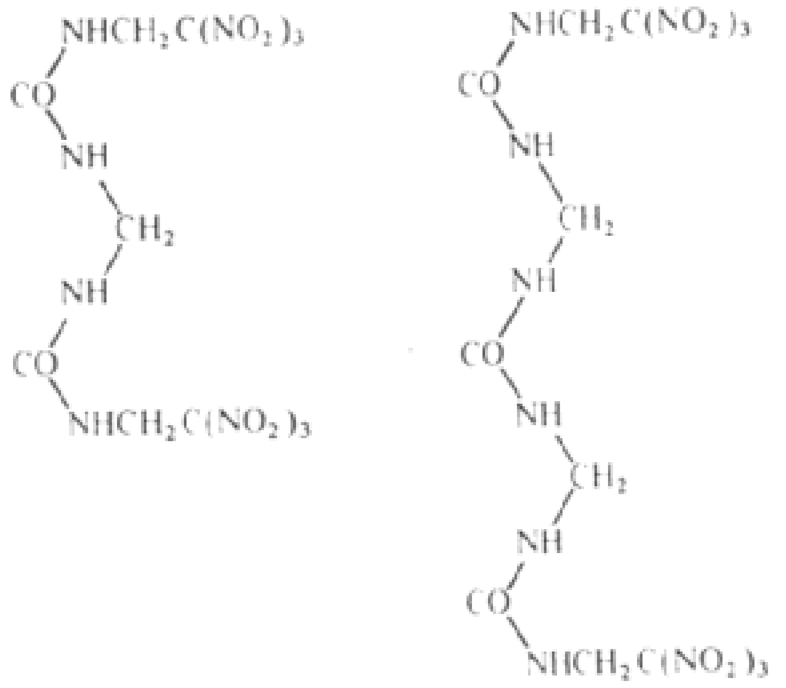
NITRO DERIVATIVES OF UREA

N,N-bis (β,β,β)-Trinitroethyl Urea (IV), p. 247

This interesting substance was obtained by Wetterholm [250] in 1951 by reaction (56):

$$2(NO_2)_3C\,CH_2OH + NH_2CONH_2 \longrightarrow (NO_2)_3C\,CH_2NH\,CO\,NH\,CH_2C\,(NO_2)_3 \qquad (56)$$

DiTeU separated as a white precipitate sparingly soluble in water. Another method consists in reacting dimethylolurea with nitroform [251]. The product is not a single compound: it contains less soluble fractions of di- and trimer, which can be removed by crystallization:



The pure DiTeU has a favourable oxygen balance:

$$C_5H_6O_{13}N_8 \longrightarrow 5\,CO_2 + 3\,H_2O + 4\,N_2. \qquad (57)$$

The explosion enthalpy is 1645 kcal/kg.

The deflagration point is 210°C, the rate of detonation 8000 m/s at density 1.62, lead block 465 cm³. It is less sensitive to impact than RDX.

A pilot plant for DiTeU, producing 30 kg/hr DiTeU, exists in Sweden at Nitro-Nobel A.G. A great advantage of the production is that no spent acid is formed.

NITROSO COMPOUNDS (Vol. I, p. 602)

Nitro-nitroso Alkanes ('Pseudonitroles')

As is known, pseudonitroles are formed by nitrosation of secondary nitroalkanes. Very little interest has been shown to this class of compounds which have been known since the classical work of Victor Meyer in 1873. For early work see [7].

More recently the mechanism for the formation of pseudonitroles and their stereo chemistry has been examined by Noland and Libers [212]. The pseudonitroles can be oxidized to gem-dinitro compounds with air or hydrogen peroxide.

Recently de Boer and Bolsman [213] examined photolysis of 1-nitro-1-nitrosocyclohexane with red light in the absence of oxygen and came to the conclusion that a homolytic fission of C − NO bond occurred at 40°C and generated a radical pair: NO and α-nitrocyclohexyl, Solvolysis occurred in different solvents. In benzene, cyclohexanone was formed as a major product and small amounts of 1,1-dinitrocyclohexane, as well as 1-nitrocyclohexene and nitrocyclohexane.

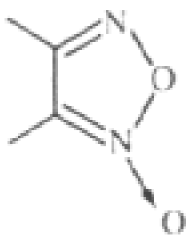
'Hexanitrosobenzene'

As mentioned in Vol. I, p. 603, hexanitrosobenzene now has the accepted structure of 'Benzotrisfuroxane'.

This was confirmed by several physico-chemical methods, such as:

X-ray diffraction [215],
X-ray photoelectron spectroscopy [216],
Vibrational spectroscopy [217],
Laser-Raman study [218],
Nitrogen NMR [219],
Carbon-13 NMR [220].

It should also be pointed out that the substances with a furoxane structure (VII):



VII

possess explosive properties [221–225].

An excellent review on furoxanes has been given by Kaufman and Picard [226].

Nitroenamines

Enamines are an interesting group of compounds, for example VIII

$$(CH_3)_2N\ CH = CH\ NO_2$$

VIII

An excellent review has recently been given by Rajappa [229]. The substances and their properties are outside the scope of the present book.

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APPENDIX

Nitromethane – Aluminium Chloride Complex

Závada, Pankova and Z. Arnold [1] described a complex of nitromethane with aluminium chloride which is a convenient form of the Friedel-Crafts catalyst [2].

Substituted Nitro Alkanes

Thermal decomposition. A considerable number of substituted nitroalkanes were prepared by Soviet chemists and their thermal decomposition was examined by Nazin and co-workers [3, 4] in view of determining their activation energy and frequency factor. Some of the results are collected in Table A1 and in a summarizing review of Nazin and Manelis [5]

TABLE A1. Energy of activation of thermal decomposition of di- and tri-nitroalkanes and their halogen derivatives

Compound	Temperature range °C	Activation energy kcal/mol	Frequency factor log B	References
CH_3NO_2	360–390	54.3	14.3	[3]
$CH_3CH(NO_2)_2$	197–227	47.1	16.7	[4a]
$CH_3CH_2CH(NO_2)_2$	215–265	48.0	16.9	
$CH_3(CH_2)_2CH(NO_2)_2$	219–244	48.2	17.0	
$C(NO_2)_4$	86–177	38.2	16.3	[4b]
$CF(NO_2)_3$	178–236	41.9	15.4	
$CCl(NO_2)_3$	120–165	36.4	15.75	
$CH(NO_2)_3$	180–200	42.4	15.9	[4c]
$CHCl(NO_2)_2$	180–200	40.6	16.1	
$CF_2(NO_2)_2$	235–270	47.4	15.9	[4d]
$CH_3CF(NO_2)_2$	214–262	47.7	17.0	
$C(NO_2)_3-C(NO_2)_3$	90–135	35.8	17.3	
$CF(NO_2)_2-C(NO_2)_3$	88–140	36.5	17.3	
$CF(NO_2)_2-CF(NO_2)_2$	107–180	42.2	18.0	
$CH_3C(NO_2)_3$	160–200	43.2	17.2	[4e]

Thermochemical properties. A monograph should be mentioned of thermochemistry of nitro compounds by Lebedev and co-workers [9]. Pepekin and co-workers examined the enthalpy of formation of dinitrophenylmethane, trinitrophenylethane fluordinitrophenylmethane [6], and fluordinitromethane [7]. The results are given in Table A2.

TABLE A2. Thermochemical data of some nitroalkane derivatives

Compounds	Enthalpy of formation in gas-phase kcal/mol	Energy of the bond C–C between phenyl or benzyl and $C(NO_2)_2$ or $C(NO_2)_3$ kcal/mol
$C_6H_5CH(NO_2)_2$	8.3	100.2
$C_6H_5CH_2C(NO_2)_3$	15.7	79.1
$C_6H_5CF(NO_2)_2$	44.2	105.1
$CHF(NO_2)_2$	56.1	

Steric Effects in Nitroalkanes

Novikov and co-workers [8] studied steric effects in mono- and polynitroalkanes. They calculated the equilibrium of configuration, energy of strains and enthalpy of atomization. Steric effects from the nitro groups increase with the increase of their number and the increase of the length of the alkyl chain.

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CHAPTER 9

DIFLUOROAMINO COMPOUNDS

As a result of searching for new explosives and in particular rocket propellants, a new group of explosives was found – that of organic compounds containing difluoroamino group – NF_2. The group can also be regarded as a modification of the nitro group, where two atoms of oxygen were replaced by atoms of fluorine.

There is now extensive patent literature covering the preparation of difluoroamino compounds and describing their potential use as high-energy propellant ingredients. However, some of the compounds possess properties which cast doubt on the safety of their preparation and handling. A striking example is the simplest member of the family with difluoroamino group, i.e. difluoroamine (NHF_2). This is a particularly dangerous compound: unexpected detonations have been reported.

It appears that interest in difluoroamino compounds is now diminishing, as far as their application as explosives is concerned. Nevertheless the chemistry of difluoroamino compounds remains very interesting.

Two routes for the preparation of difluoroamino compounds are known:

(1) through the direct fluorination of amines,
(2) through the reactions with tetrafluorohydrazine, accompanied by thermal or photochemical dissociation of this compound.

A review of the work on derivatives of nitrogen fluoride compounds including those with difluoroamino group was given by J. K. Ruff [1]. Fokin and Kozyrev [30] published an extensive review dedicated to difluoroamino compounds.

Reviews on difluoroamino compounds appeared also in Advances in Chemistry Series of American Chemical Society [34]. They were reviewed mainly for their application as rocket propellants.

DIRECT FLUORINATION OF NON-AROMATIC COMPOUNDS

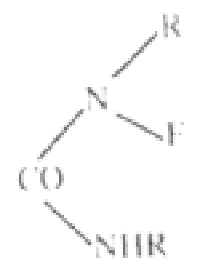
Although the first compounds with NF_2 group were obtained as early as 1936 by O. Ruff and Giese [35] the most important work started relatively recently in the early sixties. These were the indications of the possible transformation of NH_2 into NF_2 given by Lawton and co-workers [2] and Grakauskas [3].

Direct Fluorination of NH_2 and NH Groups in Aliphatic Compounds

Lawton acted on solid urea with fluorine diluted with nitrogen at 0°C and among a variety of compounds isolated a solid substance which proved to be identical with that prepared by Grakauskas [3] through the action on urea in aqueous solution with fluorine diluted with nitrogen at 0–5°C. It proved to be *N,N*-difluorourea (I). It was extracted with ether as a hygroscopic, lackrymatory solid, m.p. 43°C.

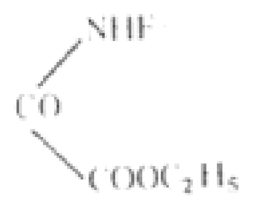
Additional examples of fluorination of compounds containing NH_2, $NHCH_3$ or NHC_2H_5 groups in an aqueous medium were later also reported [4]. They described the formation of such compounds as II–IV.

I



II

$R=CH_3, C_2H_5$



III

CH_3NF_2

IV

A compound analogous to I with SO_2 group instead of CO was prepared by fluorination of sulphonamide: $NH_2SO_2NF_2$ [5].

Difluoramine (Difluorimide) NHF_2

Difluoroamine NHF_2 was prepared by decomposition of I or III.

Difluoramine is a gaseous substance [6] with m.p. −116.4 to −117.1°C, b.p. −23.6, density $d = 1.424 - 0.00202\,t$ (d measured at −42.5°C was 1.513). It possesses extraordinary explosive properties, being extremely sensitive to impact, detonating spontaneously when cooled to −196°C in liquid nitrogen. The N–F bond strength in NHF is estimated to be 72 kcal/mol [7b].

According to Lawton and Weber [6] it was formed as one of the products of the action of fluorine diluted with nitrogen (in proportion 1:4 to 1:10) on solid urea at 0°C. The resulting liquid mixture was distilled under reduced pressure and condensation at −142°C gave NHF_2 with a yield of 30% (calculated on the fluorine used). The nondistilling residue was composed of difluorourea (I).

Difluoroamine was formed from *N,N*-difluorourea through acid hydrolysis:

$$NF_2CONH_2 \xrightarrow{H^+,\,H_2O} NHF_2. \qquad (1$$

Kennedy and Colburn [7a] obtained a small quantity of difluoroamine b acting on nitrogen trifluoride with arsenic at 250–300°C. The best method o making the compound consists in hydrolysis of trityldifluoroamine with sul phuric acid. A quantitative yield was obtained [8]. Trityldifluoroamine in turn was obtained by acting with tetrafluorohydrazine on trityl cation [9]:

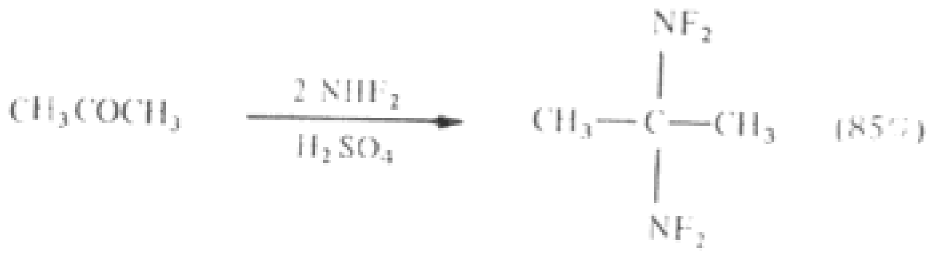
$$N_2F_4 + (C_6H_5)_3C^+ \longrightarrow \underset{\text{m.p. } 75\text{–}77^\circ C}{(C_6H_5)_3CNF_2} \xrightarrow{H_2SO_4} NHF_2 \qquad (2)$$

Difluoroamine hydrolysed under the action of bases and fluorine anion was evolved [10].

Difluoroamine forms complexes with ethers and Lewis acids, and decomposes on contact with copper, stainless steel and some organic compounds, such as urea [6].

It reacts with carbonium ions to yield *N,N*-difluoroamines [11].

Difluoroamine reacts with carbonyl compounds in acid medium to yield difluoroamino derivatives [12a], for example:



$$CH_3COCH_3 \xrightarrow[H_2SO_4]{2\ NHF_2} CH_3-\underset{NF_2}{\overset{NF_2}{\overset{|}{\underset{|}{C}}}}-CH_3 \quad (85\%) \qquad (3)$$

b.p. 73°C

and with acetylenes to yield NF_2 substituted olefins [12b].

No explosive properties of such substances were reported.

Other Non-aromatic Difluoroamines

Sharts [13] fluorinated a number of aliphatic amines.

He fluorinated hexamethylenediamine with a fluorine-nitrogen mixture (1:2) in aqueous medium in the presence of sodium bicarbonate, trichlorofluoromethane and methylene dichloride at temperatures below 2°C.

N,N,N^1,N^1-Tetrafluorohexamethylenediamine or 1,6-bis(difluoroamino)hexane (b.p. 70–75°C at 0.1 mmHg) resulted with a yield of 23%.

In a similar manner cyclohexylamine was converted into *N,N*-Difluorocyclohexylamine (the yield was 66%, based on cyclohexylamine and 23% on fluorine). It is a liquid boiling over the range 69–81°C under 80–90 mmHg.

Davis and Graves [14] fluorinated guanidine and obtained an explosive product: perfluoroguanidine $NF = C(NF_2)_2$. Rosenfeld and co-workers [15] fluorinated cyanoguanidine and obtained three major products V–VII:

$CF(NF_2)_3$

V

$$\underset{\underset{NF}{\|}}{F_2NC}NFCF_2NF_2$$

VI

$(F_2N)_2CFNFCF_2NF_2$

VII

Compounds VI (b.p. 55°C) and VII (b.p. 60°C) possess explosive characteristics.

FLUORINATION OF NITROAROMATIC AMINES

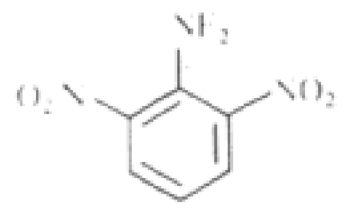
Coon and co-workers [16] have found a general synthetic procedure for the preparation of nitroaromatic difluoramines. Nitroaromatic monoamines, such as picramide and its analogues have been converted in high yield into the corresponding difluoramines in liquid hydrogen fluoride and in some cases in organic solvents, such as acetonitrile, by using fluorine diluted with nitrogen, at temperatures below 0°C.

Nitroaromatic diamines and triamines undergo similar fluorination reactions.

Dinitroanilines were fluorinated in good yield, but fluorination of non-nitrated amines (such as aniline) is accompanied by ring fluorination *ortho* to the NF_2 group.

According to the same authors the reaction of fluorination occurs through a radical mechanism.

All substances described below possess marked explosive characteristics [16].



VIII

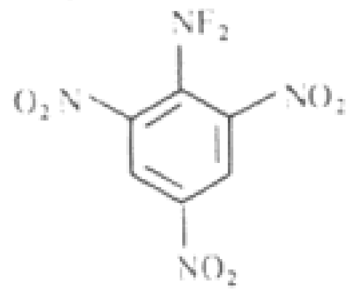
1-Difluoramino-2,6-dinitrobenzene (VIII)

This substance forms light yellow coloured needles (from 50/50 chloroform/hexane), m.p. 91–93°C.

It was obtained by fluorination of 2,6-dinitroaniline in acetonitrile at −10 to −5°C with a stream of 15% fluorine in nitrogen. The yield was *ca.* 60%.

1-Difluoroamino-2,4-dinitrobenzene

This substance was not isolated in a pure form. The liquid product of fluorination of 2,4-dinitroaniline contained 1-difluoroamino-6-fluoro-2,4-dinitrobenzene.

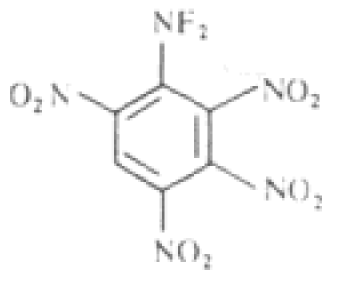


IX

1-Difluoroamino-2,4,6-trinitrobenzene (IX)

The substance forms light yellow coloured crystals, m.p. 69°C.

As mentioned already it was obtained by fluorinating 2,4,6-trinitroaniline dissolved in anhydrous hydrogen fluoride at −5° to 0°C with a stream of 60% fluorine in nitrogen. The yield was 75%.



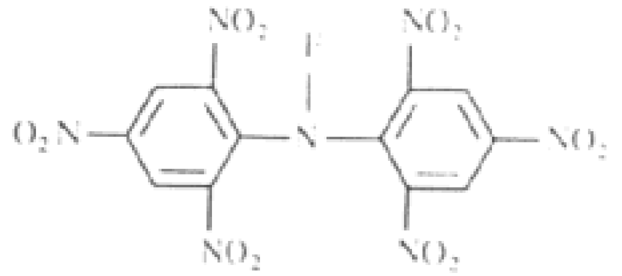
X

1-Difluoroamino-2,3,4,6-tetranitrobenzene (X)

The substance forms yellow coloured crystalline solids, m.p. 84°C.

It was obtained [16] from tetranitroaniline (Vol. I, p. 560) in the same way as 1-difluoramino-2,4,6-trinitrobenzene, the only difference being that no external cooling was used and the temperature in the course of fluorination was that of the b.p. of anhydrous hydrogen fluoride (+19°C). The yield was 75%.

Difluoraminopentanitrobenzene was obtained by fluorinating pentanitroaniline (Vol. I, p. 562) in the same way as fluorination of picramide, the only difference was that no external cooling was applied. The product was stable only in solution and could be detected by NMR spectrum. In the solid state the orange coloured crystals decomposed quickly and formed viscous oil.

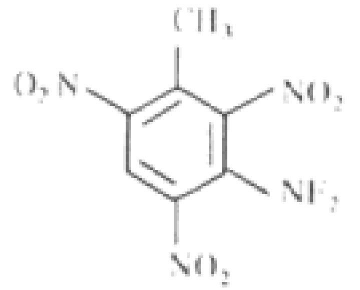


XI

Hexanitrodiphenylfluoramine (XI)

This is a crystalline, orange coloured solid, m.p. 102–105°C.

It was made from hexanitrodiphenylamine in acetonitrile solution by fluorinating with 15% fluorine at temperatures of −10 to −5°C (54% yield). It decomposed at room temperature within a few days and is stable only below −18°C.



XII

3-Difluoramine-2,4,6-trinitrotoluene (XII)

This substance forms yellow coloured crystalline solids, m.p. 111°C.

It was obtained in the same way as (IX) at −16 to −4°C with 46% fluorine–nitrogen. The yield was 78%.

Other Difluoramino Nitroaromatics

The following difluoramino nitroaromatics were also prepared [16]:

a. 3-Difluoramino-2,4,6-trinitroanisol, a yellow coloured liquid,
b. 3,5-bis(difluoramino)-2,4,6-trinitrotoluene, yellow coloured crystals m.p. 143–145°C,
c. 3-difluoramino-5-chloro-2,4,6-trinitrotoluene, yellow coloured crystals, m.p. 149–153°C,
d. 1,5-bis(difluoramino)-2,4-dinitrobenzene,
e. 1,5-bis(difluoramino)-2,4-dinitro-6-fluorobenzene. Compounds (d) and (e) were obtained in a mixture by fluorinating 1,5-diamino-2,4-dinitrobenzene.
f. 1,3,5-tris(difluoramino)-2,4-dinitrobenzene, light yellow coloured crystals, m.p. 54–56°C.

The latter was obtained in the course of fluorination of 1,3,5-triamino-2,4-dinitrobenzene along with 1,3,5-tris(difluoramino)-2,4-dinitro-1,2,3,4,5,6-hexafluorocyclohexane – a liquid product which was formed from the saturation of the benzene ring of the product (f) with fluorine.

No reference to their explosive properties was given, but private information is that they do not differ from the mother nitro compounds.

FLUORINATION THROUGH THE ADDITION OF TETRAFLUOROHYDRAZINE

Tetrafluorohydrazine NF_2–NF_2

Tetrafluorohydrazine is a gaseous substance with b.p. −73°C.

The preparation of tetrafluorohydrazine was in a way a turning point in the chemistry of difluoroamino compounds by offering a stable reactive substance which could also yield NF_2 free radicals. The enthalpy of dissociation (4)

$$N_2F_4 \longrightarrow 2\cdot NF_2 \qquad (4)$$

is very low 20 ± 1 kcal/mol [1].

Tetrafluorohydrazine was obtained by Colburn and Kennedy [17] by passing nitrogen trifluoride over copper at 375°C:

$$2\,NF_3 + Cu \longrightarrow N_2F_4 + CuF_2. \qquad (5)$$

The reaction can also be carried out with other metals, such as Fe, As, Sb and Bi. The conversion was 42–62% and the yield 62–71%.

(Nitrogen trifluoride was obtained by O. Ruff and co-workers [18] through electrolysis at 125°C of molten ammonium hydrogen fluoride: $NH_4F \cdot HF$. It is a stable, gaseous, b.p. −119°C, substance which can be hydrolysed by hot water vapour.)

It was also reported that nitrogen trifluoride could be obtained by reacting N_2O with fluorine at 700°C [19].

On other methods of preparation of tetrafluorohydrazine – see [1].

Reactivity of Tetrafluorohydrazine

Frazer [20] has shown that tetrafluorohydrazine can react with methyl and ethyl iodide in a light initiated reaction to give *N,N*-difluoroaminomethane and ethane respectively.

A number of authors reported the formation of bis(difluoroamino) compounds by the addition of tetrafluorohydrazine to unsaturated aliphatic and aromatic compounds [21–26].

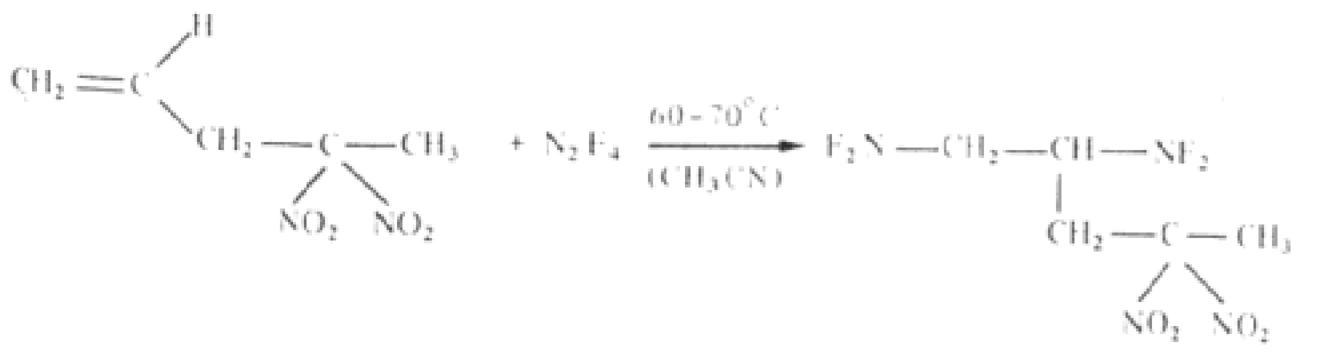
According to Cerfontain [24] tetrafluorohydrazine can react with polycyclic aromatic hydrocarbons in iso-octane as a solvent at 40°C. Thus anthracene yielded 9,10-bisfluoroamino-9,10-dihydroanthracene. The product does not show good stability, it decomposed above 130°C with a gas evolution and at 220°C yielded mainly the parent hydrocarbon. Similarly the product of the reaction of stilbene with tetrafluorohydrazine (which was 1,2-bisdifluoroamino-1,2-diphenylethane) decomposed above 80°C.

The reaction of tetrafluorohydrazine with diallyl ether was studied by Reed [26]. The main product of the reaction (48%) was di[2,3-bis(difluoroamino) propyl] ether (6)

$$(CH_2{=}CH{-}CH_2)_2O + N_2F_4 \longrightarrow \left(\begin{array}{ccc} CH_2 & - CH - & CH_2 \\ | & | & \\ NF_2 & NF_2 & \end{array}\right)_2 \qquad (6)$$

The other products were tetrahydrofurane derivatives.

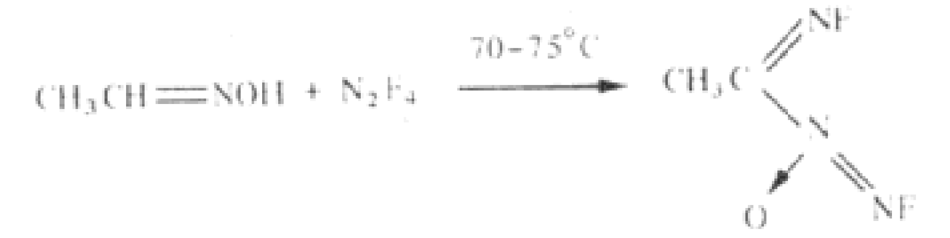
Fokin and co-workers [32] described interesting reactions of nitroalkenes with tetrafluorohydrazine. Such was the reaction of 2,2-dinitropentene-4 with tetrafluorohydrazine yielding 2,2-dinitro-4,5-bis(difluoroamino)-pentane (7) with a yield of *ca.* 36%:



(7)

The reaction is very solvent dependent. Decomposition occurred in most solvents but the best proved to be acetonitrile.

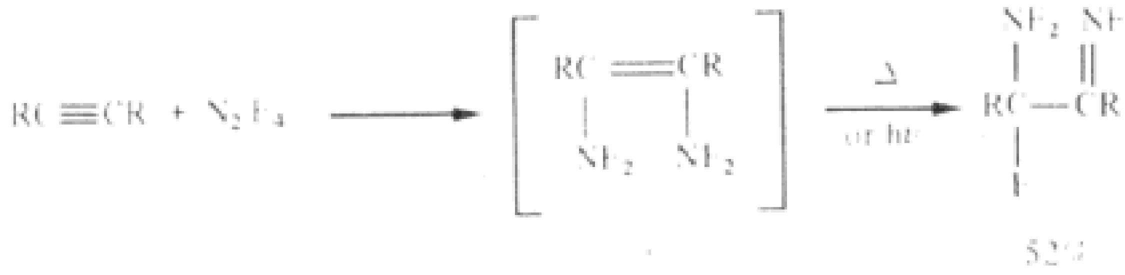
Fokin and co-workers [33] studied reactions of oximes with tetrafluorohydrazine, for example (8)



(8)

Most of the latter products are unstable. The only stable compounds were obtained from aromatic oximes.

The addition of N_2F_4 to acetylenes was studied by a number of authors [27, 28]. The reactions give ethylene derivatives unstable and readily isomerizing on further heating or under the influence of irradiation (9)



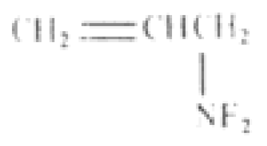
(9)

The fact that NF_2 radical formed through the equilibrium $N_2F_4 \rightleftharpoons 2\cdot NF$ absorbs at 260 mn suggests that it possesses photochemical properties. Indeed it was found that the irradiation of methane with N_2F_4 produced difluoroaminomethane (10)

$$CH_4 \xrightarrow[h\nu]{N_2F_4} CH_3NF_2 + HCN \qquad (10)$$

Similarly ethane yielded difluoroaminoethane $C_2H_5NF_2$ and CH_3CN.

Olefins also reacted with N_2F_4 under irradiation, for example propylene yielded 50% of a mixture of substituted propylene and propane (XIII–XI) [29]



$$\begin{array}{l} CH_2{=}CHCH_2 \\ \qquad\quad |\\ \qquad\quad NF_2 \end{array}$$

XIII

$$\begin{array}{l} FCH_2CHCH_3 \\ \qquad |\\ \qquad NF_2 \end{array}$$

XIV

$$\begin{array}{l} CH_2{-}CHF{-}CH_3 \\ | \\ NF_2 \end{array}$$

XV

EXPLOSIVE PROPERTIES OF DIFLUOROAMINOALKANES AND ALKENES

A few experimental data of explosive properties of difluoroaminoalkanes and alkenes were collected and theoretical calculation of their properties was given by Pepekin [31].

According to Berke and associates [43] bis-difluoroaminopropane and -butane give the rates of detonation:

$C_3H_6N_2F_4$, $\rho = 1.26$, D = 6300 m/s,
$C_4H_8N_2F_4$, $\rho = 1.20$, D = 6000 m/s.

Voskoboynikov and co-workers [44] have found similar figures for bis-difluoroaminobutane and -pentene. They also described an interesting compound: tetra-difluoroaminopentane:

$$CH_2(NF_2)-[CH(NF_2)]_3-CH_3, \rho = 1.51, D = 7000 \text{ m/s.}$$

The general conclusion is that compounds with NF_2 group show similar explosive properties as those with the same number of NO_2 groups.

Theoretical Aspects of Properties of NF_2 Compounds

A series of theoretical papers on the difluoroamino group and compounds have appeared. Their aim was to find a theoretical background for the use of difluoroamino compounds in propellants.

1. Isotopic exchange reaction of difluoroamine (NF_2H) with D_2O and trifluoro deutero acetic acid (CF_3COOD) was examined by Becker and Impastato [36].

2. The reaction of difluoroamine with Lewis Acids [37].

3. A general paper on the chemistry of difluoroamines by Craig *et al.* [38] was also published. It was dedicated to understanding the nature of N–F and N–X bonds and to obtain a picture of the relative electron distribution in X–NF_2 compounds, where X = F, Cl, H, NF_2, CH_3, C_2H_5 and CF_3. The electron affinity of cation NF_2^+ was found to be very high and by adding an electron, a relatively stable radical NF_2 was favoured. The electron distribution is more symmetrical than in anion NF_2^- and cation NF_2^+ which do not seem to be sufficiently stable.

4. In searching for high energy explosives the reactions were examined between difluoroamino compounds and

(a) organometallic compounds,
(b) nitric acid [39]. A variety of compounds were obtained in both instances, such as:
(a) azo-compounds, dialkyldifluoro-hydrazine, tertiary amine and hydrocarbon,
(b) alkyl nitrates and nitrites.

5. Reactivity of nitrogen fluorides NF_3, N_2F_4 and cis- and trans-N_2F_2 was examined by Hurst and Khayat [40]. Nitrogen trifluoride (NF_3) is inert to pure water but reacted with aqueous bases at 100°C to give nitrite and fluoride. N_2F_4 was hydrolysed slowly with water at 60–100°C. Cis- and trans-N_2F_2 were hydrolysed with water at 74° and 89°C respectively. The reactions were of the first order with respect to N_2F_2 and the major products are N_2 and O_2 [41].

Thermochemistry

Pepekin and Apin [42] calculated enthalpy of formation of 1,1-bis(difluoroamine)cyclohexane and the energy of the bond N–F. The enthalpy of formation – ΔH_f was found to be 52.5 kcal/mol and the thermochemical energy of the bond N–F was 68.4 cal.

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CHAPTER 10

ESTERS
NITRATE ESTERS
(*O*-NITRO COMPOUNDS)

Although nitrate esters continue to be widely used and are important explosives, their chemical properties are described to a much lesser extent than those of *C*-nitro compounds. This is understandable when considering the wide use of *C*-nitro compounds, particularly aromatic ones, not only as explosives but in a great variety of uses as intermediates and finished products. For this reason the excellent monograph of Patai, series edited by H. Feuer [1], does not contain a chapter on *O*-nitro compounds and the only review papers dedicated solely to *O*-nitro compounds were by Boschan, Merrow, Van Dolah [2] and Connon [3].

STRUCTURE (Vol. II, p. 1)

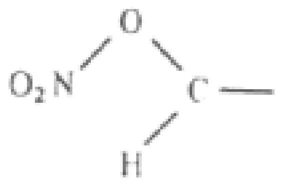
Three kinds of nitrate esters are distinguished: primary, secondary and tertiary deriving from primary, secondary and tertiary alcohols respectively:

(1) primary	CH_2-ONO_2
(2) secondary	$CH-ONO_2$
(3) tertiary	$C-ONO_2$

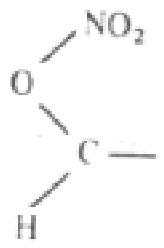
This was pointed out by T. Urbański and Witanowski (Vol. I, p. 6) who found the spectroscopic (infra red) method of distinguishing the above species which is described later in the paragraph on spectroscopy of nitrate esters.

DIPOLE MOMENTS (Vol. II, p. 3)

Recent measurements of dipole moments carried out by Lemanceau and Caire-Maurisier [4] brought some new and important conclusions to the problem of the conformation of nitroglycerine and other nitrate esters with three or four atoms of carbon in the chain. They concluded that there is less need for admitting various conformations produced by the rotation around C—C bonds of the chain $CH_2-CH-CH_2$. Instead they rationalized their results in terms of the rotation in groups $C-ONO_2$ around the bonds C–O, viz. Formulae Ia and Ib:

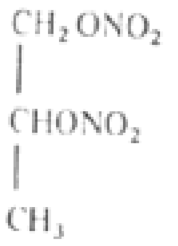


Ia



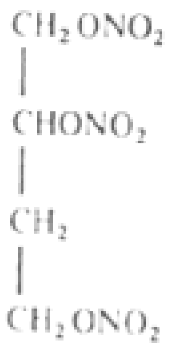
Ib

The same applies to propane-1,2-diol dinitrate (II) and butane-1,2,4-triol trinitrate (III). They also examined NMR spectra of nitrate esters – their conclusions are reported in the paragraph on NMR of nitrate esters (p. 284).



$$\begin{array}{c}CH_2ONO_2\\ |\\ CHONO_2\\ |\\ CH_3\end{array}$$

II



$$\begin{array}{c}CH_2ONO_2\\ |\\ CHONO_2\\ |\\ CH_2\\ |\\ CH_2ONO_2\end{array}$$

III

SPECTROSCOPY (Vol. II, p. 4).

T. Urbański and Witanowski [5] found that a stepwise substitution of hydrogen atoms with methyl groups in methyl nitrate lowers the frequency of asymmetric vibrations by about 5 cm^{-1} for each methyl introduced. Subsequently it is possible to distinguish between primary, secondary and tertiary simple alkyl nitrates by their ν_{as} as frequencies, viz.:

1632–1630,
1626,
1621 cm^{-1} respectively.

On the contrary ν_{sym} vibrations of simple nitrate esters (1283–1280 cm^{-1}) is unaffected by the substitution as above.

The fact observed by Pristera (Vol. II, p. 6) that the infra red asymmetric vibration band of *ca.* 1639 cm^{-1} of nitroglycerine has a shoulder was rationalized by Rossmy [6], T. Urbański and Witanowski (Vol. II, pp. 4, 6) as the result of rotational isomerism around the bond $C-\underset{\substack{|\\ ONO_2}}{C}$.

Nevertheless the shoulder can also be partly produced by the fact that the nitroglycerine molecule contains both the primary groups and the secondary *O*-nitro group. This refers also to all nitrate esters with longer chains, such as esters of erytritol and hexitols (e.g. mannitol, sorbitol), but not in esters of ethylene glycol and pentaerythritol which show a splitting of the absorption bands: [7] and (Vol. II, p. 6).

The data for infra red spectra obtained by T. Urbański and Witanowski [5, 7] were used by Czuchajowski and Kucharski [8] in the series of papers on calculation force constants. Such a theoretical approach for methyl nitrate was first given by Shlyapochnikov, Novikov and Zavilovich [9].

Czuchajowski and Kucharski examined a full range of derivatives of ethyl nitrate of the general formula $Y-CH_2-CH_2-ONO_2$. Table 45 gives comparative results of experimental values [5, 7] and their calculation [8]. Table 46 gives stretching force constants and the influence of *+I* inductive effect of the substituents *Y*.

TABLE 45. Stretching frequencies of NO_2 group in $Y-CH_2-CH_2-ONO_2$

Y	ν_{as} (NO_2) cm^{-1} exper. [4, 6]	ν_{as} (NO_2) cm^{-1} theor. [7]	ν_s (NO_2) cm^{-1} exper. [4, 6]	ν_s (NO_2) cm^{-1} theor. [7]
OH	1631	1632	1282	1284
Cl	1652 1640	1651	1280	1283
Br	1651 1641	1655	1282 1273	1284
I	1662 1640	1660	1281 1262	1284
ONO_2	1656 1643	1656	1282 1271	1273

TABLE 46. Stretching force constants in $Y-CH_2-CH_2-ONO_2$. Influence of +I inductive effect (according to Czuchajowski and Kucharski [7])

Y	K_{O-N} m dyn/A	K_{N-O} m dyn/A
OH	4.40	9.04
Cl	4.10	9.25
Br	4.07	9.29
I	3.99	9.35
ONO_2	4.07	9.29

In the next paper [10] Czuchajowski and Kucharski extended their calculations of valence force field (VFF) to compounds of the general formula *Y* $CH_2-CH_2-ONO_2$, where *Y* was NO_2, CN, ONO_2. Their calculated results in cluded the difference between gauche and trans conformers, the values o which were 1655–1652 and 1644–1641 cm^{-1} respectively and are also in agreement with the experimental data [7].

NUCLEAR MAGNETIC RESONANCE

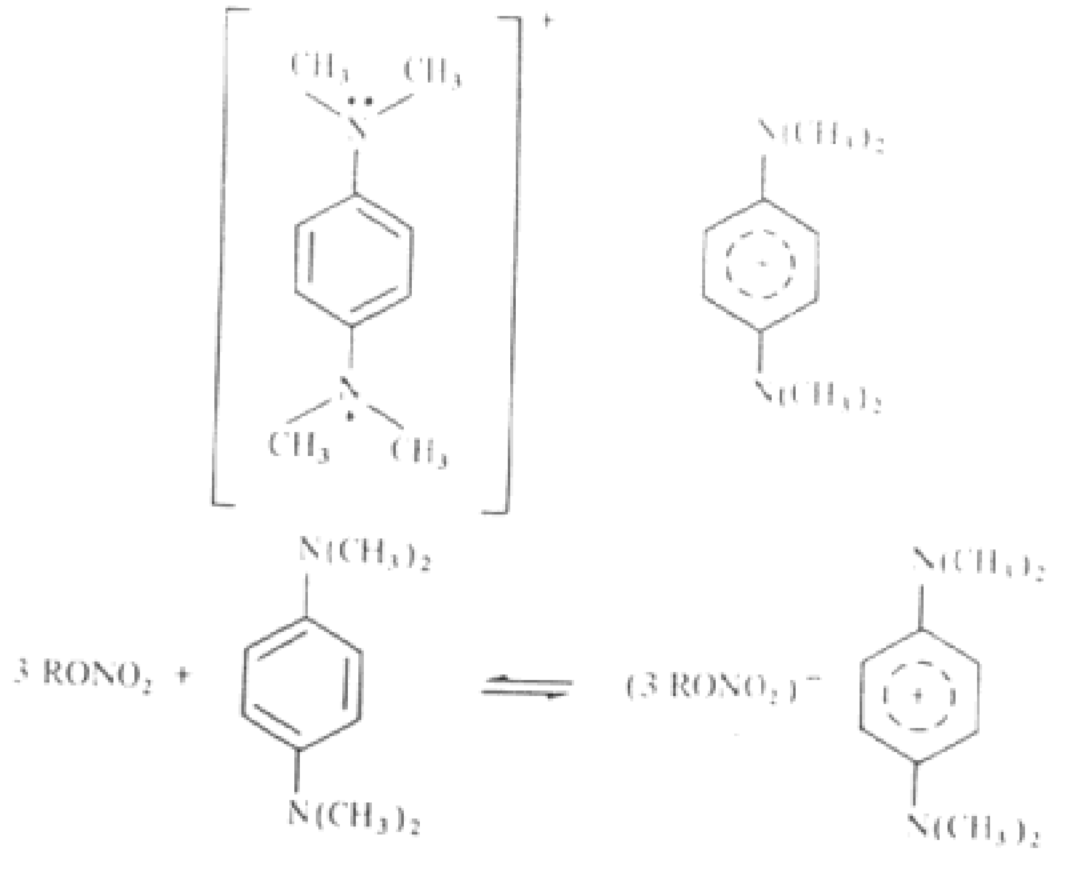
Lemanceau and Caire-Maurisier [4] examined NMR spectrum of nitroglycerine with a view to determining the conformation of the compound. The spectrum is of the type *ABCA'B'* and appears to favour the ecliptic conformation of C–ONO_2 groups.

Pobłocka, T. Urbański and Wacławek [11] examined NMR spectra of erythritol tetranitrate (an acceptor) while studying its charge–transfer complexes with bases as electron donors.

ELECTRON ATTRACTING PROPERTIES OF NITRATE ESTERS AND CHARGE–TRANSFER COMPLEXES

T. Urbański (Vol. II, pp. 167, 169) and later Witanowski [12] have shown by way of thermal analysis that some *O*-nitro compounds such as D-mannitol hexanitrate and erythritol tetranitrate can form additional complexes with aromatic nitro compounds.

In a series of papers [13–15, 22] T. Urbański, Hetnarski and Południkiewicz described charge–transfer complexes with nitrate esters as electron acceptors. Tetramethyl-*p*-phenylenediamine (TMPD) was used as an electron donor. The visible stage of the reaction between nitrate esters and TMPD in 1,2-dichloroethane as the solvent was the formation of the bluish-violet coloured radical-ion known as Wurster cation (IV) [16, 17] formed from TMPD through the loss of one electron. The presence of Wurster cation is manifested by two absorption bands in the electronic spectrum: 570 and 620 nm [17]. The authors established that at least three ONO_2 groups are needed to form one mole of IV, for example:

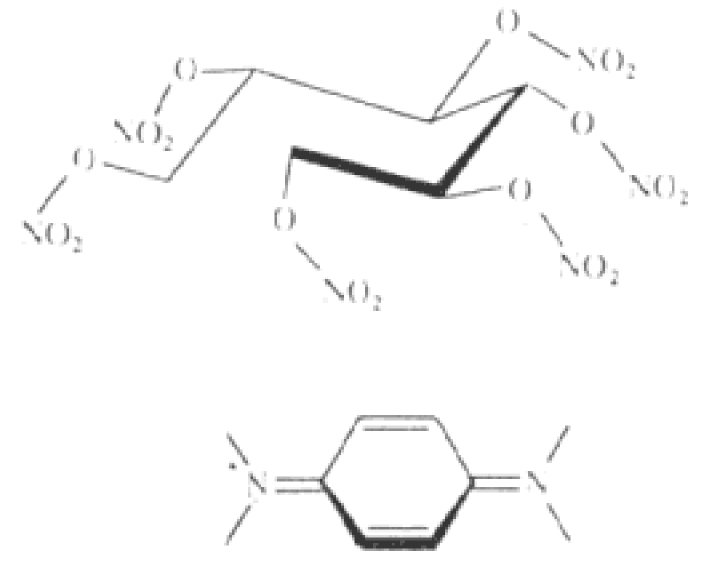


IV

The comparison of the enthalpy of the formation of Wurster cation of primary, secondary and tertiary butyl nitrate has shown that the primary ONO_2 group is the weakest electron acceptor and the strongest is the tertiary ONO_2 group the enthalpy of formation ($-\Delta H_f$) being 0.47 and 0.61 kcal/mol respectively. Nitroglycerine, pentaerythritol tri- and tetranitrates reacted with TMPD at the molar ratio 1:1. The same ratio was observed with erythritol tetranitrate but comparison with pentaerythritol tetranitrate (PETN) shows a stronger electron accepting property of the former probably due to the presence of secondary nitrate groups.

Hexanitrates of hexitols show strong accepting properties: 1 mole of hexanitrates with 2 moles of TMPD, in agreement with the rule – 3 ONO_2 groups for 1 mole of TMPD.

More detailed examination of the electronic spectra of TMPD with pentanitrates of D-xylitol, D-mannitol and hexanitrates of D-mannitol, D-sorbitol, D-dulcitol and myoinositol has shown three stages of the reaction in 1,2-dichloroethane as a solvent. At first all of them showed a rapid formation of low intensity transient bands between 909 and 1030 nm, which corresponds to an unstable CT–complex. Within 15 min (as in the case of all other nitrate esters) two bands of Wurster cation appeared. While these bands of nitrate esters persisted for a few days, both bands of pentanitrates and hexanitrates disappeared within 2 hours and were transformed into one band of 450 nm characterizing the yellow coloured relatively stable complex of the ratio 1:1 of hexanitrates to TMPD. The enthalpy of the formation of the new complex was $-\Delta H_f = 5.12$ kcal/mol, a value of the same magnitude as in many π–π complexes. Following the 'overlap and orientation principle' of Mulliken [18] the structure of the 1:1 complex was rationalized [15] being as shown on formula V. (Fig. 40, p. 308).



V

The structure of TMPD is represented here as TMPD being transformed into a quinoid compound: tetramethyl-*p*-quinonediamine dication formed by disproportions of Wurster cation. Its structure was confirmed by infra red spectroscopy.

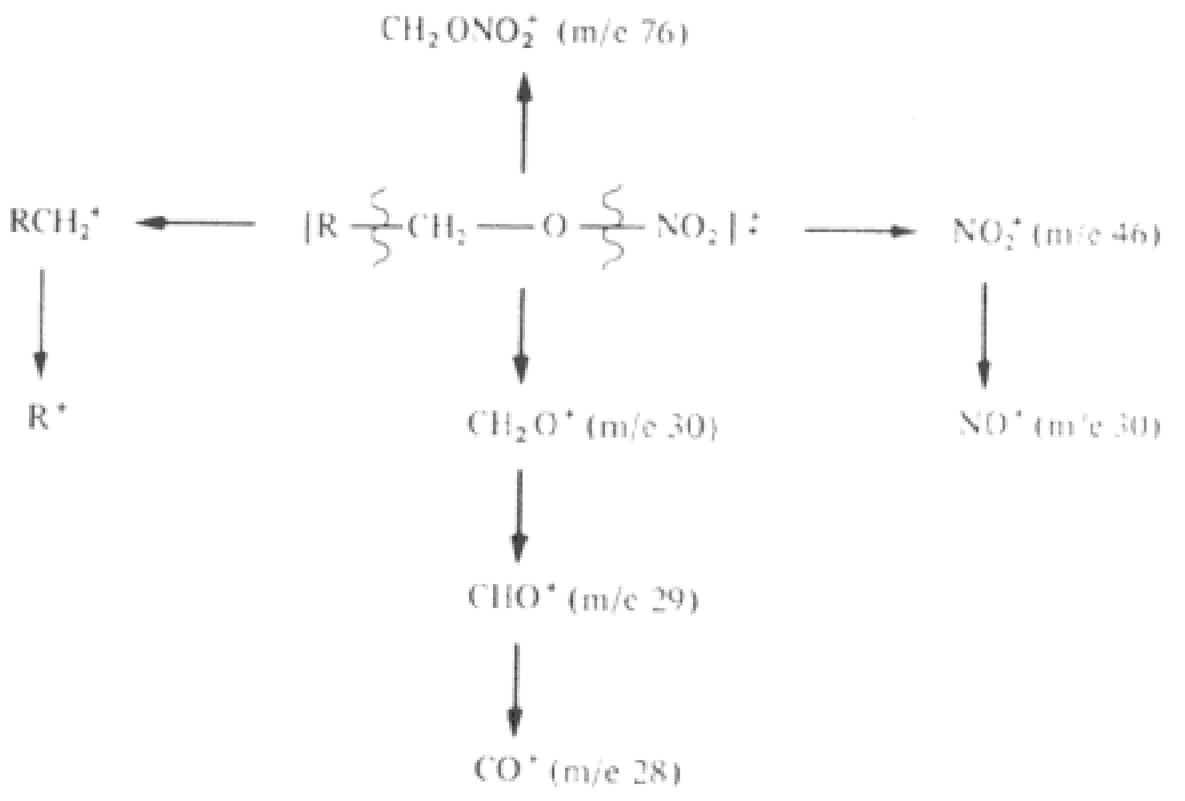
A hypothetical structure of complexes of nitrate esters with one to four nitrate groups was also advanced [19]. It was suggested that TMPD be used for analytical detection (including TLC) of nitrate esters [20].

In the light of the above work the finding of Parihar, Sharma and Varma [21] on the colour reaction of *O*-nitro compounds with potassium sulphanilate and α-naphthylamine in acetic acid should also be attributed to the oxidation of amines. The reaction produced the coloured cations and possibly charge–transfer complexes between the *O*-nitro compounds and the amine.

Further experiments were carried out on CT complexes between D-mannitol hexanitrate and pyrimidine and purine bases important in biochemical processes [22]. A summarized report has also been given on nitrate esters as electron acceptors [23].

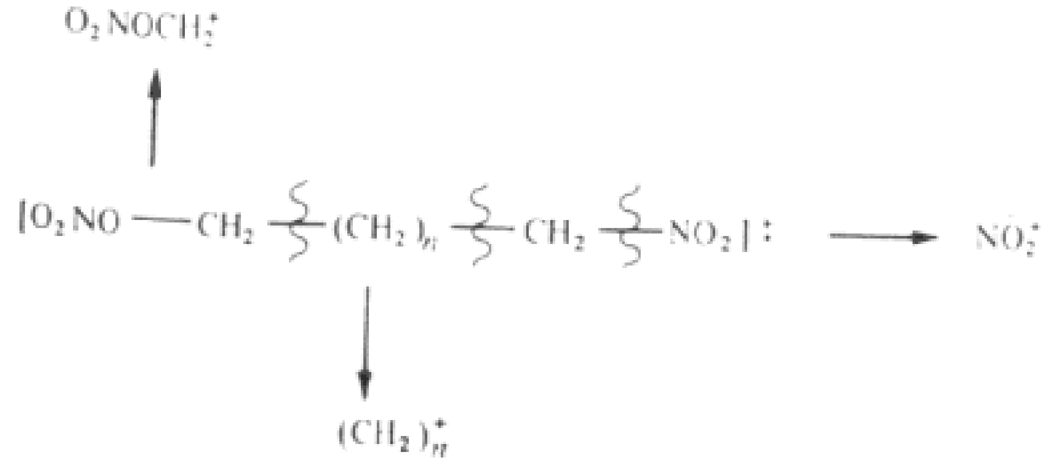
Fraser and Paul [159] examined nitrate esters by mass spectrometry. Both mononitrates and polynitrates were examined. The main conclusions of this important work are given below.

n-Alkyl mononitrates are subject to cleavage as:



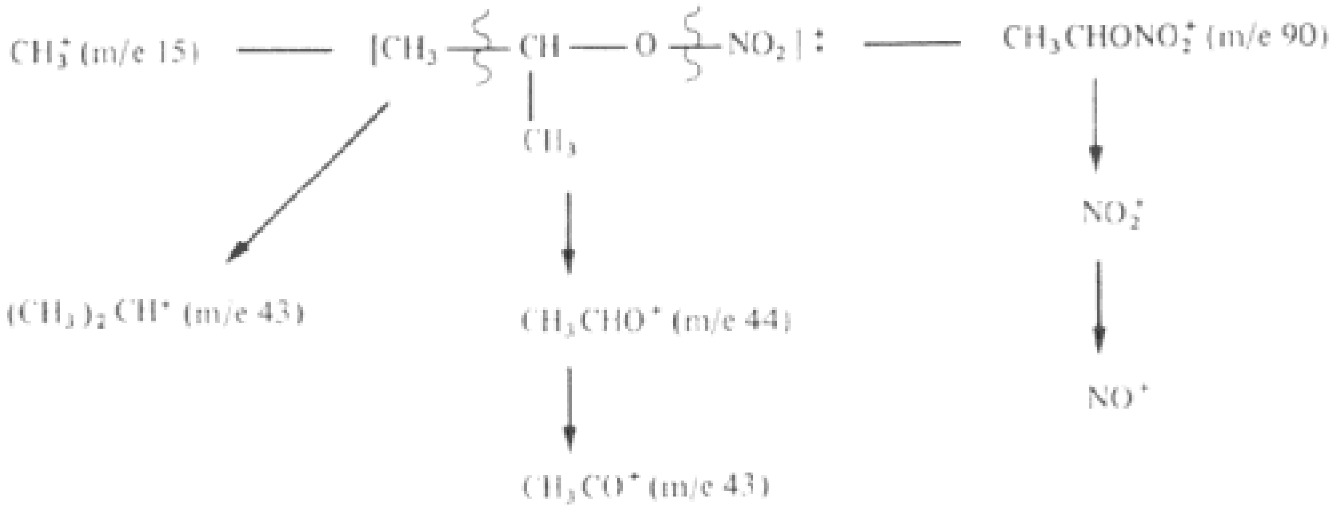
(1)

Diol dinitrates:



(2)

Branched-chain nitrates, for example isopropyl nitrate:



(3)

Nitroglycerine shows a low intensity peak of 76 m/e.

Kriemler and Buttrill [161] studied the formation of positive and negative ion-molecules from ethyl nitrate by ion cyclotron resonance technique. They found three kinds of reactions of positive ions:

(a) transfer of NO_2^+ from $CH_2ONO_2^+$ and $H_2NO_3^+$ to ethyl nitrate to form $C_2H_5N_2O_5^+$,

(b) protonation of $C_2H_5ONO_2$ by $C_2H_3^+$, $C_2H_5^+$ and CHO^+,

(c) fragmentation of protonated ethyl nitrate into $H_2NO_3^+$ and ethylene.

Negative ions have been found $C_2H_3O^-$, $C_2H_5^-$ and OH^- to produce NO_3^-.

HYDROLYSIS OF NITRATE ESTERS (Vol. II, p. 7)

Baker and co-workers (Vol. II, p. 8; [23–25]) have undertaken extensive research on alkaline hydrolysis of nitrate esters. Their results, as those of the other authors [27], were reviewed [2, 3]. They can be summarized as follows:

Nucleophilic attack on carbon (S_N1 and S_N2):

$$HO^- + RCH_2{-}O{-}NO_2 \longrightarrow RCH_2{-}OH + NO_3^-. \tag{4a}$$

Nucleophilic attack on nitrogen (S_N2):

$$HO^- + RCH_2{-}^{18}O{-}NO_2 \longrightarrow [R{-}CH_2{-}^{18}O + HONO_2] \longrightarrow RCH_2{-}O{-}H + NO_3^-. \tag{4b}$$

Nucleophilic attack on α-hydrogen (E2):

$$HO^- + RCH_2{-}O{-}NO_2 \longrightarrow RCH{=}O + NO_2^- + H_2O. \tag{4c}$$

Nucleophilic attack on β-hydrogen (E1 and E2):

$$HO^- + RCH_2CH_2{-}ONO_2 \longrightarrow RCH{=}CH_2 + NO_3^- + H_2O. \tag{4d}$$

Thus both cleavage of bonds C–O and O–N can occur.

The reaction of primary and secondary mononitrate esters are slow, for example slower than alkaline hydrolysis of carboxylic esters.

Primary nitrate esters can undergo alkaline hydrolysis mainly by two pathways (4a and 4b) and the yield of elimination reactions (4c and 4b) are, generally speaking, negligible.

Secondary nitrate esters give a more complicated picture. The dominating reaction is S_N2 but reactions (4c) and (4d) are of importance. Reaction (4c) can yield (depending on R) 8–45% of the carbonyl compound in addition to a certain amount of alkenes. A striking example was given by Baker and Easty [23] on hydrolysis of isopropyl nitrate (Vol. II, p. 13). An important contribution to the mechanism of the reaction of hydrolysis was given by Crystol and co-workers (Vol. II, p. 14) while reacting optically active 2-octyl nitrate.

Reaction (4c) E2 [24] has been used to introduce a carbonyl group into steroids [28].

Neutral hydrolysis of primary and secondary nitrates is very slow [23]. On the contrary, simple tertiary nitrate esters are readily hydrolysed [23, 27, Lucas and Hammett (Vol. II, p. 8)] to yield either alcohol (S_N1) or olefin (E1). Both go through the tertiary carbonium ion.

The four modes of hydrolysis can explain the reaction of nitrate esters with other nucleophiles such as ammonia and amines, hydrazine (Vol. II, p. 12), hydroxide and alkoxide ions (S_N1 and S_N2). Here the esters can act as alkylating agents.

Alkaline hydrolysis at 25°C of glycerol trinitrate, 1,2-glycerol and 1,3-glycerol dinitrates, 1-glyceryl and 2-glyceryl mononitrates with CO_2 free aqueous calcium hydroxide was studied by Capellos and co-workers [103]. They found that 2-glyceryl mononitrate isomerized on hydrolysis to 1-glyceryl mononitrate and 1,2-glycerol dinitrate isomerized to the 1,3-dinitrate before the hydrolysis was accomplished. 1,3-Glycerol dinitrate furnished on hydrolysis glicydyl nitrate in agreement with the reactions described in Vol. II, p. 128.

Nitrate ester hydrolysis is not catalysed by mineral acids to an appreciable extent [29, 26]. This is in contrast to nitrite esters which readily hydrolyse in an acid medium. According to Dewar [30] nitrate esters are protonated preferentially at the alkoxy oxygen according to equation (5a):

$$R{-}ONO_2 + H^+ \overset{\text{fast}}{\rightleftharpoons} R{-}O^+{-}NO_2 \xrightarrow{\text{slow}} ROH + NO_2^+ \tag{5a}$$

The last stage of the reaction is inhibited by the large positive heat of the dissociation [3].

In concentrated sulphuric acid nitrate esters are almost completely dissociated according to equation (5b):

$$RONO_2 + 3H_2SO_4 \longrightarrow ROSO_3H + NO_2^+ + H_3O^+ + 2HSO_4^-. \tag{5b}$$

Such a system can be used as a strong nitrating agent (Vol. I, pp. 15, 122). The nitration of an active methylene group with nitrate esters was basically described in Chapter I.

An interesting method of hydrolysis of nitrate esters to alcohols was given by Pews [158]. It consists in refluxing nitrate esters with formic acid followed by refluxing with methanol. Pentaerythritol trinitrate yielded pentaerythritol.

REDUCTION OF NITRATE ESTERS (Vol. II, p. 18)

The review on nitrate esters [2] should be mentioned here. The following are agents which can be used to recover the original alcohols: $LiAlH_4$, sulphides, H_2 on Pd/charcoal, Raney Ni, Pt. The reduction on platinum can go as far as to the formation of ammonia from ONO_2. Grignard reagent can be also used to reduce nitrate esters [31]. Reduction has been used to remove the *O*-nitro group which served for protection of OH during the synthesis of some steroids [32, 33].

Polarography can be used as an analytical method of quantitative determination of *O*-nitro groups. It was applied to simple esters [34] and to nitroglycerine [35].

CONVERSION OF NITRATE ESTERS INTO NITROALKANES

Bachman and Connon [37] described an interesting reaction of conversion of nitrate esters into nitroalkanes according to (6):

$$RONO_2 + NaNO_2 \xrightarrow{\text{solvent}} RNO_2 + ROH\ (\text{from RONO}) \tag{6}$$

The reaction of nitrate esters with metal nitrites (e.g. sodium nitrite) was carried out in a suitable solvent at temperatures below 100°C. The nature of solvent is decisive to the yield. In the instance of *n*-propyl nitrate the best result (42% of 1-nitropropane) was obtained by keeping the reagents for one hour at 45°C in hexamethylphosphamide. The rest of the nitrate ester was converted to the original alcohol (54% of *n*-propyl alcohol in the described example).

The reaction has little value for the preparation of nitroalkanes, but is of theoretical importance as it indicates the reactivity of nitrate esters. It should be added that J. B. Levy [59] has found that thermal decomposition of nitrate esters resulted in the formation of small amounts of nitroalkanes. Thus the formation of nitroalkanes from nitrate esters seems to merit a more detailed examination of the mechanism of the conversion and decomposition.

FORMATION OF NITRATE ESTERS (Vol. II, p. 20)

The review by Van Dolah and co-workers [2] should be mentioned. Owing to the fact that sulphuric acid in a nitrating mixture promotes hydrolysis of nitrate esters, it is often desirable to nitrate alcohol with nitric acid alone in the presence of urea. The method was used on a large scale to make iso-propyl nitrate [36]. Urea obviously is a scavenger of nitric oxides and nitrous acid – compounds which can lead to oxidation and often dangerous decomposition.

Other nitrating agents which are the source of NO_2^+ ion can also be used (Chapter I).

An interesting method of making nitrate esters consists in reacting dinitrogen pentoxide with alcohols in a vapour phase as developed by Bachman and Connon [3, 37]. A continuously working laboratory nitrator was described by Connon [3]. Here N_2O_5 is produced as a dilute mixture with oxygen by reacting $NO_2(N_2O_4)$ with ozonized oxygen and has a composition according to the diagram (7):

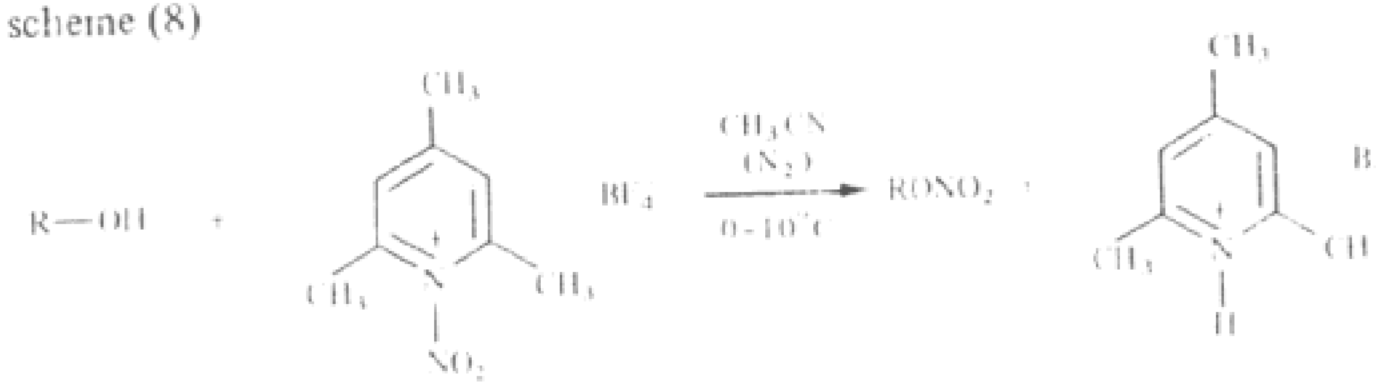
$$NO_2 + O_3 \rightleftharpoons NO_3 + O_2 \longrightarrow N_2O_5. \tag{7}$$

The addition of N_2O_4 to alkene oxide can also produce nitrate esters. E. White and Feldman [38] reacted with a solution of N_2O_4 on sodium butoxide–butanol at −75°C, and received butyl nitrate with a yield of 89%. The reaction is also an example of N_2O_4 acting according to equation (16), Chapter I, as ion pair nitronium nitrite ($NO_2^+ + NO_2^-$). The order of adding reagents is critical: the reversed nitrosation can occur due to the action of N_2O_4 in the capacity of nitrosyl nitrate ($NO^+ + NO_3^-$) – equation (17), Chapter I. This was substantiated by Bachman and Connon [3, 37]. They also found that sodium hydroxide can be used instead of sodium butoxide.

A convenient laboratory method for the preparation of nitrate esters consists in acting with silver nitrate on alkyl bromide or iodide in nitromethane or nitrobenzene [2] or acetonitrile [3]. Kornblum and co-workers [39] made an extensive study of the stereochemistry and mechanism in the reaction of silver nitrate (and nitrite) with alkyl halides. Their conclusion can be summarized: the optically active nitrate esters (as well as nitrite esters) are produced with an inversion. Thus optically active 2-bromooctane when treated with silver nitrate gives 2-octyl nitrate of the inverted configuration regardless of the solvent. With α-phenylethyl chloride however, the steric course of the reaction is solvent dependent: in ethyl ether and in benzene α-phenylethyl. nitrate is produced with retention of configuration but in acetonitrile or petroleum ether the nitrate ester is produced with the inversion. The authors came to the conclusion that the reaction of silver salts with alkyl halides is rationalized as concerted S_N1–S_N2 processes.

Nitrate esters are formed as by-products in the reaction of alhyl bromide or iodide with silver nitrite [40]. By using a temperature below 0°C the formation of nitrate ester can be prevented [41].

Olah and co-workers [42] suggested a convenient and safe method for the preparation of alkyl nitrates (particularly polynitrates) via transfer nitration of alcohols (polyols) with *N*-nitrocollidinium tetrafluoroborate according to scheme (8)



(8)

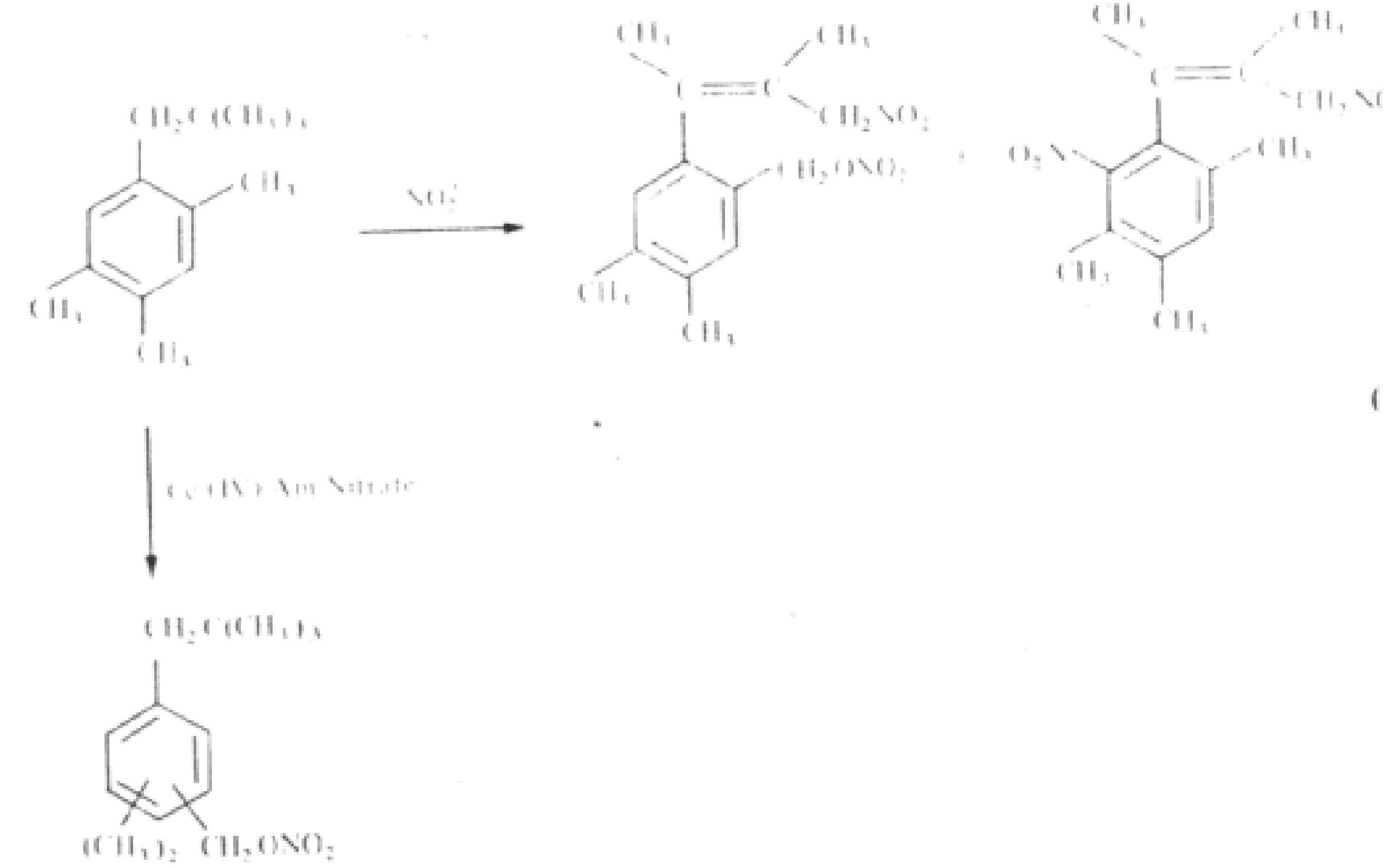
The yield is 41–100%, thus ethyl nitrate, glycol dinitrate and nitroglycerine can be obtained in theoretical yield.

Among the other methods of formation of nitrate esters the reaction discovered by Franchimont [43] of the action of nitric acid on nitramines is of importance:

$$CH_3NHNO_2 \xrightarrow{HNO_3} CH_3ONO_2 + N_2O. \tag{9}$$

The reaction should be taken into consideration when examining the formation of nitramines including Cyclonite.

Interesting reactions of the formation of nitrate esters consist in the action of some nitrating agents on alkanes and alkyl groups. Titov and Shchitov [44] established that cyclohexane, *n*-heptane and *n*-octane react with dinitrogen pentoxide to yield cyclohexyl, 2-heptyl and 2-octyl nitrates respectively. Suzuki and co-workers [45] described the action of an excess of nitric acid or cerium ammonium nitrate on 2.4.5-trimethylneopentylbenzene and found that compounds were formed with one of the methyl groups subjected to nitro-oxidation according to abridged scheme (10)



(10

In another series of experiments Suzuki and associates [46] found a similar reaction of nitration $CH_3 \rightarrow CH_2ONO_2$ by acting with nitrous acid on pentamethyl derivatives of acetophenon.

Nitrate esters can also be made by the oxidation of nitrite esters (Vol. I, p.2). This reaction can also be carried out through a photolysis of nitrite esters. Such is, for example, the photolysis of octyl nitrite in heptane saturated with oxygen of the probable mechanism as below [47, 48]:

$$C_8H_{17}ONO + h\nu \rightleftharpoons C_8H_{17}O\cdot + NO, \qquad (a)$$

$$2NO + O_2 \rightleftharpoons 2\,NO_2, \qquad (b) \qquad (11)$$

$$C_8H_{17}O\cdot + NO_2 \rightleftharpoons C_8H_{17}\,ONO_2. \qquad (c)$$

The yield was 50%.

Bachman and Connon [49] have shown that simple nitrite esters can be partly oxidized to corresponding nitrate esters by mixtures of N_2O_4 and oxygen which probably react as N_2O_5 or free radical NO_3. The same authors [37] obtained nitrate esters by reacting nitrite esters with a mixture of N_2O_4 with ozonized oxygen according to (7). Octyl nitrite gave a 70% yield of the nitrate as well as 30% octanoic acid. When octyl nitrite reacted with dilute ozonized N_2O_4 (which reacted as N_2O_5) in a counter current reactor [3] the yield of octyl nitrate could be as high as 97%.

GAS-CHROMATOGRAPHY OF ALKYL NITRATES

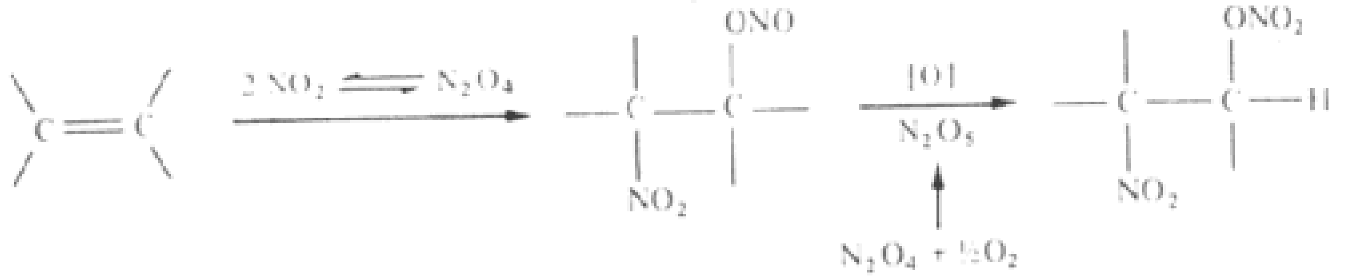
Although analytical problems are not discussed in the present book, it is appropriate that some information should be given, as the problem of the presence of nitrate esters, for example in air, is connected with problems of safety.

Alkyl nitrates can be separated and identified by gas–liquid–chromatography. Ethylene glycol succinate was used as the partition liquid and Celite C22ak was used as support [155]. Gas–liquid chromatography was used to determine nitrate esters in the presence of aromatic nitro compounds [156]. An improvement was made in the gas-chromatography by using an electron capture detector with tritium source [157].

ALKENES AS A SOURCE OF NITRATE ESTERS

As pointed out in Vol. I, p. 146 nitrate ester of β-nitroethanol can be formed by passing ethylene into a nitric–sulphuric acid mixture, and a side reaction is the formation of ethylene glycol dinitrate. However in most experiments nitronitrate ester is the minor product of the reaction. The reactions of alkenes with N_2O_4 were described in the excellent review paper by Shechter [50]. The classic work of N. Levy, Scaife *et al.* (Vol. I, pp. 594–5): [51–53] should be mentioned here, as well as those of Lachowicz and Kreuz [54], Bonetti and co-workers [55], Stevens [56].

Connon [3] summarized their results in two schemes. The simple version is (12).



(12)

Here the oxidizing agent can be N_2O_5 or $\cdot NO_3$ which can be formed by the action of oxygen on $NO + NO_2$ [57].

An interesting method for the formation of an iodo nitrate ester consists in acting with $Hg(NO_3)_2$ and iodine on alkene [58].

NITRATE ESTERS AS EXPLOSIVES (Vol. II, p. 2)

Relatively little work has been dedicated to the examination of such problems as the rate of detonation of nitrate esters, except in the instance of new compounds or those which are not yet sufficiently known. They are now reported in a description of the said compounds. On the contrary, considerable work has been done on thermal decomposition of nitrate esters. Particularly numerous are papers by Soviet authors mainly those of Andreev and his School collected in three monographs [60–62]. The data on the energy of activation of thermal decomposition of nitrate esters and the frequency factors are collected in Table 47 [63–65]. The calculated figures are remarkably similar for all nitrate esters and also are in agreement with those formerly found for nitroglycerine – Vol. II, p. 50. It should also be pointed out that the energy of activation is greatly influenced by the temperature of experiments – see [76, 77].

Determination of stability remains largely unchanged and is much the same as described in Vol. II, p. 23. The 'Heat test' (Abel test) is frequently used to determine the purity of nitrate esters such as nitroglycerine, glycol dinitrate, DGDN and nitrocellulose because of its simplicity [66].

Fraser [67] examined the stability of nitrate esters by determining the hydrolysis rates of the esters using sodium hydroxide in 90% ethanol at 30° and 60°C. The reactions are all second order in both nitrate ester and hydroxide ions. As the measure of the stability of an ester Fraser took the initial specific rate of hydrolysis. His results are summarized in Table 48.

He concluded that stability increases as the length of the carbon chain increases and is further enhanced by the introduction of an α-methyl group. Alkyl substitution in β-position has a smaller but similar effect. The replacement of a hydrogen by methyl or substituted methyl group decreases the rate of hydro-

TABLE 47. Energy of activation of nitrate esters

Compound	Energy of Activation kcal/mol	log B	Temperature ranges °C	References
Ethyl Nitrate	39.0	15.5	100 170	64b
Nitroglycerine	39.0	15.4	80–140	64c
Ethylene Glycol Dinitrate (Nitroglycol)	39.0	14.5	80 140	64c
Diethylene Glycol Dinitrate	42.0	16.5	80–140	64c
1,2-Propylene Glycol Dinitrate	40.3	15.8	72 140	65
1,3-Propylene Glycol Dinitrate	39.1	14.9	72 140	65
1,4-Butylene Glycol Dinitrate	39.0	15.1	72 140	65
2,3-Butylene Glycol Dinitrate	41.6	16.7	72 140	65
Mannitol Hexanitrate	38.0	15.9	80 140	64c
PETN	40.0	15.8	80 140	64c
Nitrocellulose (13.35% N)	39.2	15.0	100 170	63
Collodion Cotton	38.0	14.4	70 140	64a

TABLE 48. Initial second order rates of hydrolysis of nitrate esters [67]

Compounds	$10^5 k_1$ 30°C	60°C
Methyl nitrate		11.2
Nitroethyl nitrate	1050	
n-propyl nitrate		2.9
n-butyl nitrate		2.9
iso-butyl nitrate		1.6
Ethylene glycol mono-nitrate	168	2700
Ethylene glycol dinitrate	160	
1,3-Propane diol dinitrate	58.7	1300
1,4-Butane diol dinitrate		16.0
DGDN		140
Triethyleneglycol dinitrate (TEGDN)		340
1,2-Propane diol nitrate	54	4650
1,3-Butane diol nitrate	20	
2,3-Butane diol nitrate	2.9	66
Metriol trinitrate (trimethylol-methylmethane trinitrate)	69	
Nitroglycerine	24000	
1,3-Glycerol dinitrate	4500	66200
1-Glycerolmononitrate	2150	51000
2-Glycerolmononitrate	920	20500
Nitro-iso-butyl glycerol trinitrate	128000	
PETN	34	2700

lysis (compare the rate of *n*-propyl and iso-butyl nitrates, nitroglycerine and metriol trinitrate).

The recent novel use of nitrate esters (in addition to their primary role as constituents of high explosives and propellants) is also directed towards improving the ignition and burning of liquid fuels, for example isopropyl nitrate (p. 306). Curme [68, 69] suggested the addition of polyethylene glycol nitrate and polypropylene nitrate as an addition to liquid fuel. Currently experiments are being carried out in Brasil on adding a small proportion (*ca.* 3%) of nitroglycerine to ethanol used as engine fuel (p. 299).

BIOLOGICAL ACTION OF NITRATE ESTERS

According to Von Oettingen [70] nitrate esters oxidize haemoglobin to methaemoglobin and, by depression of the muscles in the vascular walls, cause a peripheral vasodilatation resulting in lower systolic blood pressure, and increased pulse and respiratory rates. The maximum permitted concentration in working places differs for different nitrate esters: a typical example is nitroglycol with a maximum permitted concentration of 1.5 mg/m^3.

GLYCEROL TRINITRATE (NITROGLYCERINE (Vol. II, p. 84))

Setting Point

Some new data have appeared on the physical properties of nitroglycerine. Such is the determination of the setting point by Andreev and Bezpalov [71] on highly pure nitroglycerine. Nitroglycerine was purified by molecular distillation at 40–50°C under pressure of 10^{-4}–10^{-5} Torr. After two or three distillations the setting point +13.1 was found. The authors considered this method for the purification of nitroglycerine to be the most efficient and the safest.

However Meyer [72, 73] gives slightly higher setting points for nitroglycerine:

+13.2 [72] and +13.2–13.5 [73] for stable modification,
+ 2.2 [72] and + 1.9–2.2 [73] for labile modification.

Vapour Pressure (Vol. II, p. 43)

The data on vapour pressure of nitroglycerine were collected by Meyer [72, 73] as being:

0.00033 millibar at	20°C
0.0097	50
0.13	80
0.31	90

Absorption Spectra (Vol. II, p. 45)

The shoulder on the band of asymmetrical and symmetrical vibrations is due to the rotational isomerism [4–7]. Also it should be attributed to the fact that nitroglycerine contains both primary and secondary nitrate groups which according to T. Urbański and Witanowski [5] give different frequencies of asymmetric vibrations (p. 281).

Chemical Properties and Stability (Vol. II, pp. 46–47)

Thermal decomposition of nitroglycerine (and other similar nitrate esters) has been studied intensively by Soviet Union authors and their work has been described in collective volumes [61, 62] and the monograph by Andreev [60].

Here are the main conclusions of some of these important works as presented by Andreev and Bezpalov [71, 74]. They examined the action of water (at 80°, 100° and 120°C) and nitric acid (at 100°C).

Figure 37 shows the decomposition of nitroglycerine in the presence of 0.03% of either nitric acid or water or both, as compared with pure nitroglycerine. The decomposition was recorded by the pressure which developed inside the closed vessel. The strongest action was produced by nitric acid alone, less active was pure water and still less active nitric acid with water. The authors explain it in terms of different rates of hydrolysis and oxidation–reduction processes.

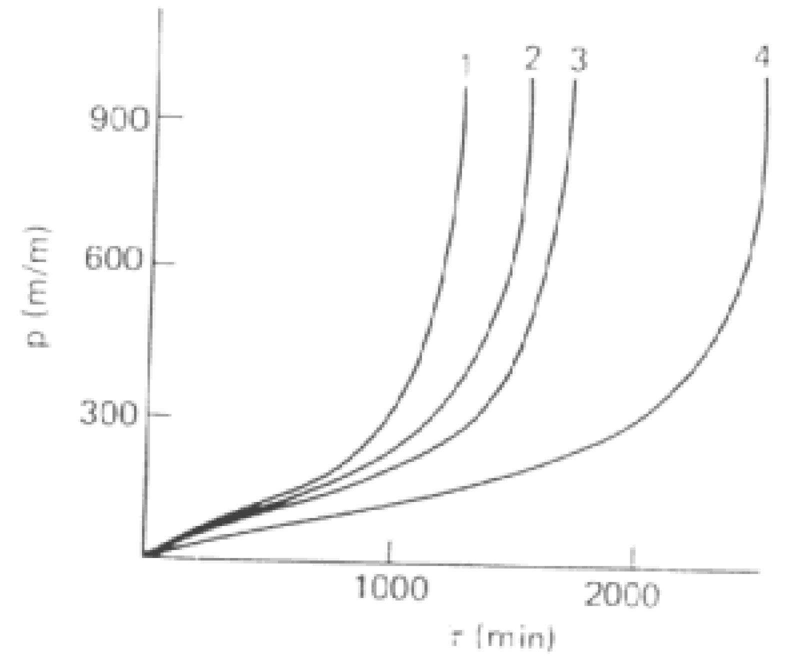


FIG. 37. Influence of a small quantity of water and nitric acid (0.3%) on decomposition of nitroglycerine at 100°C [74]. 1. NG + nitric acid. 2. NG + nitric acid + water. 3. NG + water (0.3%). 4. pure NG.

Larger quantities of nitric acid (0.13–1.5%) with water produce a characteristic shape for the curve of decomposition – Fig. 38. It comprises three stages:

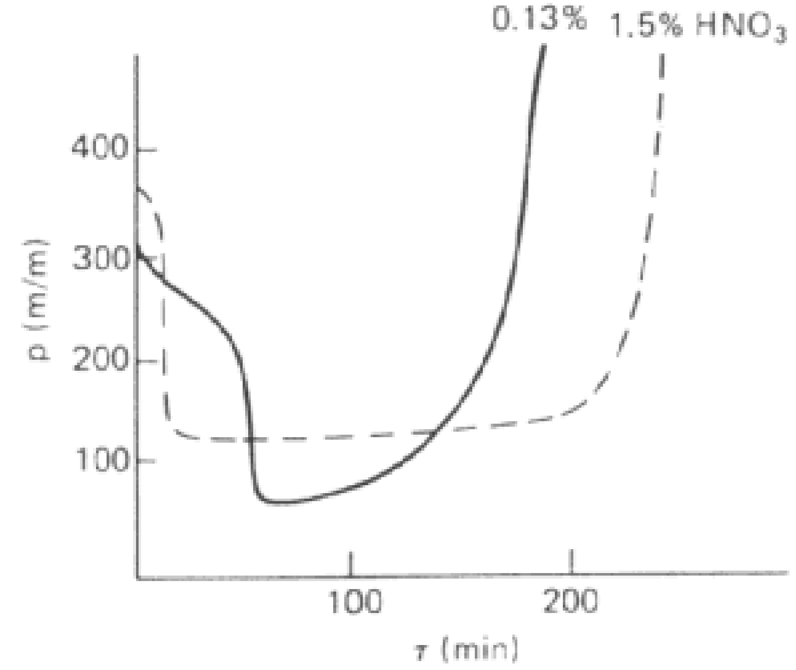


FIG. 38. Influence of nitric acid (0.13% and 1.5% HNO_3) on decomposition of nitroglycerine in the presence of water [74].

(a) induction period under constant pressure,
(b) rapid fall of pressure, due to the reactions between the products of hydrolysis,
(c) increased pressure due to decomposition and oxidation.

The practical conclusion drawn by the authors was that moist nitroglycerine may become dangerous in storage if it contains traces of acid, for example, from insufficient washing.

Svetlov [75] examined the thermal decomposition of pure nitroglycerine in the range of 80–140°C. Two stages have been found. The first is not influenced by the products of the reaction. This is followed by the second stage when the products of the decomposition greatly influence the rate of the reaction. This is presented in Fig. 39. The value of log $\Delta p/\Delta\tau$ is greatly influenced by δ-density inside the container of the sample.

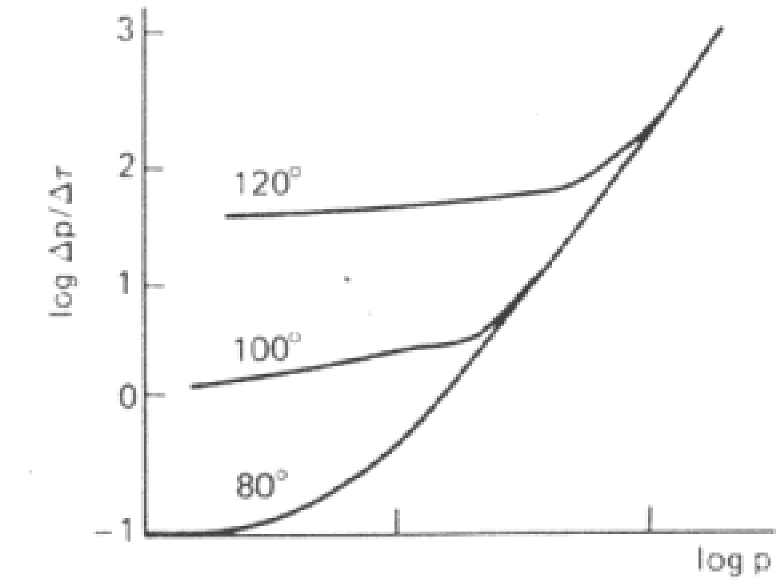


FIG. 39. Influence of gaseous products from nitroglycerine at density δ = 0.03 on its decomposition at 80–120°C [75].

Gorbunov and Svetlov [76] confirmed these findings for the temperature range 80–140°C. The energy of activation depends on the range of temperatures: at 80–140°C and 100–140°C it was found to be 28 kcal/mol and 32 kcal/mol. As previously pointed out (p. 293) the energy of activation is greatly influenced by the temperature range of experiments. Thus Wenograd [77] found value $E = 21.8$ kcal/mol for nitroglycerine at temperatures 300–1000°C.

Gorbunov and Svetlov [76] also examined the role of water in the decomposition of nitroglycerine. Thus water has a very strong influence particularly at higher temperatures, whereas nitric acid increases the rate of decomposition at lower temperatures. As a consequence Gorbunov [78] determined the solubility of water in nitroglycerine at 20–90°C. It varies from 0.26% at 20°C to 0.97% (weight %) at 120°C. The solubility increases when nitroglycerine contains some (0.3–0.6%) nitric acid.

As already reported, Fraser and Paul examined nitrate esters, among them nitroglycerine, by mass spectrography [159].

Recently Caire-Maurisier and Tranchant [160] examined thermal decomposition of nitroglycerine at 110°C using NMR, infra red and mass spectrometry and gas chromatography techniques. Mass spectrometry fragmentation suggested the formation of such fragments as: N_2^+, NO^+, NO_2^+, CO^+, CO_2^+, CH_2O^+, $CH_2ONO_2^+$, CH_2-CHO^+, $CHO-CH_2ONO_2^+$ and fragments with a nitrite ester group, for example $CHONO-CH_2NO-CH_2ONO^+$, $CHONO-CH_2ONO^+$.

Sensitivity to Impact

Bowden and Yoffe [79, 80] pointed out the role of small trapped gas bubbles in the sensitivity of both liquid and solid explosives. The adiabatic compression of small trapped gas bubbles creates 'hot spots' manifested by high temperature. Also friction occurs at the surface of the containing walls, on grit particles or between the crystals of explosives and forms an additional factor governing the sensitivity of explosives to impact.

This was confirmed by a number of authors, their work has been collected in monographs by Afanasyev and Bobolev [81] and Dubovik and Bobolev [82] and in the paper by Coley and Field [83]. The collapse of air bubbles is shown to lead to an increase of sensitivity of liquid explosives by:

(a) local increase of the deflagration velocity and
(b) generating a pressure pulse which is capable of producing hot spots.

This explains the data on the high sensitivity to impact of liquid nitroglycerine and relatively low sensitivity of solid nitroglycerine (Vol. II, p. 53).

The air bubbles produce a type of micro-Munroe jet oriented in the direction of the shock.

Burning of Nitroglycerine

Nitroglycerine burns readily in open vessels under atmospheric pressure. When confined it burns more readily under reduced pressure, for example 0.5 atm. When confined in a tube nitroglycerine burns under atmospheric pressure if the diameter is larger than 0.5 mm. The rate of burning at the critical diameter of 0.5 cm is 0.14 cm/sec. [60]. Andreev and Bezpalov [84] indicated that the critical diameter of burning of nitroglycerine under pressure within the range 20–100 atm is still reduced. They pointed out that three diameters exist:

d_1 – the smallest which allows normal burning,
d_2 – the largest which allows normal burning, beyond which extinguishing can occur due to turbulent phenomena and heat losses,
d_3 – the increase of that diameter gives normal burning.

Under atmospheric pressure the diameters d_1, d_2 and d_3 are 0.5, 2.6 and 7.5 mm respectively.

The increase of viscosity of nitroglycerine by dissolving nitrocellulose reduce the ability of nitroglycerine to burn under turbulent conditions and reduces th critical diameter. The same author gave critical diameters of:

Ethylene glycol dinitrate	1.0 mm
DGDN	5 mm

The ability of nitroglycerine to burn is now being utilized (on a large experi mental scale) to improve the burning of ethanol being used as a fuel for ca engines in Brasil. A small proportion (*ca*. 3%) is added to ethanol for this pu pose, so far with a positive result [108].

Explosion and Detonation of Nitroglycerine (Vol. II, p. 51)

Andreev [85] described his experiments on the thermal decomposition nitroglycerine and the possible transformation into an explosion. The decon position is speeded up by the reaction products. The rate of decompositi depends very much on the concentration of the products and much less on t temperature, in agreement with former findings of Roginskii (Vol. II, pp. 47 48).

Two different rates of detonation of nitroglycerine (explosion and deto ation) (Vol. II, pp. 54–55) became the subject of experiments and discussio for example, Taylor [86], Häuseler [87] and Soviet workers [88, 89]. It has al been shown that the reaction front in homogeneous liquid explosives becom distorted under conditions close to failure [9, 91].

Coley and Field [83] discussed the LVD (low velocity detonation) in liqu explosives. According to the author of the present book the LVD should called not the detonation, but the explosion (Vol. II, pp. 54–55). In order to create confusion the term LVD will be accepted. Coley and Fields [83] pointed out that LVD in liquid explosives systems is a stable reaction regime, readily initiated by shock pressures of a few kilobars with propagation velocity of the order of 2000 m/s. The thermodynamic theory of detonation is not applicable to this regime since the pressures involved are too small for direct shock heating of homogeneous explosive to be significant. According to Coley and Fields new experiments have shown that the presence of gas or vapour filled cavities within the explosive is an essential requirement for initiation and propagation of LVD [91–95].

In liquid explosives bubble size becomes an important factor – this was pointed out by Coley and Field [84]: small bubbles facilitate the transfer to LVD.

Zimmer [96] came to the conclusion that the LVD of nitroglycerine (1500–1600 m/s) could be manifested by a spiral mode of propagation. (It should be pointed out that T. Urbański [97] expressed the view that non-homogeneous explosive mixtures can show a spiral way of detonation.) According to Zimmer the irregularities of the LVD are caused by the interaction of incident and reflection waves forming Mach waves under certain conditions. An analogy can be drawn between the spiral way of detonation of gas-mixtures [98–102] and spiral way of detonation of solid–liquid systems.

The critical diameter in a steel tube is 24 mm according to Meyer [72, 73].

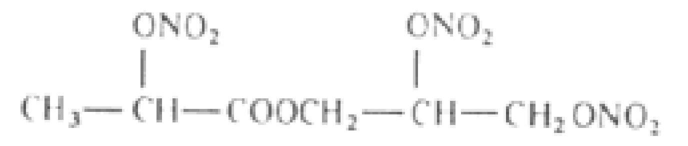
Specifications for glycerine and nitroglycerine are given in Chapter XI on the manufacture of nitroglycerine.

GLYCEROL DINITRATES ('DINITROGLYCERINE') AND DERIVATIVES

'Dinitroglycerine' is a common impurity present in nitroglycerine. Most frequently it is glycerol 1,3-dinitrate. 1,2-Isomer is usually present in negligible quantity. Krasiejko [104] isolated the dinitrates by TLC and spectrometrically determined the nitrites obtained by hydrolysis of dinitrate. (The chromatography of nitroglycerine has been described in a few papers prior to the work of Krasiejko [105–107].)

Glycerol dinitrate does not currently have a practical application.

Glycerol-nitrolactate Dinitrate (VI) [72, 73]

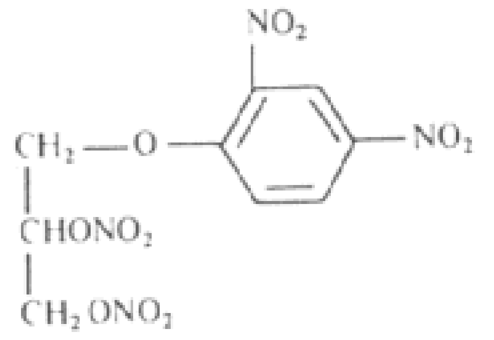


$$CH_3-\overset{\overset{ONO_2}{|}}{CH}-COOCH_2-\overset{\overset{ONO_2}{|}}{CH}-CH_2ONO_2$$

VI

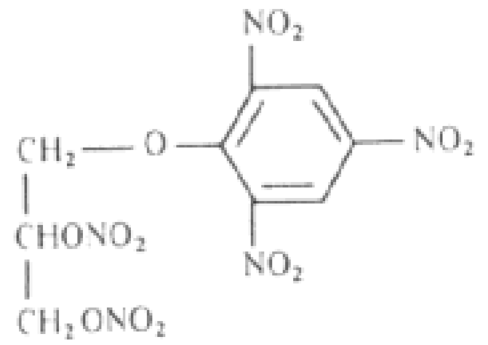
This is an oily substance of density 1.47 and ignition temperature 190°C obtained by the nitration of glycerol mono lactate. It is a good gelatinizer of nitrocellulose.

Glycerol 2,4-Dinitrophenylether (VII) and Trinitrophenylether (VIII) Dinitrates [72, 73]



VII

m.p. 124°C



VIII

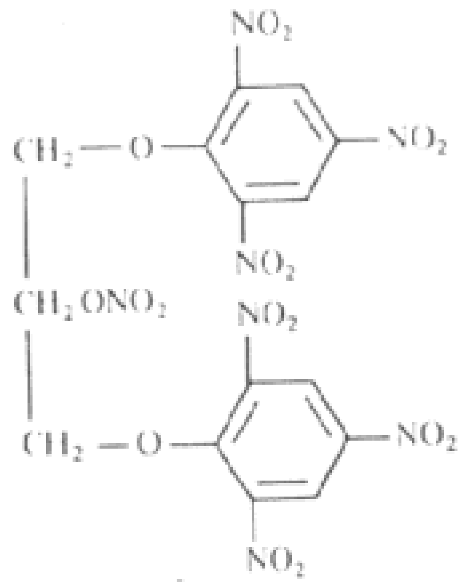
m.p. 128.5°C

Here are some pertinent data on the properties of the substances:

	VII	VIII
Ignition temperature	205–210°C	200–205°C
Lead block	320 cm^3	420 cm^3
Sensitivity to impact	0.8 kpm	0.4 kpm
Gelatinization of nitrocellulose	poor	none

Both compounds VII and VIII can be obtained by the nitration of *o*-nitrophenylglycerol ether and phenyl glycerol ether respectively.

Hexanitrodiphenylglycerol Mononitrate (IX) [72, 73]



IX

m.p. 160–175°C

The wide range of melting temperatures indicates the decomposition of the substance during heating. The substance gives lead block test of 355 cm^3. It is much less sensitive to impact than VII and VIII due to the presence of only one *O*-nitro group. It was obtained by dissolving glyceryl diphenyl in nitric acid followed by mixing the solution with nitric–sulphuric acid.

Mixed Esters of Glycerol

Among esters of glycerol with nitric and organic acids the most important appears to be Glycerol Acetate Dinitrate (X) described by Meyer [72, 73]

$$\begin{array}{l} CH_2ONO_2 \\ | \\ CHOCOCH_3 \\ | \\ CH_2ONO_2 \end{array}$$

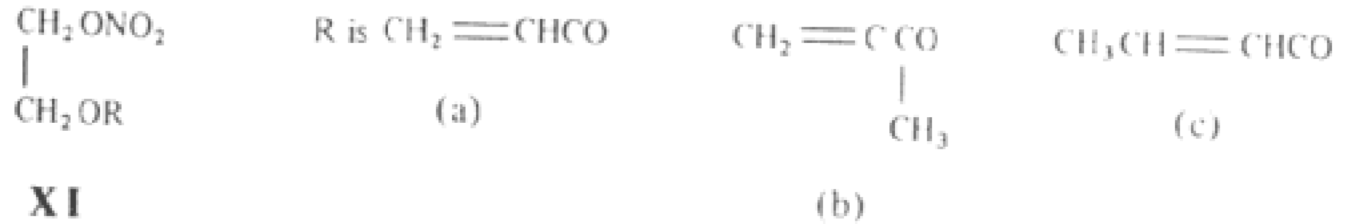
X

This is an oily substance of density 1.42 with ignition temperature 170–180°C. It gives lead block test 200 cm^3. It was prepared by nitration of acetylglycerol with mixed acid rich with nitric acid.

GLYCOL NITRATES

Ethylene Glycol Mononitrate (2-Nitratoethanol) (Vol. II, p. 142)

Glycol mononitrate has aroused a certain amount of interest. Twist and Baughan [109] examined the vapour pressure of the solution of this substance, and of a number of other nitrate esters, and found the deviations from Raoult laws to be of the same order as those observed by Chédin and Vandoni for nitrocellulose [110]. Prior to this work Marans and Zelinski [111] prepared a number of mixed esters of the type XI where R are unsaturated acyls apt to polymerize and thus to give combustible polymers.



$$\begin{array}{l} CH_2ONO_2 \\ | \\ CH_2OR \end{array} \qquad \text{R is } CH_2{=}CHCO \ (a) \qquad \begin{array}{l} CH_2{=}C\,CO \\ \quad\ | \\ \quad CH_3 \end{array} \ (b) \qquad CH_3CH{=}CHCO \ (c)$$

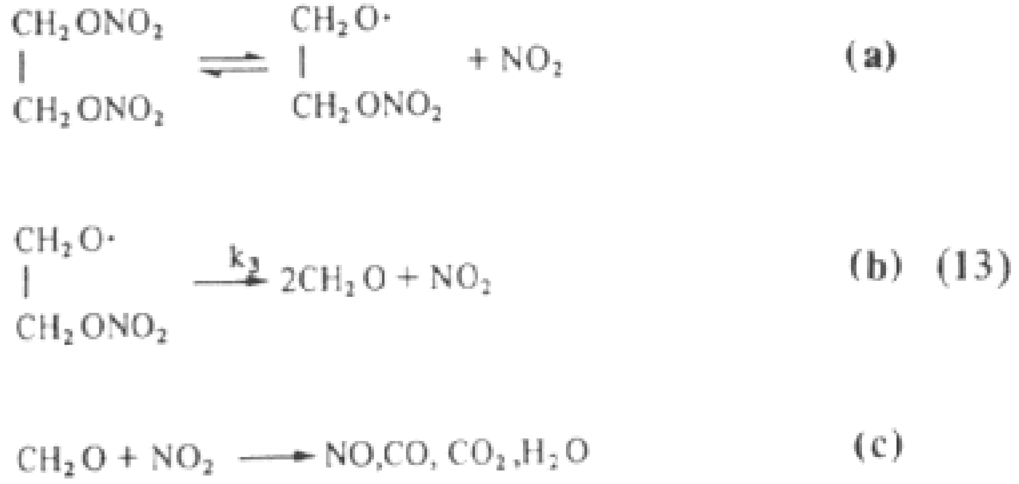
XI

They acted on 2-nitratoethanol with chlorides of acrylic (a), methacrylic (b) and crotonic (c) acids in the presence of cuprous chloride as a polymerization inhibitor. The radical polymerization was initiated by benzoyl peroxide in nitrogen atmosphere. It lasted 20 min at 100°C. In the absence of a catalyst polymerization occurred at 20°C in the course of a few days. This observation is in agreement with the finding reported in Vol. II, p. 19 that nitrate esters can catalyse polymerization reaction, contrary to *C*-nitro compounds (Chapter IV).

Ethylene Glycol Dinitrate ('Nitroglycol') (Vol. II, p. 142)

Relatively less attention is now paid to ethylene glycol dinitrate. It is currently used in mixture with nitroglycerine for low freezing dynamites but some mining explosives, used in countries with harsh winters, contain nitroglycol alone.

Kondrikov [112] rationalized thermal decomposition of ethylene glycol dinitrate by diagram (13):



$$\begin{array}{l} CH_2ONO_2 \\ | \\ CH_2ONO_2 \end{array} \rightleftharpoons \begin{array}{l} CH_2O\cdot \\ | \\ CH_2ONO_2 \end{array} + NO_2 \qquad \text{(a)}$$

$$\begin{array}{l} CH_2O\cdot \\ | \\ CH_2ONO_2 \end{array} \xrightarrow{k_2} 2CH_2O + NO_2 \qquad \text{(b)} \quad (13)$$

$$CH_2O + NO_2 \longrightarrow NO, CO, CO_2, H_2O \qquad \text{(c)}$$

Ethylene glycol dinitrate is more toxic than nitroglycerine because of its higher volatility. According to Meyer [72, 73] the maximum permitted concentration in a work place is 1.5–1.6 mg/m^3.

Diethylene Glycol Dinitrate (Vol. II, p. 149)

Diethylene glycol dinitrate – DGDN has currently become the most important (next to nitroglycerine and nitroglycol) *O*-nitro compound, much in use in 'double base' propellants. The great advantage of DGDN is its relatively low sensitivity to impact and subsequently safer handling than nitroglycerine and good solubility of nitrocellulose. The disadvantage is in the danger produced by spent acid (Vol. II, pp. 152–153).

Svetlov [113] examined thermal decomposition of DGDN in the liquid phase in the temperature range 60–150°C. He calculated the energy of activation – see Table 47 (p. 294).

Lurge and Svetlov [114] examined the decomposition of DGDN in the presence of oxygen, NO_2 and NO, H NO_3 and oxalic acid at 80–120°C and found that nitric and oxalic acids can increase the rate of decomposition up to one hundred times. Oxygen also increases the rate of decomposition but to a much smaller extent. The first stage of the reaction consists in binding oxygen, probably due to the formation of peroxides. The latter decompose at a later stage.

The specification for diethylene glycol for nitration is given in Chapter XI.

Triethylene Glycol Dinitrate (Vol. II, p. 154)

This substance was used (together with diethylene glycol dinitrate) in Germany during World War II for making double base propellants. It is less volatile than diglycol dinitrate but more soluble in spent acid (Vol. II, p. 155).

The specification for triethylene glycol for nitration is given in Chapter XI.

Butine-2-diol-1,4 Dinitrate

$$O_2NOCH_2C \equiv CCH_2ONO_2$$

XII

This substance was obtained by T. Urbański and Tarantowicz [115]. The aim was to produce an explosive of a greater power considering that the acetylenic bond increases exothermic properties of the substance. In lead block it gave a better performance (385 cm^3) than tetryl and ethylene glycol mononitrate.

It is an oily substance of density (at 20°C) 1.408. On a hot plate, temperature 245–380°C, it gave a violent explosion similar to that of nitroglycerine. Below 245°C it evaporated and above 380°C took on a spheroidal shape and burned quietly. It is more sensitive to impact than nitroglycerine, and is a good solvent for nitrocellulose.

The substance gives a negative heat test (Abel test): at 80°C potassium iodide-starch paper was coloured after 3 min.

The diol dinitrate (XII) was obtained in a standard way by nitrating in the acid mixture composed of 40% nitric and 60% sulphuric acid at 18–22°C. The yield was 70–75% of the theoretical.

NITRATE ESTERS OF MONOHYDROXYLIC ALCOHOLS
(Vol. II, p. 160)

The main interest in nitrate esters of monohydroxylic alcohols lies in their application as rocket fuels. Subsequently a thermal decomposition of nitrate esters is examined. Kondrikov [112] gave the following diagram (14) of the thermal decomposition of nitrate esters of a general formula RCH_2ONO_2:

$$\begin{array}{lll} RCH_2ONO_2 \longrightarrow RCH_2O + NO_2 & \textbf{(a)} & \\ RCH_2O \longrightarrow R\cdot + CH_2O & \textbf{(b)} & \\ CH_2O + NO_2 \longrightarrow NO, CO, CO_2, H_2O & \textbf{(c)} & \\ RCH_2O + NO \longrightarrow RCH_2ONO & \textbf{(d)} & \textbf{(14)} \\ RCH_2O + NO \longrightarrow RCHO + NOH & \textbf{(e)} & \\ 2NOH \longrightarrow N_2O + H_2O & \textbf{(f)} & \end{array}$$

A few other schemes of thermal decomposition are given with the description of particular nitrate esters.

All the mono-nitrate esters give a colour reaction with tetramethyl-*p*-phenylene-diamine due to Wurster cation [13–15, 22a]. The colour remains for several days.

With regard to the nitration of alcohols attention should be drawn to the work of Eremenko [140] who pointed out the role of undissociated nitric acid in the *O*-nitration mechanism.

Methyl Nitrate (Vol. II, p. 160)

Some properties of methyl nitrate, such as the thermal decomposition and explosive properties are given in Vol. II. Some additional data are given by Meyer [72, 73]:

boiling point	65°C
density	1.217
heat of explosion	1462 kcal/kg
volume of gases	873 l/kg
critical diameter in a steel tube	18 mm

Methyl nitrate was found to be present in the products of the decomposition of azomethane (CH_3–N=N–CH_3) when the latter substance was subjected to ultraviolet irradiation [116]. This was due to an intermediate formation of CH_3O_2 radical which reacted with NO to yield the nitrate ester:

$$CH_3O_2^{\cdot} + NO \longrightarrow CH_3O\cdot + NO_2 \longrightarrow CH_3ONO_2. \tag{15}$$

Ethyl Nitrate ($C_2H_5ONO_2$) (Vol. II, p. 163)

Ethyl nitrate is currently an important component of liquid rocket fuel. In that respect considerable work is being done to elucidate the mechanism of thermal decomposition by Pollard, H. S. Marshall and Pedler [151]. Some fragments of their mechanism are as follows (16):

$$\begin{array}{l} C_2H_5ONO_2 \longrightarrow C_2H_5O\cdot + NO_2 \\ C_2H_5O\cdot \longrightarrow CH_3CHO + H \\ C_2H_5O\cdot \longrightarrow HCHO + CH_3^{\cdot}, \text{etc.} \end{array} \tag{16}$$

Considering the formation of a number of simple molecules and free radicals, such as $CH_3^{\cdot}$, $CH_3O\cdot$, NO, NO_2, CO, CO_2 several less defined reactions can take place, for example, the formation of nitrite esters [2]:

$$\begin{array}{l} C_2H_5O\cdot + NO \longrightarrow C_2H_5ONO, \\ CH_3^{\cdot} + O \longrightarrow CH_3O\cdot, \\ CH_3O\cdot + NO \longrightarrow CH_3ONO, \text{etc.} \end{array} \tag{17}$$

Nitrite esters are marked by their relatively low stability (p. 318).

Meyer [72, 73] gives some additional data on the properties of ethyl nitrate:

melting point	−102°C

heat of explosion	913 kcal/kg
volume of gases	1227 l/kg
lead block test	420 cm³

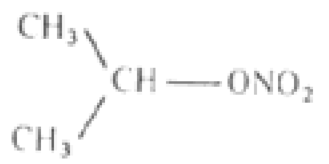
For the activation energy see Table 47.

The preparation of ethyl nitrate follows the same rule as that of methyl nitrate: nitric acid should be free of nitrous fumes by adding urea (Vol. I, p. 162).

n-Propyl Nitrate (Vol. II, p. 165)

n-Propyl nitrate has found an application as a liquid fuel in rockets according to Meyer [72, 73]. The same source gives data on the properties of the substance.

Iso-Propyl Nitrate (Vol. II, p. 165)



XIII

As previously pointed out a practical application has been found for iso-propyl nitrate. It was originally believed [117] that the substance could only be made from iso-propyl iodide and silver nitrate. Direct nitration was found to yield mainly acetone due to the oxidation of the secondary alcoholic group. However a process of continuous nitration of iso-propyl alcohol in the presence of urea has been described by Imperial Chemical Industries patents [36]. iso-Propyl alcohol and urea were introduced into nitric acid (over 40% HNO_3) at its boiling temperature and a current of air stirred and removed unstable products. According to Desseigne [118] the method gave *ca.* 80% yield. He used nitric acid of over 50% HNO_3 at 108–110°C.

iso-Propyl nitrate is in use as an engine starter fuel [119] and for rockets [121].

Gray and co-workers [120] examined the decomposition of iso-propyl nitrate at elevated temperatures:

$$\text{i-}C_3H_7ONO_2 \longrightarrow 1.5\,CO + 0.5\,CO_2 + CH_4 + H_2 + 0.5\,H_2O + 0.5\,N_2 \qquad \textbf{(18a)}$$

with the thermal effect $-\Delta H = ca.$ 86 kcal/mol. Gray *et al.* [121] also examined the decomposition of iso-propyl nitrate at elevated temperatures (290–1380°C). In the absence of oxygen the reaction can be depicted by equations:

$$\begin{aligned} &\text{i-}C_3H_7ONO \longrightarrow \text{i-}C_3H_7O\cdot + NO_2 \\ &\text{i-}C_3H_7O\cdot \longrightarrow CH_3^{\bullet} + CH_3CHO \\ &CH_3^{\bullet} + NO_2 \longrightarrow CH_3NO_2. \end{aligned} \qquad \textbf{(18b)}$$

Acetaldehyde, nitrogen dioxide and nitromethane are main products of the decomposition. In the presence of oxygen methyl radicals yield formaldehyde. Acetaldehyde is very reactive and by abstraction of hydrogen yields acetyl which is the principal source of CO and CO_2:

$$\begin{aligned} &CH_3CO \longrightarrow CH_3^{\bullet} + CO \\ &CH_3CO + NO_2 \longrightarrow CH_3^{\bullet} + CO_2 + NO. \end{aligned} \qquad \textbf{(19)}$$

POLYHYDROXYLIC ALCOHOL ESTERS (Vol. II, p. 166)

Butane-1,2,4-triol Trinitrate (Vol. II, p. 166)

Meyer [72, 73] gave some data on the properties of the substance, such as:

freezing point	−27°C
density	1.52
oxygen balance	−16.6%
heat of explosion	1420–1470 kcal/kg.

1,2,4-Butanetriol is nitrated to trinitrate with a nitric–sulphuric acid mixture. The nitrated product shows good stability. It is less volatile than nitroglycerine and according to Meyer is in use for tropic-proof double base powder.

Erythritol Tetranitrate, Erythrol Tetranitrate (Vol. II, p. 100)

Meyer [72, 73] gives some data:

melting point	61.5°C
deflagation point	154–160°C with a violent explosion
density	1.6
heat of explosion	1443 kcal/kg
volume of gases	704 l/kg.

It has an intense magenta colour with tetramethyl-*p*-phenylene-diamine due to Wurster cation [13–17].

Pentitol Pentanitrates (Vol. II, p. 168)

D-Xylitol pentanitrate with tetramethyl-*p*-phenylene-diamine (TMPD) gives a blue colour due to the formation of Wurster cation after which another charge-transfer complex is formed by 2 moles of xylitol pentanitrate and 1 mole of TMPD dication formed from Wurster cation [13–17].

D-*Mannitol Pentanitrate* (Vol. II, p. 170)

D-Mannitol-1,2,3,5,6-pentanitrate (m.p. 81–82°C) is prepared by heating hexanitrate of mannitol with pyridine [120]. Denitration occurs with the evolution of nitrogen dioxide. D-Mannitol pentanitrate reacts with TMPD in much the same way as D-Xylitol pentanitrate forming a charge–transfer complex of 2 moles of mannitol pentanitrate and 1 mole of the dication [15].

D-*Mannitol Hexanitrate* (Vol. II, p. 168)

According to Elias and Hayward [123] the nitration of D-mannitol to hexanitrate can be carried out with N_2O_5 vapour at 0 ± 2°C under reduced pressure. After two hours the hexanitrate was formed with 100% yield.

The charge–transfer between D-mannitol hexanitrate and TMPD is best presented on Fig. 40 according to T. Urbański *et al.* [15]. Curve I shows a CT colourless complex at *ca.* 1030 nm which disappears after 5 min, and two maxima of Wurster cation (570 and 620 nm) appear. The intensity of the latter increased in the course of 15 minutes (curve II).

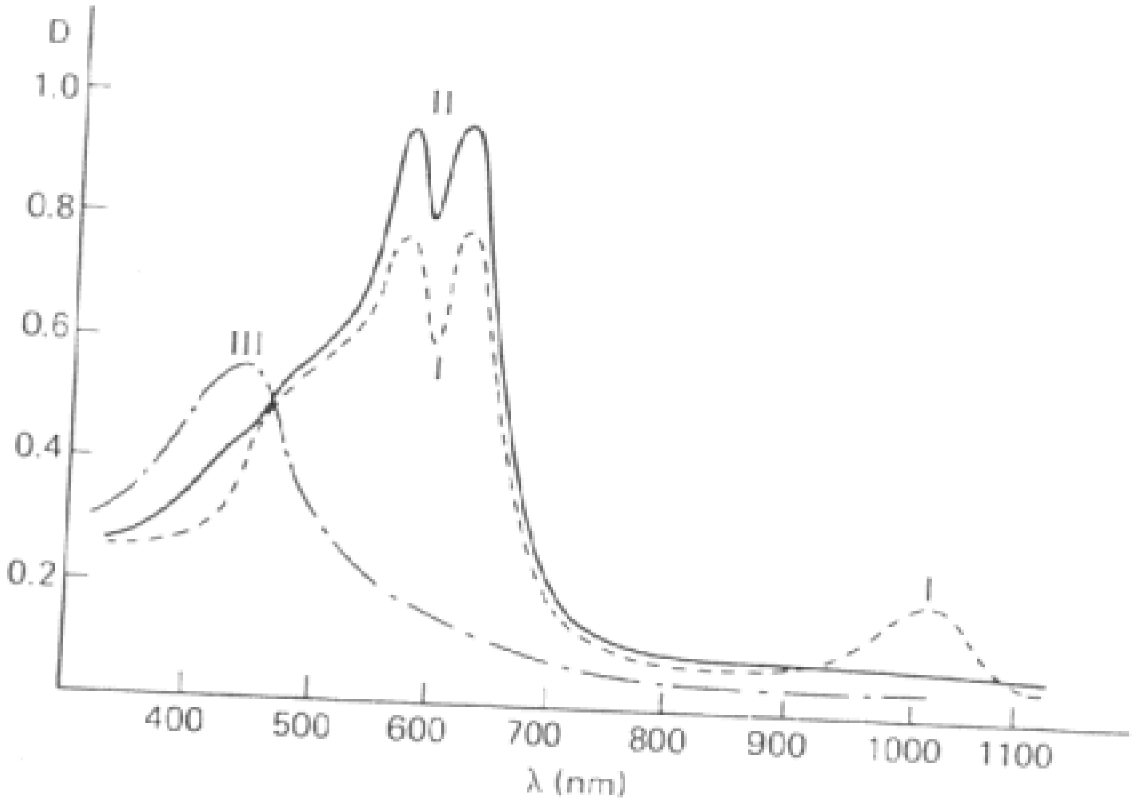
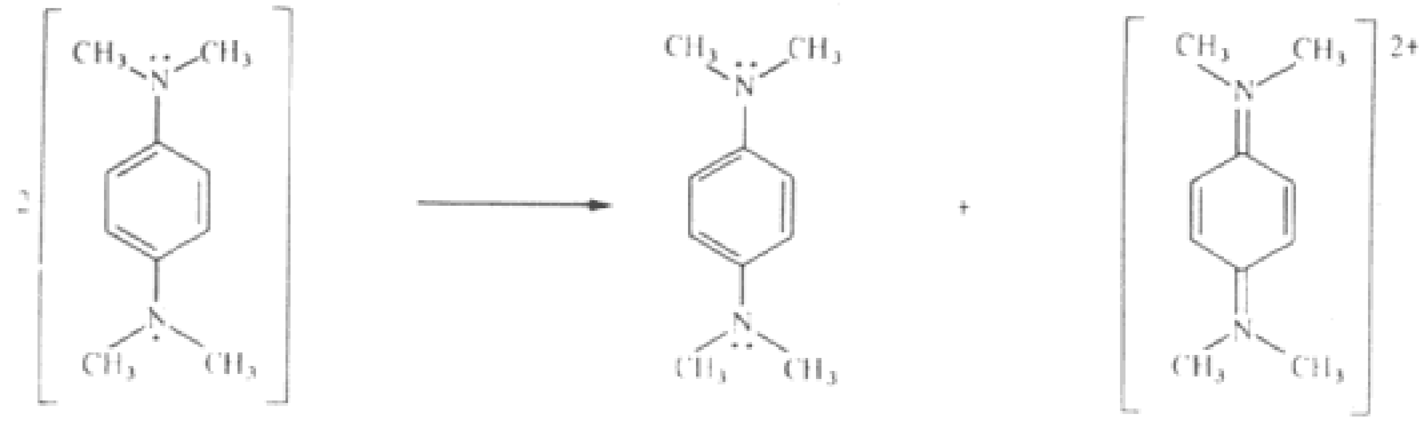


FIG. 40. General shape of electronic spectra of hexanitrate of D-mannitol and tetramethyl-*p*-phenylenediamine charge transfer phenomenon.

After 2 hours both maxima vanished and a new maximum at 450 nm appeared (curve III). The yellow coloured complex is formed from 1 mole of mannitol hexanitrate and 1 mole of TMPD dication. The dication is formed as the result of the disproportionation between the Wurster cation and TMPD:



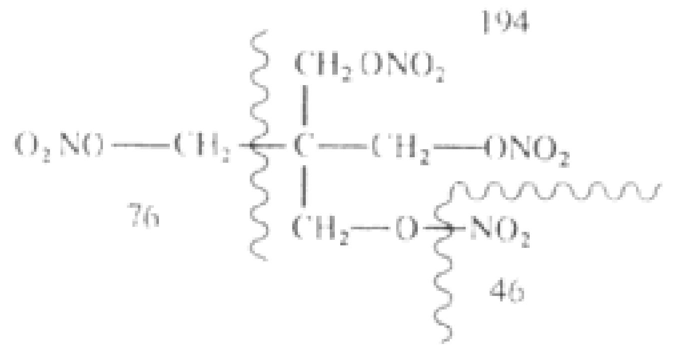
(20)

The stereochemistry of the complex is rationalized by diagram V (p. 285).

It was suggested that a six-member chain of mannitol hexanitrate was coiled into a pseudo-ring. It is not surprising if one considers that long chain organic substances in solution have a tendency to be coiled. This is based on thermodynamical analysis, dipole measurements etc. [124].

Lurye and Svetlov [125] examined the thermal decomposition of mannitol hexanitrate in the temperature range 80–140°C. They came to the conclusion that the decomposition of molten hexanitrate occurred in two (at least) stages. The first stage is manifested by splitting off nitrogen dioxide. This stage follows the equation of Arrhenius (Table 47). After that secondary reactions occur – mainly of oxidation accompanied by hydrolysis with formed water.

Mass spectrometry showed the decomposition occurs according to XIV [159]



XIV

Meyer [72, 73] gives some data on the explosive properties of D-mannitol hexanitrate:

heat of detonation	1420 kcal/kg
volume of gases	694 l/kg
deflagration point	185°C

*Dulcitol (*D- *or* -L-*galactitol) Hexanitrate and* D-*Sorbitol hexanitrate* (Vol. II, pp. 171, 172)

Both substances can be obtained with 85 and 94% yield respectively by nitrating dulcitol and D-sorbitol with N_2O_5 vapours under reduced pressure at 0 ± 2°C [123].

Both substances form charge–transfer complexes with tetramethyl-*p*-phenylenediamine in much the same way as D-mannitol hexanitrate [14, 15, 22a].

PENTAERYTHRITOL TETRANITRATE (PETN) (Vol. II, p. 175)

Some new data on the properties of PETN have been reported by Meyer [72, 73]:

melting enthalpy	36.4 kcal/kg
specific heat	0.26 kcal/kg
density	1.76

An important practical problem is how to obtain PETN in a crystalline shape which would allow an easy flow to a high bulk density, that is, greater than 1.2 g/cm³. The needle habit gives the lowest bulk density which can be used for certain purposes.

A fairly wide range of particle sizes can be obtained by adding water to an acetone solution of PETN and a bulk density of 1.1–1.2 can be reached. It is known that various sizes of crystals make the better filling of a container possible and can give a higher density.

Duncan [126] described experiments on crystal size and shape of PETN by its recrystallization.

To produce the substance having a high specific surface area $S_0 = 10$ to 20×10^3 cm²/g suitable for detonators a 'shock crystallization' was used. Pure PETN was dissolved in acetone (1:5) and the solution dropped into aqueous ethanol at *ca.* −30°C. The resulting crystals are much different in sizes (0.5–16 μ) and irregular shapes from spheres to needles. A modification of the method can be used by introducing a 10% solution of pure PETN in acetone–ethanol into ethanol–acetone (1:2) cooled to −20°C.

Crystallization from DMSO produces crystals which are too large. On the contrary, crystallization by spraying saturated acetone solution into an air tunnel gives very fine spherical particles when the tunnel walls are struck.

Duncan also gives a new table of the solubility of PETN in some solvents (Table 49).

The size of crystals increases by keeping them at 90–120°C for several hours (e.g. 20–30 hours).

Chromatography (TLC) showed very small spots of hexanitrate of dipentaerythritol (DPEHN), and in some cases octonitrate of tripentaerythritol (TPEON) and pentaerythritol trinitrate.

T. Urbański [127] suggested recrystallization to add a protective colloid such as an acetone solution of nitrocellulose (low viscosity grade collodium cotton).

TABLE 49. Solubility of PETN in wt.% according to Duncan [12b]

Solvent	Temperature °C 0	20	25	30	40	50	60
Methanol		0.46			1.15		2.60
Chloroform		0.09					
Carbon tetrachloride		0.096		0.108	0.118	0.121	
1,2-Dichloroethane		1.5		4.1	11.2		14.2
1,1,2,2-Tetrachloroethane		0.18		0.27	0.40	0.58	
2-Methyl-1-propanol	0.07	0.195			0.415		1.205
Nitromethane	3.34		8.89				
Ethyl acetate		13.0		17.0	22.0	31.0	
β-Ethoxyethyl acetate		1.5		4.1	7.6	11.2	14.2

PETN was examined by mass-spectroscopy [128]: electron impact gave two fragments: 76 and 46.

Field ionization fragments: 194, 76, 74 are depicted by scheme XIV.

Thermodynamic Properties and Thermal Decomposition of PETN

Dinegar and Stammler [129] determined enthalpies connected with the volatility of PETN. The enthalpies of sublimation and of vapourization were:

35 ± 3 kcal/mol and
19 ± 2 kcal/mol respectively.

A considerable number of papers have been dedicated to the thermal decomposition of PETN. They were reviewed by Andreev [71]. He quoted the work of Robertson [130] who examined the decomposition of PETN in the temperature range: 161–233°C, the energy of activation was

$$E = 47 \text{ kcal/mol}, \quad \log B = 19.8.$$

For a 5% solution of PETN in dicyclohexylphthalate at 171–238°C the values of E and B were:

$$E = 39.5 \text{ kcal/mol}, \quad \log B = 16.1.$$

Robertson analysed gaseous products while keeping PETN for 2 min at 210°C. He found (in mol %): 0.51 NO_2, 2.11 NO, 0.42 N_2O, 0.07 N_2, 0.09 H_2, 0.93 CO, 0.28 CO_2 and formaldehyde and water.

He suggests that the first stage of the decomposition of PETN consists in splitting off NO_2, after which $-CH_2O$ is removed as formaldehyde.

A different approach to the thermal decomposition of PETN was given by T. Urbański [131–133]. The shape of the curve of the induction time against the temperature is given in Fig. 41, much the same as in Vol. I, Fig. 13, p. 50 for nitroglycerine.

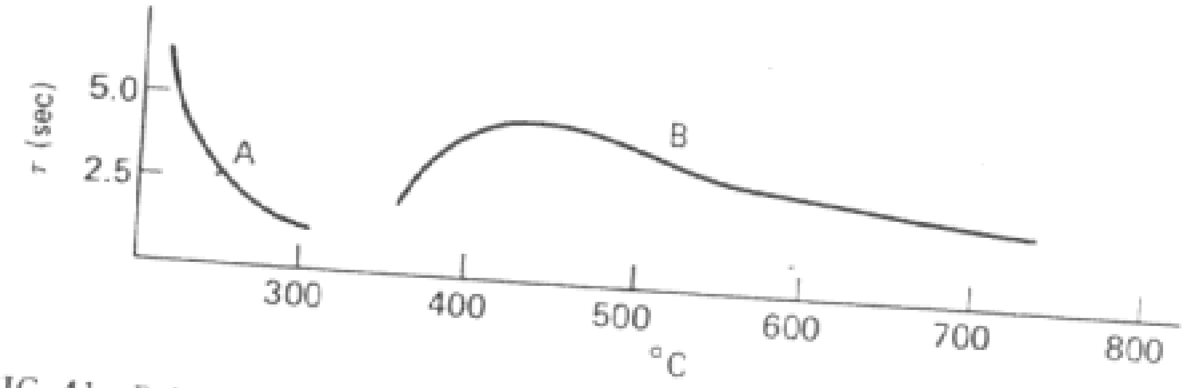


FIG. 41. Behaviour of PETN at high temperatures according to T. Urbański [131–133]. Induction period τ is given against the temperature. Curve B corresponds to spheroidal shape of the molten substance.

Curve A is of the usual shape induction period/temperature below 350°C. Curve B gives the induction period when the molten substance takes spheroidal shape. The activation energy was found to be:

E = 22.4 kcal/mol for the temperatures 240–310°C
E = 4.5 kcal/mol for the temperatures 460–790°C.

Wenograd [77] in the temperature range 400–1000°C established the energy of activation as E = 20.4 kcal/mol. Evidently the energy decreases with the increase of temperature.

Andreev and Kaidymov [134] published a review on the thermal decomposition of PETN and a description of their own results. Their data for activation energy are given in Table 47. They confirmed the results of T. Urbański and co-workers (Vol. II, pp. 181–183) and similarly of Tonegutti [135] and Bourjol [136] that the addition of aromatic nitro compounds to PETN lowers the stability of the latter. In all experiments it was shown that decomposition in the liquid phase, that is, the molten system, engenders faster decomposition than that of the solid phase.

According to the author of the present book lowering of the stability has the result that on melting the substance passes to a higher energy level with an increased entropy.

Differential Scanning Calorimeter (DSC) was used by Rogers and Dinegar [165] in combination with X-ray and microscopy to find the reason for anomalous behaviour in the heat of fusion of PETN crystallized by different methods. Microscopy revealed the existence of at least three crystal habits of PETN: (1) 'tetragonal', (2) needle, (3) irregular plates. Their heats of fusion ΔH_t were:

(1) 36.5–37.4 cal/g
(2) 36.5–37.7 cal/g
(3) 31.7–33.2 cal/g

Differences in heat of fusion was attributed to the lattice energy changes resulting from random inclusions within the lattice.

Explosive Properties

An interesting finding was made by Institut Franco-Allemand de Recherches de St. Louis [166] that the rate of detonation of PETN takes different values along different crystal axis:

(001) 8424 m/s
(110) 8887 m/s.

T. Urbański and Galas [137, 138] examined the rate of detonation of PETN with various liquids. The results with two liquids which do not dissolve PETN: water and glycerol are given in Table 50. The general trend of the change of the observed rate of detonation with the addition of a liquid is given in Fig. 42.

TABLE 50. Detonation of PETN with water and glycerol [137–138] in tubes 20/26 mm diameter, detonator No. 8 with 10 g PETN

Proportion of liquid	Density		Rate of detonation m/s		
	Total	Real ρ_r	observed V_o	at density ρ_r V_r	Difference $V_o - V_r$
Water					
0	1.45	1.45	7275	7275	0
5	1.45	1.38	7250	7055	195
10	1.45	1.31	7445	6810	635
20	1.45	1.16	7130	6250	930
30	1.44	1.01	6645	5530	1115
Glycerol					
5	1.40	1.33	7350	6880	425
10	1.40	1.26	7355	6080	1745
30	1.45	1.02	7675	5620	3055
35	1.45	0.94	7280	5230	2050

The observed rate of detonation of the explosive with the liquid was V_o and the total density 1.45. By adding a liquid and keeping the same total density (density of the mixture) the real density of the explosive was lowered to ρ_r which at this density gives the rate of detonation V_r. Hence V_o-V_r is the increase in the rate of detonation by adding the liquid. This is fully discussed in Chapter XIII (Table 60).

Dinegar, Rochester, Horton and Johnson [145] examined the shock sensitivity of PETN and came to the conclusion that the nature of the gas in a small scale 'gap-test' influences the sensitivity of PETN. Thus He, Ar, N_2 and CO_2 have a desensitizing effect, whereas oxygen sensitized the compressed charges.

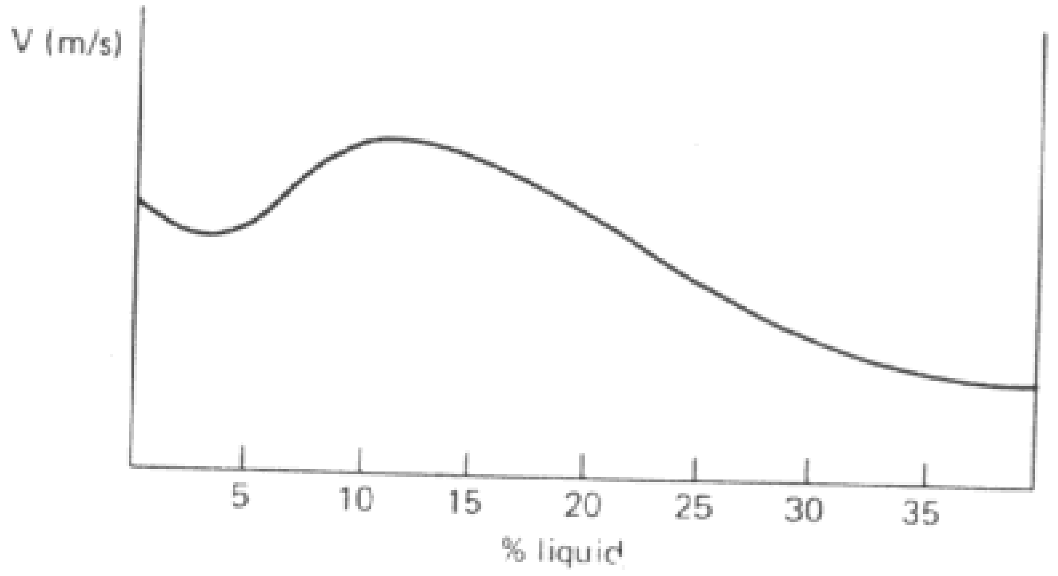


FIG. 42. Rate of detonation of systems: high explosive – non-explosive liquid, e.g. PETN or RDX and water or glycerin.

Nitration of Pentaerythritol (Vol. II, p. 185)

It is known that the nitration of pentaerythritol on an industrial scale is carried out mostly with nitric acid alone, without sulphuric acid. Therefore, it was necessary to establish the solubility of PETN in nitric acid of different concentrations and at different temperatures. Such data were given by Camera and Mauro [139] and are collected in Table 51. The same authors established the solubility of dipentaerythritol hexanitrate (Vol. II, p. 195) – Table 52.

TABLE 51. Solubility of PETN in nitric acid [139] in g of the substance in 100 g of the solution

% HNO_3	Temperature °C					
	0	10	20	30	40	50
60	0.018	0.041	0.109	0.352	0.645	0.880
65	0.036	0.113	0.322	0.778	1.020	1.300
70	0.075	0.134	0.302	0.845	1.570	2.240
75	0.069	0.124	0.265	0.557	1.340	2.650
80	0.106	0.195	0.335	0.650	1.291	2.775
85	0.190	0.329	0.585	1.056	1.957	3.849
90	0.441	0.762	1.318	2.314	4.036	7.156
95	1.060	1.825	3.023	4.822	8.090	12.609

Nevertheless, some industrial methods are still using mixtures of nitric and sulphuric acids and an important paper by Eremenko [140] has been published in which he gives an analysis of the role of nitric acid in nitric–sulphuric acid mixtures as applied to the *O*-nitration of alcohols in general and of pentaerythritol in particular. He gave a critical review of the work of Ingold and coworkers [141, 142] and their suggested mechanism of *O*-nitration based on reactions:

TABLE 52. Solubility of DiPEHN in nitric acid [139] in g of the substance in 100 g of the solution

% HNO_3	Temperature °C		
	0	10	20
60	0.024	0.064	0.222
65	0.080	0.246	1.099
70	0.271	0.530	1.455
75	0.526	0.926	2.309
80	1.358	2.693	5.798
85	4.674	7.911	18.23
90	18.26	26.17	38.02
95	30.51	46.43	54.64

$$H_2NO_3^+ \rightleftharpoons NO_2^+ + H_2O \qquad \text{(a)}$$

$$NO_2^+ + ROH \rightleftharpoons ROH{\cdot}NO_2^+ \qquad \text{(b) (21)}$$

$$ROH{\cdot}NO_2^+ + NO_3^- \longrightarrow RONO_2 + HNO_3. \qquad \text{(c)}$$

Eremenko questioned this trend of the reactions particularly in view of the facts described in Chapter I that nitric acid still possessed the nitrating ability at a concentration where the presence of NO_2^+ ions are excluded. With regards to *O*-nitration this was described by T. Urbański and Hackel [143]. By nitrating pentaerythritol and some ^{18}O labelled alcohols, Eremenko came to the conclusion that molecular, undissociated electrolytically nitric acid can be an agent for *O*-nitrating alcohols. He depicted this in diagram – Fig. 43 (in weight per cents) referred to *O*-nitration of pentaerythritol.

A summary of his conclusions, based on the analysis of the curves, is given here: region I limits the composition of the nitrating mixtures which transform

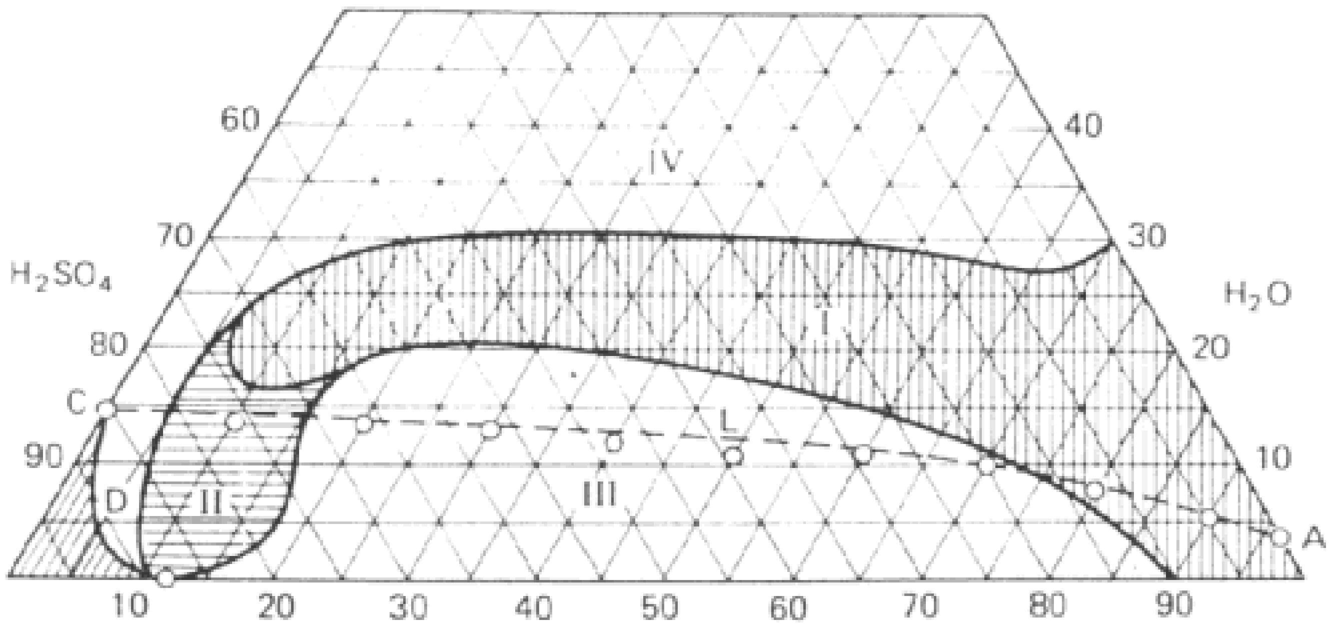
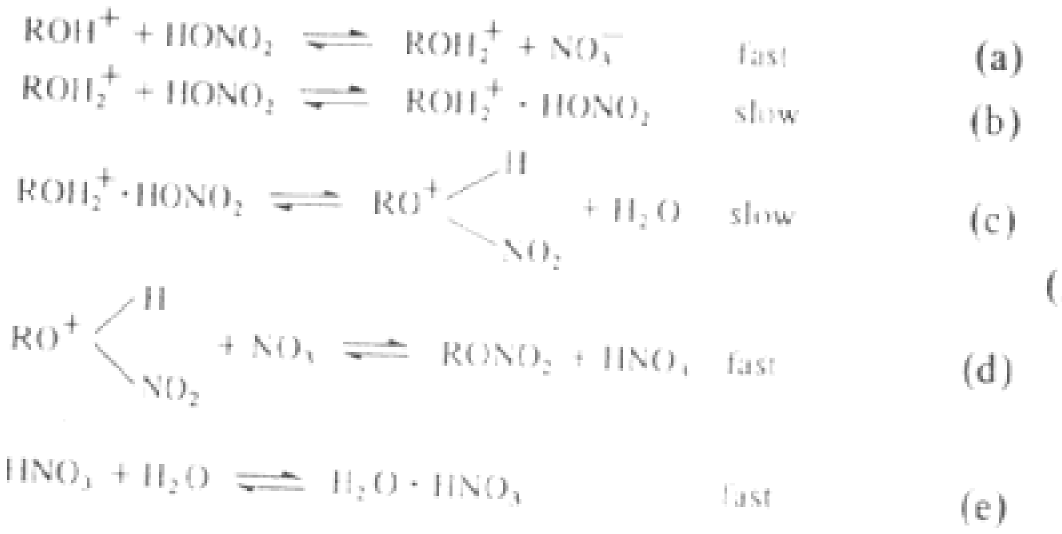


FIG. 43. Regions of the formation of pentaerythritol tetranitrate by nitrating mixture [144].

pentaerythritol into PETN with 94–98% yield without the formation of esters of sulphuric acid as intermediates. In region II the formation of PETN goes through the acid sulphates. In III tetranitrate is formed only in 10–50% yield with side reaction of oxidation accompanied by violent evolution of nitrogen oxides. In region IV *O*-nitration does not occur.

ALC curve shows the limit of the detection of NO_2^+ ions and the small region limited by curve CD shows the complete dissociation of nitric acid into NO_2^+ [144] and Vol. I, Fig. 9, p. 25 (in mol %). One can see that 'pure' *O*-nitration can occur in region I which is beyond the detectable NO_2^+ concentration.

Eventually Eremenko suggested the scheme of *O*-nitration (22):



$$ROH^+ + HONO_2 \rightleftharpoons ROH_2^+ + NO_3^- \quad \text{fast} \quad (a)$$
$$ROH_2^+ + HONO_2 \rightleftharpoons ROH_2^+ \cdot HONO_2 \quad \text{slow} \quad (b)$$
$$ROH_2^+ \cdot HONO_2 \rightleftharpoons RO^+\begin{matrix}\diagup H\\ \diagdown NO_2\end{matrix} + H_2O \quad \text{slow} \quad (c)$$
$$RO^+\begin{matrix}\diagup H\\ \diagdown NO_2\end{matrix} + NO_3 \rightleftharpoons RONO_2 + HNO_3 \quad \text{fast} \quad (d)$$
$$HNO_3 + H_2O \rightleftharpoons H_2O \cdot HNO_3 \quad \text{fast} \quad (e)$$

(22)

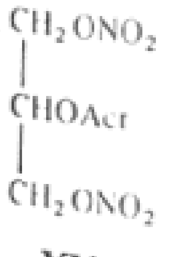
Proof of the accuracy of the scheme is also in the observed fact that the oxygen of nitrated alcohol remains in the nitrate. This was substantiated by nitrating alcohols labelled with ^{18}O.

MIXED PENTAERYTHRITOL AND GLYCEROL ESTERS (Vol. II, p. 191)

Recently a number of papers and patents have appeared which describe mixed esters of pentaerythritol and glycerol. Particular attention has been paid to esters containing one group of an unsaturated acid such as acrylic or methacrylic acid to produce an ester which could polymerize. The obvious aim is (in addition to that previously mentioned: Vol. II, p. 191): to produce combustible synthetic polymers, capable of being used as rocket propellants.

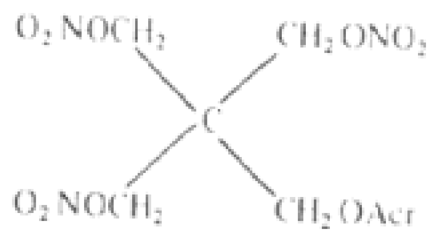
Mixed ethylene glycol esters have already been described (XI).

Wassmann [146] obtained mixed esters of glycerol and pentaerythritol as follows (Acr = acryl, methacryl):

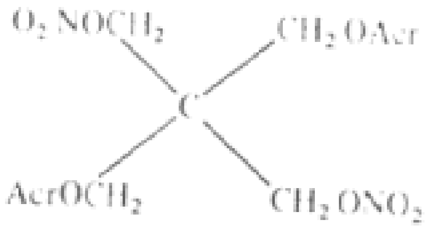


$$\begin{matrix}CH_2ONO_2\\ |\\ CHOAcr\\ |\\ CH_2ONO_2\end{matrix}$$

XV



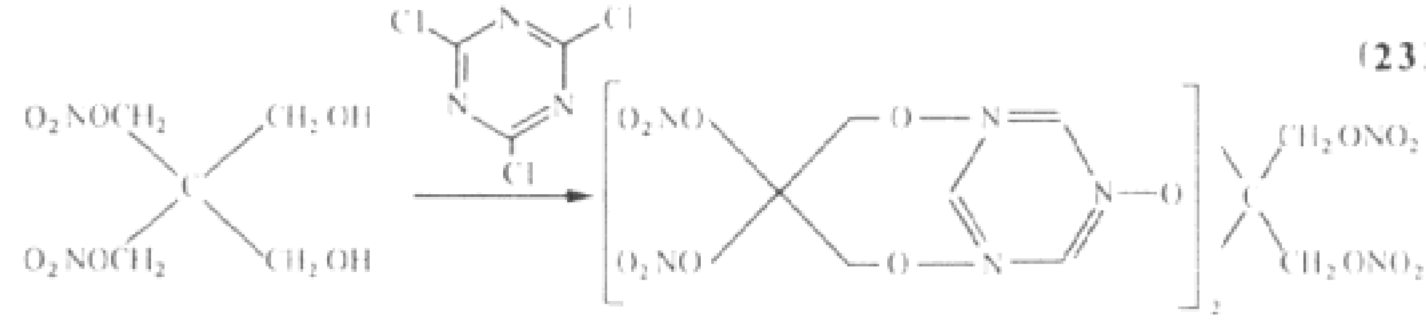
XVI



XVII

That will be mentioned in Chapter XXII dedicated to solid rocket propellants.

An interesting reaction of pentaerythritol dinitrate (PEDN) was reported by Matuszko and Chang [147]. It consists in reacting PEDN with cyanure chloride:



(23)

The reaction can serve as an analytical method of detecting PEDN.

METHOD OF PREPARATION OF PETriN and PEDN
(according to [148] and [149])

Pentaerythritol (80 g) was dissolved at 5°C in a *ca*. 6 times larger quantity of sulphuric acid (67%). CH_2Cl_2 (*ca*. 50 parts) was added followed by the addition of the nitrating mixture composed of sulphuric acid (98%) (72 g) and nitric acid (96%) (232 g) at 5°C. After mixing for 75 min, water (1000 cm^3) was added. The organic phase was neutralized with 10% $NaHCO_3$, evaporated to dryness and the solid was extracted with ether to eliminate PETN which was not dissolved.

The solution was cooled to −60°C to eliminate the precipitated impurity. On evaporation the trinitrate – PETriN (40 g) resulted. It contained some PETN and PEDN and was purified while removing PEDN by dissolving it in water.

The part insoluble in water was crystallized from CH_2Cl_2. Finally pure PETriN was obtained by distillation under reduced pressure. Under 1 mmHg a fraction of 155–160°C was collected. Precaution should be taken: it can explode at 175°C. It has m.p. 27–28°C (Vol. II, p. 194).

The aqueous solution was evaporated to dryness and furnished PEDN.

Camera [149] draws attention to the fact that PETN in spent acid is readily subjected to hydrolysis leading to the formation of tri- and dinitrate of pentaerythritol at different temperatures (20 and 40°C) and concentration of nitric acid (70–90%).

He calculated the constants of equilibria:

$$\frac{[\text{PE-TRi N}]\ [HNO_3]}{[\text{PETN}]\ [H_2O]} = K_1$$

$$\frac{[\text{PE-Di N}]\ [HNO_3]}{[\text{PE-Tri N}]\ [H_2O]} = K_2$$

The values of K_1 and K_2 are given in Table 53.

TABLE 53

Concentration $\%HNO_3$	K_1 20°C	K_1 40°C	K_2 20°C	K_2 40°C
70%	0.996	1.362	0.608	0.726
80%	0.873	1.395	0.606	0.721
90%	0.950	1.396	0.749	0.838

The solubility of PETriN and PEDN in nitric acid of different concentrations is given in Table 54.

TABLE 54. Solubility of tri and dinitrates of pentaerythritol according to Camera [149]

Concentration $\%HNO_3$	Temperature °C 20° PETri N	20° PEDN	40° PETri N	40° PEDN
60	0.032	0.040	0.179	0.265
65	0.099	0.102	0.309	0.370
70	0.094	0.079	0.511	0.486
75	0.085	0.054	0.456	0.337
80	0.103	0.049	0.441	0.245
85	0.160	0.054	0.629	0.246
90	0.283	0.060	1.081	0.267
95	0.376	0.038	1.344	0.157

NITRITE ESTERS (O-NITROSO COMPOUNDS)

Nitrite esters (O-nitroso compounds) are usually not discussed as explosives. They are relatively unstable compounds but may possess some significance as products of the decomposition of *O*-nitro compounds according to Gray [150] and Pollard *et al.* [151].

Chemical and physico-chemical properties of O-nitroso compounds have been extensively studied by Steacie since 1934 [152] and described in a monograph [153].

An important work on the chemical stability and decomposition of ethylene dinitrite and glycerol trinitrite was done by Kondrikov [154]. Their activation energies were found to be:

at 170–190°C, $E = 35.6$ kcal/mol, $\log B = 13.8$
and at 143–160°C, $E = 41.6$ kcal/mol, $\log B = 17.8$ respectively.

The decompositions of the former can be depicted by diagram:

$$\begin{array}{l} CH_2ONO \\ | \\ CH_2ONO \end{array} \longrightarrow 2CH_2O + 2NO. \qquad (24)$$

ESTERS OF OXY-ACIDS OF CHLORINE (Vol. II, p. 447)

Esters of oxy-acids of chlorine have not received any practical application owing to their very high sensitivity to impact and friction, but they are interesting from a theoretical point of view.

A few papers have appeared on the use of alkyl perchlorates, especially methyl perchlorate as alkylating (particularly methylating) agents [162]. Kevill *et al.* [163] established that methyl perchlorate in acetonitrile is a much weaker methylating agent than for example trifluoromethanesulphonate.

Geminal Diperchlorates

Baum [164] obtained geminal diperchlorates by reacting carbonyl compounds with perchloric acid in halogenated hydrocarbons: for example acetone and perchloric acid in chloroform yielded an oily product within a few minutes. This was 2,2-diperchloratopropane $(CH_3)_2C\ (OClO_3)_2$. It can be distilled: b.p. 52°C/0.1 mmHg.

It is very hygroscopic. Differential thermal analysis shows one exotherm peak at 159°C and second at 202°C which ended in an explosion at 250°C.

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APPENDIX

N-OXIDES (N→O)

An attention was recently drawn to explosive properties of N-oxides: N-hydroxyimidazole N-oxide (m.p. 183°) and its N-methoxy derivative [1]. The earlier finding [2] also reported that a care should be taken when purifying N-oxides by distillation. Thus low molecular weight N-oxides should be considered as possessing explosive properties.

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CHAPTER 11

PRODUCTION OF NITRATE ESTERS

(Vol. II, pp. 62–125, 185)

NITROGLYCERINE (NG)

No fundamental progress on methods of the manufacture of NG can be recorded. The main efforts have been concentrated on the problem of increasing the safety of the processes by using perfect automation with remote control devices, avoiding immediate contact between personnel and dangerous parts of the process and the reduction of the quantity of explosive in the working place. All these requirements can be achieved with continuous methods, although batch processes are still in use.

Continuous and semi-continuous methods are as described in Vol. II:

(1) Schmid (p. 99),
(2) Schmid-Meissner (p. 104),
(3) Raczyński (p. 106),
(4) Biazzi (p. 107),
(5) N.A.B. Injector Process (A.B. Gyttorp) (p. 114),
(6) Semi-continuous method of Jarek (p. 120).

Of the above methods 1, 2, 4 and 5 have been widely used in many countries. A novel method (7) has been described and is known as:

(7) Hercules Tubular Nitrator described by McKinney [1] and in *Encyclopedia of Explosives* [2].

Hercules Tubular Process

This description is based on that given in the Encyclopedia [2]. A continuous stream of glycerine flows through a tubular path to a tubular reaction zone where it meets a stream of precooled nitrating acid. The tubular reaction zone is uncooled, the temperature is controlled by regulating the temperature of precooled nitric acid and also the proportion of nitratic acid to glycerine. It is desirable to cool the mixture of nitrate ester and spent acid to facilitate the separation of the nitrated product.

The diagram of the system is presented in Fig. 44. Nitrating acid passes through pump 1 to the cooler, and valves 2 to 6 and meets glycerine in the counter current which enters through valve 3, pump 4 and valve 5 to the same place 6.

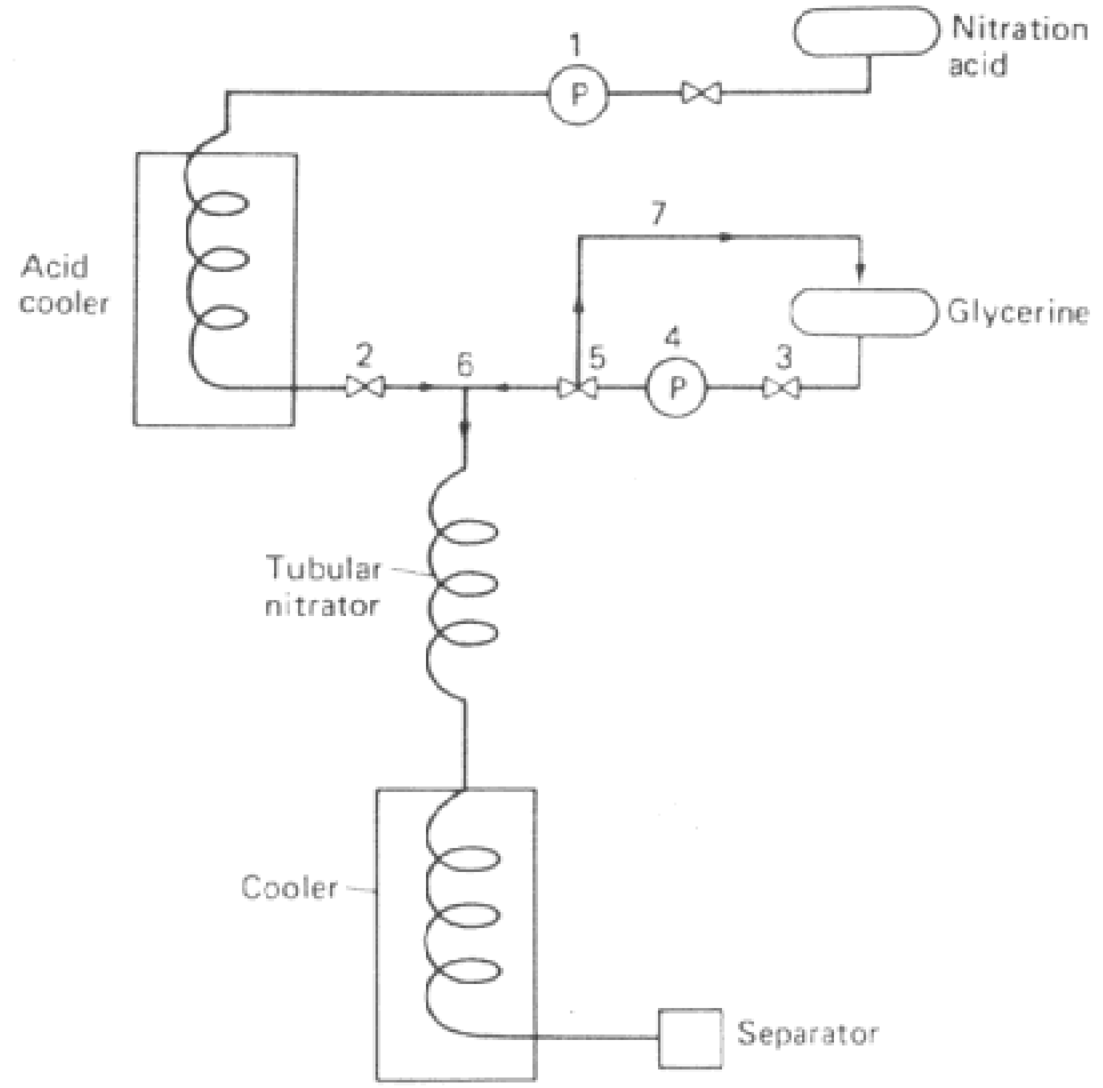

FIG. 44. Hercules Co. tubular nitrator of glycerine [2].

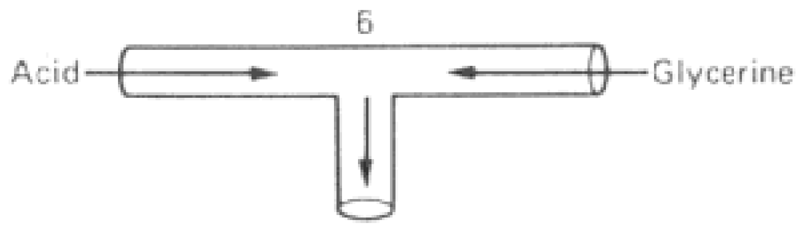

FIG. 45. T – tube for nitration of glycerine (Hercules Co.) [2].

Nitration starts in 6 and continues in the tubular nitrator before entering the cooler and finally the separator. Valve 5 is a quick opening by-pass valve. In the case of an emergency valve 5 is turned to stop the flow of glycerine to the nitrator 6 switching through 7 to the glycerine container.

Figure 45 shows a diagram of the 'mixing tee' 6.

The nitrating acid in the Hercules Tubular Process is composed of 18–40% HNO_3, 45–70% H_2SO_4 and 11–17% H_2O. The preferred acid to glycerine ratio is 10–12 parts of acid per one part of glycerine.

Stow [3] improved the method by introducing a centrifugal separator of nitroglycerine from the spent acid.

The method can be used to both: nitration of glycerine, glycerine–ethylene glycerol mixture, diethyleneglycol or ethylene glycol.

Biazzi Process (Vol. II, p. 107)

The detailed description of the process given in Vol. II remains valid with a few additions described by Biasutti [4]. Figures 48 and 49 (Vol. II, pp. 108, 111) are still valid, and the main points which introduce some additional, novel information are given here.

Mixed acid and glycerine are stored externally in separate tanks and are transferred by means of centrifugal and gear pumps to small feed tanks. From the feed tanks the reactants are sent to the nitrator by means of two positive displacement pumps driven by the same electric motor. Two speed variators allow change in the total flow rate as well as the ratio between acid and glycerine. The glycerine feed pipe in the nitrator, fitted with a multi-nozzle distributing head is retractable and can only be extended if all safety conditions are fulfilled. The feed arrangements are such that the acid and glycerine are quickly submerged, emulsified and forced down the nitrator through the central space formed by the cooling coils. Part of the emulsion overflows into the separator and part returns to the vortex in the nitrator fluid. Cooling is achieved by sodium nitrate brine circulating through helical coils. The reaction temperature is kept constant by thermostatic control of the brine valve.

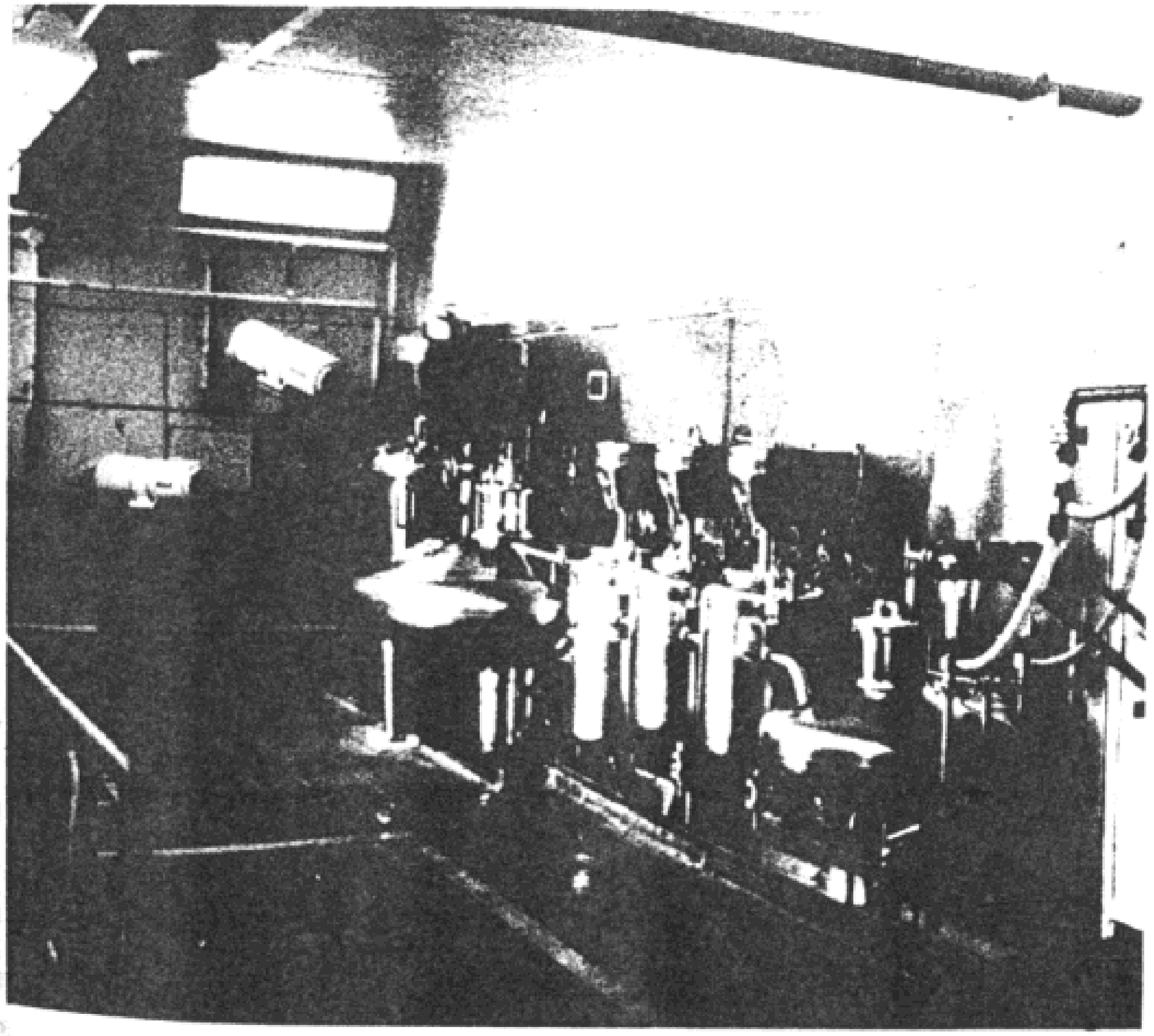

FIG. 46. Nitration of glycerine plant of M. Biazzi S.A. (Courtesy M. Biazzi S.A.).

The intensity of mixing in the nitrator by the turbine is such that the emulsion of nitroglycerine in the acid cannot be initiated by a No. 8 blasting cap. The turbine is driven by V-belts of a motor mounted in a room separated from the nitration unit by a partition wall.

The bottom of the nitrator is provided with a quick opening flap valve placed considerably off the axis which can be operated manually or pneumatically for quick draining of the contents into a large tank full of water.

Control of the Nitration

The emulsion overflowing from the nitrator enters the separator through a short section of pipe in which a special electrode is fitted for the measurement of the Redox-potential of the spent acid against a reference sample of mixed acid. The Redox-potential of the spent acid has a direct relation to the HNO_3 and HNO_2 content in this acid composed of $HNO_3-HNO_2-H_2O$ and can serve as a control on the extent that nitration follows the normal course without too many oxidation reactions and deviations from the normal course. It was first introduced by Öhman in 1938 [5]. He applied the method for the control of the nitration of glycerine [6–8], glycol and similar compounds [9] and eventually to the nitration of aromatic hydrocarbons [10]. More recently the method was extended by Camera [11] to the control of the nitration of pentaerythritol. See also a general description by Biasutti [12].

The Redox-potential of the system (1)

$$HNO_3 + 2H^+ \longrightarrow HNO_2 + H_2O \tag{1}$$

can be expressed by equation (at 20°C):

$$e = e_0 + 0.0291 \log \frac{[HNO_3]\ [H^+]^2}{[HNO_2]\ [H_2O]}\ , \tag{2}$$

where e_0 is the potential of the standard electrode. Considering that HNO_2 is relatively small and HNO_3 is constant at 20°C a simplified equation (3) can be used [13]:

$$e\ O\ e_0 = 0.0291 \log [HNO_2]. \tag{3}$$

The reference sample [11] is composed of

H_2SO_4 49.1%

HNO_3	48.3%
HNO_2	0.3%
H_2O	2.3%.

Nitrous acid is introduced into this solution in the form of $NaNO_2$.

By recording the value of *e* in mV the operator can see whether the trend of the reaction is normal. If the value of *e* deviates too much from normal, the nitration should be stopped by cutting the inflow of glycerine and, if necessary, the inflow of the mixed acid.

The following are some values of *e* in −mV given by Camera [11]:

TABLE 55. Values of *e* in mV

%HNO_3	%HNO_2			
	0.01	0.1	0.5	0.8
90	164	192	208	222
80	282	306	325	332
70	366	394	410	417

The permissible values of *e* should be established by experiments.

Separation of NG from the Spent Acid

From the tangential separator NG flows to the washing vessels and then to a storage tank. The spent acid flows from the base of the separator to its storage tank through a variable overlow valve by means of which the height of the nitroglycerine–spent acid interface may be controlled. This adjustment is effected automatically through a float on the spent acid layer in the separator. A small amount of water is added to the overflowing spent acid to avoid further separation of NG as in the system of Nathan *et al.* (Vol. II, p. 95).

Alkaline Washing of NG

Sodium carbonate solution is introduced to the first washing vessel by gravity. The automatic feed control is obtained by means of a pH-meter with its electrode placed at the outlet of the first washer. The soda water/NG emulsion passes through two additional washers for completion of the neutralization reaction. From the last washer the emulsion flows to a Biazzi separator. The wash water flows to a catch tank for the recovery of the last portions of unseparated NG.

Technical Data of Biazzi Method (Vol. II, p. 114)

Nitrator	
Heat Transfer Coefficient	700 kcal/m^2.h. °C
Ratio Coil Volume to Useful Volume	80/100
Ratio Coil surface to Useful Volume	10 m^2/100 l
Ratio Useful Volume to Production Capacity	110 l/1000 kg/h NG
Ratio NG content to Production Capacity	70 kg/1000 kg/h NG
Throughput of Emulsion through Turbine Wheel	10 m^3/min
Average Retention Time	4 min
Draining Time	8 sec
Separator	
Ratio total Volume to Production Capacity	800 l/1000 kg/h NG
Ratio Separated NG to Production Capacity	40 kg/1000 kg/h NG
Ratio total NG to Production Capacity	170 kg/1000 kg/h NG
Average Retention Time (NG)	10 min
Average Retention Time (Spent Acid)	50 min
Draining Time	20 sec
Washers	
Ratio NG/Production Capacity	50 kg/1000 kg/h NG
Retention Time (NG)	3 min

Safety Measures

When the Biazzi unit has to be shut down, it is necessary to remove all the NG from the nitrator–separator system. This is done by introducing spent acid from an overhead storage tank into the bottom of the nitrator until all the NG has been displaced through the overflow of the separator. A level sensor automatically stops the displacement process as soon as all the NG leaves the separator.

In general layout and design the possibility of the retention of a minute quantity of NG is eliminated. All the vessels are highly polished internally to prevent the adherence of NG to rough surfaces.

There are two control rooms. One is near the nitrator house in a 'control bunker', another is further away in a remote control room at a safe distance. The latter is provided with instruments to start, supervise Redox, pH NG–water emulsion and a device to shut down the unit. Both control rooms are provided with TV sets. Signals between the two houses are both electric and pneumatic, although controls on the nitration unit are only pneumatic. The remote control room is operated in case of emergency and necessity or breakdown of the automatic system.

The 'control bunker' is provided with a number of 'push buttons'. They are:

Preparation button. By pressing this button the nitrator and separator are filled with water, the pumps are started, brine is circulated through the cooling coils etc. When all red lights on the alarm panel are out the unit is ready to start.

The start button is then pressed, the glycerine pipe is extended to the nitrator, glycerine and mixed acids begin to flow at the selected production rate between the nominal rate (100%) and reduced to 50%.

The stop button causes the glycerine and acid flow to end and the glycerine pipe is retracted. One minute later the automatic shut-down sequence starts and continues until all the nitroglycerine has been evacuated from the building.

An alarm sounds in the case of irregularities.

The early history of the Biazzi invention was given by Biasutti [12].

Injector Nitration Process (Vol. II, p. 114)

Brunnberg [14] gave a brief description of the method and its early history.

Because of the high temperature of glycerine or glycerine–glycol mixture the viscosity is considerably reduced and helps the action of the injector. The temperature rise through nitration is 46–48°C. The influx of the alcohol is automatically regulated and registered. Only one second after the two components are mixed, cooling of the emulsion begins, first in a coil with cold water or brine and then in a tubular cooler with brine to reduce the temperature to +15°C.

The nitrate ester is separated in a centrifuge of 4–8 kg capacity. The spent acid contains 0.1% emulsified NG and by adding 4–5% water the nitroglycerine remains in the solution (Vol. II, p. 95).

The acid NG from the centrifuge runs to an injector where it is mixed with 8% aqueous solution of sodium carbonate. It is transported to a special degassing vessel, where CO_2 is evolved. After that the emulsion passes to two wash columns provided with perforated discs made of stainless steel. Mixing is achieved by air inlet to the column, from the second column the emulsion runs to a specially designed wash centrifuge. The stabilized nitrate ester runs to an injector and is transported as a non-explosive aqueous emulsion to a separate storage building.

From the point of view of safety, the main advantage of the injector method is the very small quantity of nitrate ester present in the reaction space and the very short reaction time (*ca.* 1 second). After the reaction has ended, the quantity of nitrate ester is too small to be able to detonate. If nitration is stopped, the emulsion flows downward, leaving the apparatus empty, cleaned by nitrating acid and subsequently there is no need for a safety tank for draining nitrate ester and acid in the case of emergency.

If the power fails or the reaction temperature becomes too high, a valve for the inlet of air to the injector opens automatically and prevents the alcohol being sucked into the injector. If the electric current returns, the nitration process cannot restart by itself.

Centrifugal separation of NG is safe on condition that lubrication is carried out according to instructions.

The injection nitration is supervised by remote control.

Safety Problems (Vol. II, p. 122)

Safety problems have already been tackled in the general description of processes. Biasutti [15] described over 20 accidents in nitroglycerine manufacture.

In the batch process two accidents were caused by faulty mixing. Thus in Gransberg, Sweden in 1955, the supply of compressed air to stir the content of the nitrator was stopped. Glycerine started to decompose which produced a heat evolution and hot acid together with decomposing organic substances entered the separator and detonated the charge of nitroglycerine in the separator (probably over 1000 kg).

Also in continuous methods of nitration faulty functioning of mixing in the nitrator has caused a few accidents. Another cause of accidents in continuous methods was the malfunctioning of the automation device which produced an inflow of the wrong proportions of glycerine and acid. Thus two accidents with the Schmid method (in Gyttorp, 1933 and in Bofors, 1953) and one with the Biazzi system (Kaohsiung, Taiwan, 1966) were caused by an insufficient proportion of acid in the unit. Insufficiently trained personnel can also be responsible for accidents where the production is fully automatic and requires skilled workers (e.g. wrong calibration and incorrect setting of control instruments).

A process for drying nitroglycerine with calcium chloride was probably the cause of an explosion of stored nitroglycerine in Schlebusch (1956). It is believed that drying with calcium chloride evolved enough heat to produce the decomposition of the substance.

Generally speaking storage of nitroglycerine should be avoided. The continuous methods were originally ended by batch processes of weighing and mixing nitroglycerine. By fully continuous methods no storage would be required. According to Biasutti [12] in Japan and Sweden for the manufacture of commercial explosives of *ca.* 500 kg/hr, only 40 kg of NG and 20 kg of dynamite can be present at any time.

A separate danger of handling nitroglycerine has recently been described. It consists in choe combined with adiabatic compression of minute air bubbles. The first described accident of this kind took place at Asa in Japan (1962). Meticulous study revealed that in the suction tube the air bubbles were originally under 0.1 atm, later the pressure increased to 1 atm. which caused a rise in the temperature by 300°C. A similar accident took place with a 'water hammer' it suddenly opening a water pipe which produced an adiabatic compression of air

(Marions, Illinois, 1968). A few more accidents produced by compressing air bubbles have also been reported [15].

Biasutti [16a] reported statistics of accidents which [16b] are given in Table 56.

TABLE 56. Accident statistics in ng manufacture

Number of accidents	Section
31	Nitration–Separation
66	Washing and Storage
13	After-Separation and Handling of Spent Acid
4	Wash Water Handling
2	Decontamination
15	Transportation

Accidents in the nitration–separation section were mostly due to self-decomposition of the NG–spent acid mixture following incorrect nitration ratio (9 cases), insufficient stirring (4 cases), leakage of cooling brine in the nitrator (2 cases), self-decomposition because of impure raw materials, instability of spent acid used for displacement. A high number of accidents during the washing and storage of NG have occurred mainly in older batch processes where the two sections were installed in the same building.

A great number of accidents have been caused by human error, for example the opening or closing valves on NG (9 cases), stumbling when carrying buckets full of NG (4 cases) shock of metal pieces (6 cases). Chemical decomposition was the cause of the explosion of nitroglycerine sludge accumulated at the bottom of settling tanks. External causes – lightning – caused 7 accidents. Spent acid decomposition was the source of 10 accidents. Here 5 cases were due to the decomposition of NG dissolved in the acid. Accidents in transportation were caused by stumbling, fall of buckets, shocks and derailments or collisions on mechanical transportation (6 cases). Transportation through water-injection was the cause of 8 accidents. This was due to adiabatic compression of air bubbles. Since the introduction of the safe water-injection method, where rapid energetic changes are avoided, the transportation by water-injection became much safer.

DIETHYLENE GLYCOL DINITRATE (DGDN) (Vol. II, p. 149)

As previously mentioned this compound was extensively used in World War II for making double base powder. It was made by the nitration of diethylene-glycol by methods similar to those used for the nitration of glycerine, preferably at higher temperatures (Vol. II, p. 151).

The specificiation of diethylene glycol for nitration was given by Meyer [17]:

Clear colourless liquid, density (20/4) 1.1157–1.1165
neutral to litmus
boiling analysis: five drops not below 241°C,
distillation at 246.5°C,
end not above 250°C
moisture: no more than 0.5%
residue after burning: no more than 0.02%
acidity (as H_2SO_4): no more than 0.01%
chlorides: traces
saponification number: not above 0.02%
reducing substances (test with ammonia solution of $AgNO_3$): none
viscosity at 20°C: 35.7 cP
Content of monoethyleneglycol – no more than 2%.

TRIETHYLENE GLYCOL DINITRATE (Vol. II, p. 154)

As already pointed out, the substance was used in double-base propellants in Germany during World War II.

Meyer [17] gives the specification of the glycol used for nitration (compare with the data in Vol. II, p. 154):

density (20/4) 1.230–1.234
boiling: do not start below 280°C,
90% distilled not over 295°C
moisture: no more than 0.5%
chlorides: traces
acids (H_2SO_4): no more than 0.02%
saponification as Na_2O: no more than 0.05%
reducing matters: none.

MANUFACTURE OF PENTAERYTHRITOL TETRANITRATE (PETN) (Vol. II, p. 185)

Relatively little can be added to the description of the methods of PETN manufacture. Continuous methods are mostly used in modern plants (see also Fig. 74, Vol. II, p. 188).

The nitration characteristics of pentaerythritol (PE) can be summarized as follows:

1. Use of low temperature of nitration with nitric acid (d 1.50),
2. Ease of separation of PETN from the spent acid by the fact that the product is a crystalline solid, and ease of washing it from the acid,

3. High sensitivity of PETN to impact which should always be kept in mind,
4. Instability of the spent acid.

Pentaerythritol (PE), 'nitration grade'. According to 'Biazzi SA' [18] PE should possess the following characteristics:

M.p.	263 ± 1°C
Humidity	max 0.2%
Crystal size	min dia. 0.025 mm max dia. 1.0 mm
Formic acid	absent
Dust	absent
Water insoluble parts	max 0.2%
Ashes	max 0.01%
Monopentaerythritol	96.5–98.5%
Dipentaerythritol	0.7–1.3%

The following is the description given by Biazzi SA [18] on the continuous nitration of PETN – Fig. 47 with two nitrators.

The dry pentaerythritol (PE) of specified granular size and quality (see the specification above) from (1) loaded into a feeding hopper (2) is fed into the first nitrator (3) by means of a vibrating system giving a constant flow rate. The feeder is provided with a variator making it possible to modify the feeding rate. Simultaneously a continuous flow of nitric acid (98.5% HNO_3) is introduced into the nitrator in the right proportion (5:1).

From the first nitrator the suspension of PETN nitric acid enters the second nitrator (4). The temperature 15–20°C is maintained by a freon filled jacket and controlled by the cooling agent valves. The nitric acid is fed into the first nitrator from a constant-level overhead tank (5). The contents of the nitrators are stirred by paddle type stirrers, driven by electric motors which are located outside the building or in a separate motor room. Gas from the nitrator is washed with water in a column (6).

Camera [19] discussed the control of the safety of nitration of pentaerythritol with nitric acid by Redox measurement as described in Chapter X.

The PETN suspended in the spent acid overflows from the second nitrator into a continuous vacuum filter (7). The spent acid goes through a filter into an intermediate vacuum tank equipped with a strainer retaining all the PETN which may escape from the filter. From the tank the acid is pumped to storage by means of a diaphragm pump controlled by a level switch in the intermediate vacuum tank.

From the filter PETN is transferred to the dissolution neutralization and crystallization equipment by a water jet. Although the nitration of Pentaerythritol (PE) should be regarded in itself as a relatively safe operation compared to the nitration of glycerine and trinitration of toluene, there is a certain amount of danger particularly from the storage of spent acid for a longer time. This is the result of hydrolysis of PETN to lower nitrated PE, that is, PETriN and PEDN described by Camera [20]. The lower nitrated products can be relatively readily oxidized and this of course is manifested by the formation of nitrous acid.

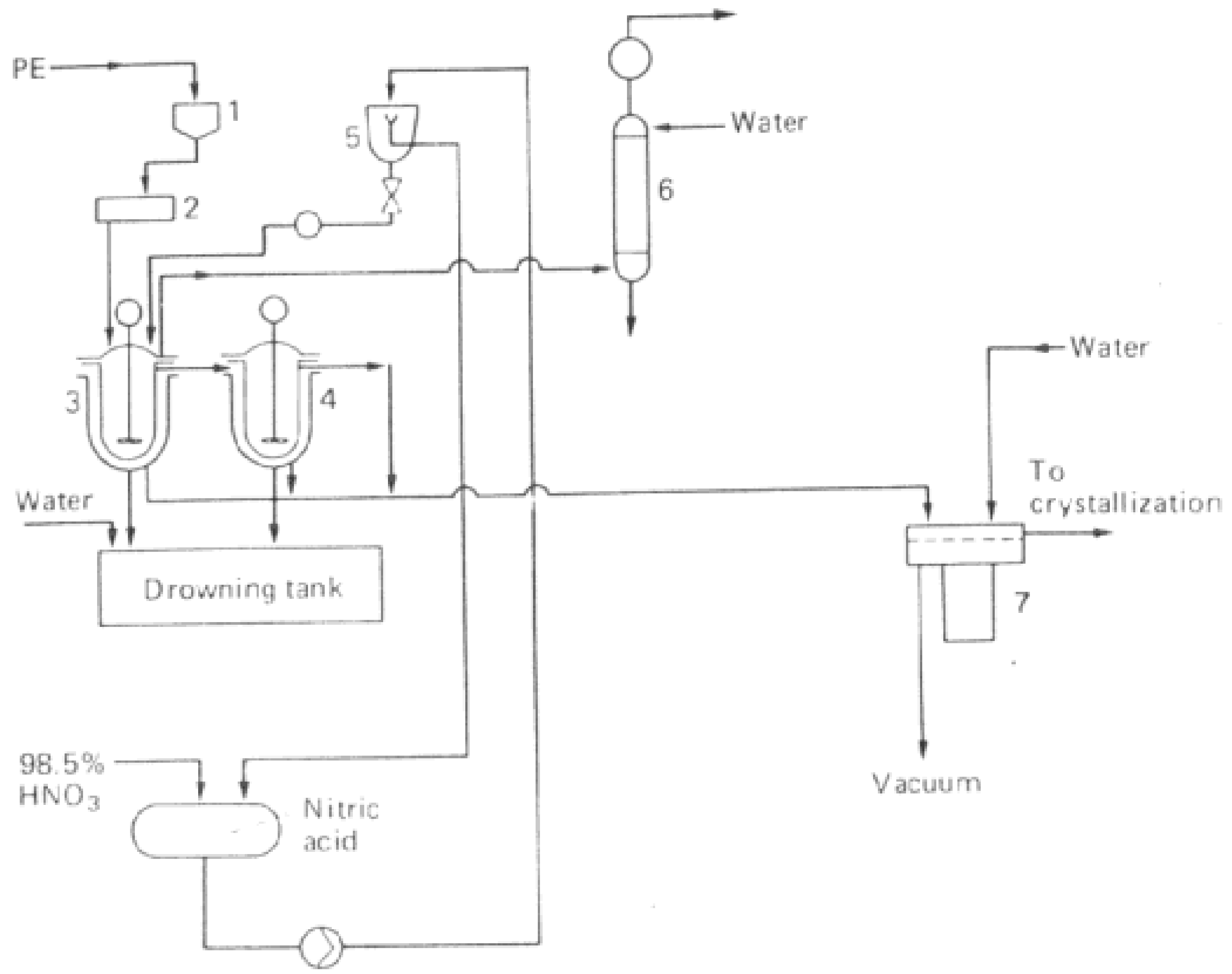

FIG. 47. Simplified flow sheet of Biazzi method of making PETN (Courtesy M. Biazzi S.A.)

One of the important requirements for the safety of nitration of PE is keeping the right proportion of nitric acid to PE (5:1).

A few accidents with PETN described by Biasutti [15] were very instructive. A typical accident happened through a faulty rotameter giving a wrong dosage of the acid in the continuous method of the manufacture of PETN. Insufficient quantity of the acid produced a considerable increase in the temperature in the nitrator and a violent decomposition of PETN [21].

The sensitivity of PETN to shock was the cause of another accident. This happened when the crust of the explosive was removed from the stirrer with a steel chisel. This was against the regulation which required the use of a solvent (acetone) and either wooden or plastic tools [22].

The storage of spent nitric acid is dangerous particularly in a concentration of 75–80% [23] or from other sources 65–75% [24]. The probable cause of the 'fume off' of the spent acid is hydrolysis of the lower esters followed by oxidation as described above.

However, Ramaswamy and Subba Rao [23] suggested a 'controlled fume-off' as a means of avoiding the danger of keeping spent acid. Two methods were recommended both by injecting live steam:

(1) keeping the temperature at 70 ± 2°C;
or (2) at 95–100°C with an additional injection of N_2 or air.

This is fully discussed in Chapter XIII dedicated to the treatment of spent acids.

Purification of PETN

The usual method for the purification of PETN consists in crystallization from acetone (Vol. II, pp. 188–189).

A description of crystallization as given by Biazzi SA [18] is as follows. PETN is continuously introduced from the filter into a stainless steel dissolving apparatus provided with a hot water heating jacket and a stirrer. The required amount of acetone is continuously fed from a constant-level overhead tank together with ammonia gas for neutralization. The neutralized solution of PETN in acetone flows continuously into a series of continuous crystallizers equipped with stirrers and jackets. The crystallization is carried out by adding a well determined quantity of water. The contents of the last crystallizer flow continuously on a continuous vacuum filter where most of the waste acetone is removed. The dilute acetone is collected into an intermediate vacuum tank from which it is pumped to the acetone recovery unit.

The moist and recrystallized PETN falls continuously from the filter into the containers for further use.

The plant is provided with an electro-pneumatic safety system which signals all emergencies during the operation and sets the automatic safety devices in action if the intervention of personnel fails.

The material balance of the Biazzi process is given below for 1000 kg of produced PETN [18]:

PE was used in quantity	450 kg
Nitric acid (as 100% HNO_3)	2250 kg (not including recovery)
Acetone *ca.*	300 kg
Ammonia (as 100% NH_3)	1.5 kg
Process water	12 000 l.

By-products and wastes:

Spent acid (81–84% HNO_3) 1650 kg for recovery

Acidic waters: 3750 kg which should be neutralized and sent to the drains.

Acetone (30%) water: 9250 kg to be sent to acetone recovery plant.

Specification of the final product (PETN).

M.P. min. 140°C
Abel heat test at 30°C: min. 30 minutes
Nitrogen content: min. 14.5%
Insoluble in acetone: max. 0.1%
Bulk density: max. 800 ± 80 g/litre
Acidity: max. 0.005% (HNO_3)
Ash: max. 0.05%
Water (for the safety in transportation and manipulation); max. 20%.

US standards have slightly different requirements.

According to Roth [25] PETN for military use in the USA shall correspond to data as below:

Melting point: 141° ± 1.0°C.
Nitrogen content: min. 17.5%
Acetone insoluble material: max. 0.10%
Acidity or alkalinity: max. 0.01%

120°C vacuum stability: the max. amount of gas evolved in a 20 hour test should not exceed 5 ml.

Granulation. PETN should comply with the granulation requirements shown on Table 57.

TABLE 57. Sieving of PETN (US specification)

US Standard Sieve No.	Percent Passing through the Sieve Class 1	Class 2	Class 3	Class 4
30			95 min	100 min
80	100 min			
100	85 min	96 min		20 max
140	55 max			
200	30 max	80 max 65 min	30 max	

With regard to the safety of crystallization attention should be paid to the danger of explosive acetone–air mixtures which have been responsible for some accidents [26]. In some countries (e.g. Japan) purification of PETN is carried out by heating PETN with water in autoclaves in a manner similar to that for nitrocellulose (Vol. II, pp. 411–413). However, an explosion occurred when PETN was heated with 30% water in an autoclave [26]. The accident was probably produced by overheating.

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CHAPTER 12

CARBOHYDRATE NITRATES

CELLULOSE AND CELLULOSE NITRATES (NITROCELLULOSE)

(Vol. II, pp. 213, 234, 293, 321, 362, 393)

With regard to cellulose two more collective volumes have appeared [1] which are the continuation of the former ones edited by Ott, Spurlin and Graffin. However, most of the text is now dedicated to the biosynthesis of cellulose and modifications of cellulose which are outside the scope of the present book. Only one chapter written by Hiatt and Rebel [2] refers to esters of cellulose, including nitrocellulose and the information given by these authors is used in the present volume.

With regard to the present advances in the chemistry of cellulose an excellent review has been given by Shafizadeh [3]. He also refers to the folded chain structure of cellulose [4, 5] and of the structure of elementary fibrils [6].

Cellulose for nitration. In most European countries wood cellulose is now used for nitration (Vol. II, p. 364). The success of the nitration of cellulose from wood depends on a high proportion of α-cellulose in wood cellulose. According to Petropavlovskii, Krunchak and Vasilyeva [7] the yield of nitrocellulose highly depends on the α-cellulose content and can be proportional to this content. Some authors [8] consider that lower quality of nitrocellulose from wood-cellulose is due to the presence of hemi-celluloses (mainly pentosanes) in it.

Nevertheless wood cellulose has a lower molecular weight than cotton cellulose, which explains the lower molecular weight of nitrocellulose from wood. Some attempts have been made to produce a higher quality nitrocellulose from wood by carrying out the nitration in two stages, for example [9] but this technique did not seem to find a wider application although the semi-continuous method of nitration of Bofors-Nobel-Chematur (see p. 346, Fig. 48) includes the nitration in two stages:

(1) Pre-nitration,
(2) After-nitration.

Structure of Cellulose Polymer and Determination of Molecular Weight
(Vol. II, pp. 261–278)

The structure of cellulose has only relatively recently been tackled through the examination of its trinitrate, that is, nitrocellulose of *ca.* 14% N. Trinitrate of cellulose was chosen as a readily available cellulose ester, soluble in polar solvents, of an almost unique unbranched polymer chain structure having a broad range of molecular weights manifested by the degree of polymerization 250–9000.

Holtzer, Benoit and Doty [45] undertook the task of fractioning samples of nitrocellulose with 13.8–14.1% N. *n*-Hexane was added dropwise while stirring to 0.2% solution of nitrocellulose in acetone and several fractions were obtained. Their molecular weight was determined by light scattering, viscosity and osmotic pressure measurement.

Light scattering gave the following figures:

(1) Weight average molecular weight: $\bar{M}_n$ = 2 640 000–77 000
(2) Number average molecular weight: $\bar{M}_n$ = 1 320 000–4500.

Thus the polydispersity $\bar{M}_w/\bar{M}_n$ is *ca.* 2. However most commercial samples of nitrocellulose have a high polydispersity: 2.5–3.5. (For the description of $\bar{M}_w$ and $\bar{M}_n$ and their calculation see [46].)

Measurement of viscosity gave lower figures. The above results were confirmed by Hunt, Newman, Scharaga and Flory [47]. Their figures for the molecular weight of fractions were lower: 575 000–40 000. Canadian workers [48] obtained figures of 2 500 000–650 000. Their method of fractionation consisted in adding water to the solution of nitrocellulose in acetone [49].

The conclusion from the above experiments was that:

(1) molecular weight of nitrocellulose (e.g. 400 000) is much higher than that of most vinyl synthetic polymers,
(2) the cellulose skeleton in nitrocellulose is manifested by an unusually stiff chain.

Both these characteristics are responsible for the very high viscosity of nitrocellulose solutions.

Recently British authors [50] described a simple method of determining number-average and weight-average molecular weight of 12.6% N pyro nitrocellulose. The measurement was made with a 3% solution in acetone/ethanol. The viscosity is related to the number-average and weight-average molecular weight. By adding *ca.* 7% lead β-resorcylate a fractional increase in the viscosity was found, which is a function only of number-average molecular weight. Once calibration has been made against osmotic pressure measurements and intrinsic viscosity, both number- and weight-average may be measured rapidly.

Pyrolysis of Nitrocellulose

Ettre and Varadi [51] examined pyrolysis of nitrocellulose (no nitrogen content was given) between 300° and 950°C. The decomposition yielded almost completely gaseous products: CO_2, CO, nitrogen oxides, CH_4, H_2O, lesser amounts of nitrogen (increasing with temperature) and small quantities (below 2%) of ethylene, acetaldehyde, methanol, ethanol and methyl acetate. The latter four compounds were not found at 900–950°C. A small solid residue which formed between 300° and 500°C yielded gaseous products above 500°C.

At 175–250°C a solid residue was produced which decomposed only partly to volatile products when heated to 600°C. This indicated the difference between the composition of products formed at 300–500°C and at 175–250°C.

Osada and Hara [53] examined the action of UV radiation on nitrocellulose and found that evolution of NO_2 and NO occurred. In oxygen atmosphere nitrocellulose absorbed oxygen which promoted denitration and depolymerization. Also salts of di- and trivalent iron promote depolymerization.

Thermochemical Properties of Nitrocellulose (Vol. II, p. 313)

The National Bureau of Standards [41] reported their results for determining heat of combustion and heat of formation of dinitrate- and trinitrate of cellulose (Table 58).

TABLE 58. Heat of combustion and formation of nitrocellulose [41]

Compound	Heat of combustion cal/g	Heat of formation cal/g
Cellulose Dinitrate	2614.4–2616 and 2606.0–2608.6	715.3–712.8
Cellulose Trinitrate	2190.7–2188.7 and 2179.5–2178.1	523.4–525.4

Nitration. As pointed out in Vol. II (p. 321) the only industrial method of nitrating cellulose consists in using a nitric acid–sulphuric acid nitrating mixture. The other nitrating mixtures, such as nitric acid/phosphoric anhydride, nitric acid/acetic anhydride, nitric acid/chlorinated hydrocarbons were in use occasionally on a laboratory scale to solve some problems connected with the nitration of cellulose. Thus Bennett and Timell [10] confirmed the work of Bouchonnet, Trombe and Petitpas (Vol. II, p. 344) that the nitration of cotton dust with a mixture of nitric acid–acetic acid–acetic anhydride (in proportion 43:32:25) at 0°C can yield fully nitrated cellulose, that is, cellulose trinitrate of 14.14% N.

Thinius and Thümmler [11] obtained highly stable nitrocellulose of 13.8–14.0% N by nitrating cellulose with solutions of nitric acid in chlorinated hydrocarbons (see Vol. II, p. 346).

With regard to the mechanism of the nitration of cellulose, two modes were suggested for the formation of esters of cellulose (Vol. II, pp. 239–242). One of the mechanisms suggests gradual introduction of NO_2 groups: at the beginning on the surface of micells followed by a step-wise deeper penetration. Another mechanism suggests simultaneous reactions of OH groups with nitric acid. The latter mechanism seems now to be accepted according to Hiatt and Rebel [2].

Sakata and Komatsu [12] used infra red and X-ray techniques to study the mechanism of the nitration of cellulose with nitric and phosphoric or sulphuric acid. Their conclusion can be summarized as follows. Nitric acid penetrates into crystallites and most OH groups simultaneously react with the reagent in the presence of phosphoric acid. In the presence of sulphuric acid the accessibility of OH groups gradually increases. The part of the molecule which has not reacted shows the same pattern as the original unnitrated micell.

Kunz, Kompolthy and Balogh [13] examined the trend of the nitration of mechanically pulverized cellulose. They found that the nitration obeys the same rule as the nitration of starch, reported by Kunz and Toth (Vol. II, p. 430). The same dependence: reaction time on the reaction temperatures exists in both cases and the degree of nitration plot on triangle diagram (Vol. II, pp. 333–336, 429) are identical, without the typical one phase system for nitrostarch due to the solution of starch in nitrating mixtures rich with nitric acid. A correlation exists between the activity of nitric acid (Vol. I, pp. 28–30) and the duration of the reaction. The reaction was fully accomplished in 8–13 minutes depending on the composition of mixed acids. It was found that the introduction of one NO_2 group into the cellulose molecule develops 1696 ± 85 kcal/mol. This figure consists of the actual heat of reaction of nitration and the heat of absorption of nitric acid by cellulose (see Vol. II, p. 358).

Mixed Esters: Nitrates and Sulphates

It is well known that the low stability of nitrocellulose is often attributed to the presence of sulphates of cellulose, usually in the form of mixed esters: nitrato-sulphates (Vol. II, pp. 293–298). A number of patents [1] have attempted to obtain nitrocellulose free of sulphates by nitrating cellulose with nitrating mixtures composed of nitric acid and salts of nitric acid, such as magnesium nitrate [14] much in the way described in Vol. II, pp. 346–347.

The analytical method of determining the quantity of sulphate groups in nitrocellulose was given by Dawoud, Saad an Attia [15] who used a quick analytical method of determining sulphate esters of cellulose:

(1) by the ignition of samples in a calorimetric bomb,
(2) by titrometric determination of sulphate using Thorin titration method with $BaClO_4$.

The conclusion of this important work is given here. Unstabilized samples of 12.2%, 12.52% and 13.3% N have shown 0.68%, 0.44% and 0.37% SO_4 respectively.

Finished commercial products showed only trace quantities of SO_4:

nitrocellulose of 12.2% from linters: 0.01%
nitrocellulose of 12.16% from wood cellulose: 0.02%
nitrocellulose of 13.2% from linters: 0.03% SO_4.

Attention should be drawn to the work of Castorina, Helf, Aaronson and Kaufman [52] who examined the nature and amount of sulphate present in nitrocellulose and mechanism of its removal during stabilization by using the radioactive tracer – sulphur 35. Thus nitrocellulose of 13.35% contained 0.84% sulphate. After 56 hours of boiling in acid it was reduced to 0.05%. The latter could not be removed. The authors concluded that *ca.* 90% of sulphate in unstabilized nitrocellulose is removable sulphuric acid and the remainder is sulphate ester which is difficult to remove.

Nitration of wood meal with N_2O_5 vapour at 0° to –2°C *in vacuo* was also described [16].

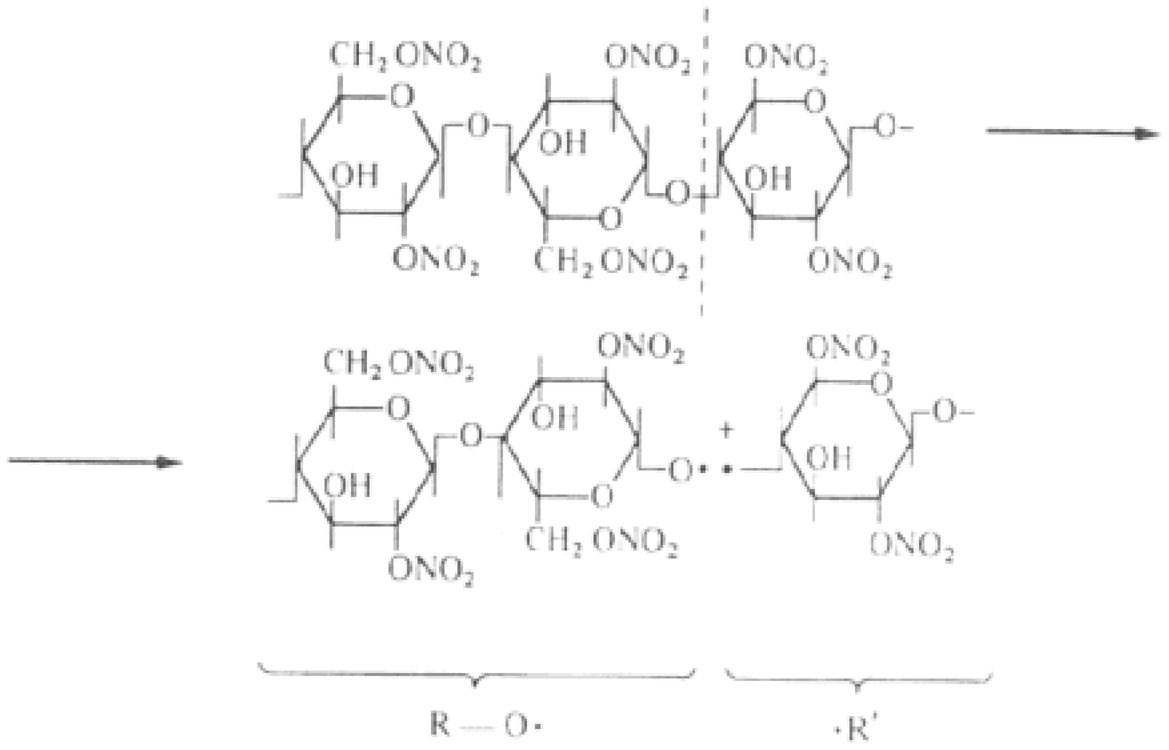
Stabilization of Nitrocellulose

As described in Vol. II, p. 393 stabilization comprises washing and boiling nitrocellulose in kiers (if necessary an additional kiering in autoclave), pulping in beaters or mills (refiners) followed by final boiling and washing.

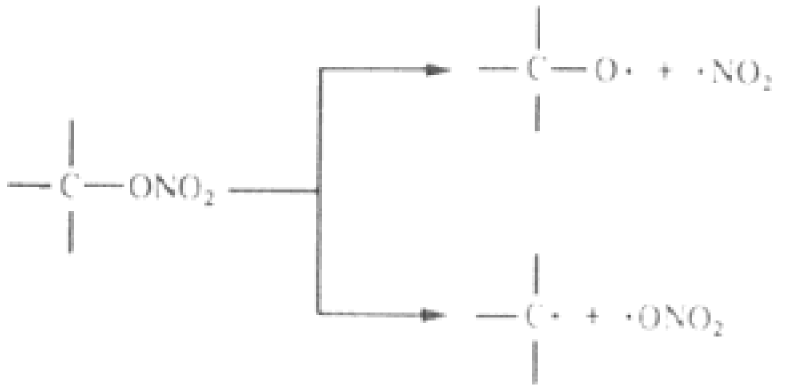
Hess and Trogus (Vol. II, p. 241) have shown that boiling nitrocellulose increases the regularity of the structure of the obtained molecule. A very important part of stabilization is pulping the nitrated fibres. Mechanical cutting of the fibres into shorter ones produces a depolymerization manifested by a decrease in the viscosity of the solutions of nitrocellulose (Vol. II, p. 276).

Steurer and Hess [17] have already calculated that the kinetic energy from the impact of balls (in a colloid ball mill used by Staudinger – Vol. II, p. 276) on cellulose fibres should be sufficient to rupture covalent bonds in cellulose such as C–C, C–O. Breaking such bonds requires energy of the order 80–90 kcal. This statement was substantiated by Swedish authors [18] who found experimentally that the covalent bonds in cellulose, as above, can be ruptured by mechanical action (in an agate ball mill). It has been known since 1895/96, thanks to the work of Bruley (Vol. II, p. 276), that pulping nitrocellulose reduces the viscosity of its solutions, but only now the experimental facts can be explained in terms of breaking the covalent bonds. This was done by T. Urbański

[19] who suggested a sequence of reactions given in scheme (1). First breaking a bond between pyrane ring can occur forming free radicals (a) RO· and R'·. Also a rupture of the bond $-C-O-NO_2$ can occur forming free radicals $-C\cdot$, $-C-O\cdot$, $\cdot ONO_2$ and $\cdot NO_2$ (b) All free radicals can react with water to yield: $R-OH$, $R'-OH$ and $-C-OH$, $-CH$, $HONO_2$ and HNO_2 (c)



(1a)



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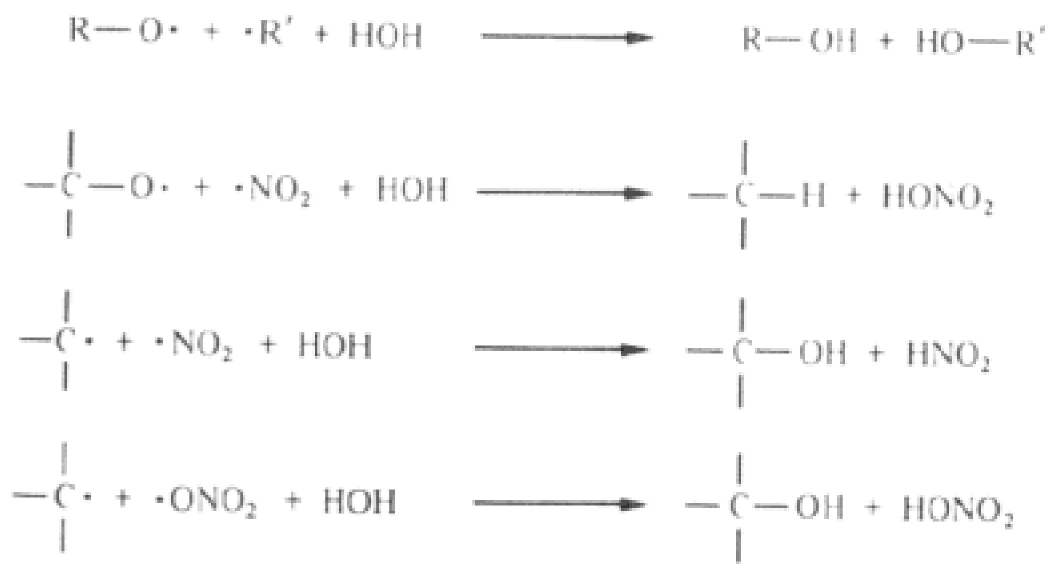

(1c)

This scheme explains both the reduction of the viscosity and a slight denitratio of nitrocellulose during the pulping (Vol. II, p. 276) and the presence $Ca(NO_3)_2$ and $Ca(NO_2)_2$ in water in beaters. Calcium salts are being forme from calcium carbonate added to the water in the course of the work of beater

Degradation of polymers by mechanical action (tribo- or mechano-chemistr is now generally accepted and has been described in two monographs [20, 21].

Knecht Compound

The structure of "Knecht compound" has been examined by T. Urbański ar Żyszczyński [54]. On the basis of infra red spectra they came to a conclusic that the cellulose moiety of the Knecht Compound is partly oxidized and shov the presence of a carbonyl group similar to that of oxycellulose (Vol. II, p. 321

Manufacture of Nitrocellulose. Continuous Methods

As pointed out in Vol. II, p. 391 numerous attempts have been made introduce continuous methods of cellulose nitration. In addition to those me tioned in Vol. II, the following continuous methods were reported by Hiatt ar Rebel [2]: Plunkett [22], Plunkett and McMillan [23], Reinhardt [24]. Rar sey [25] described a continuous method with nitric–phosphoric acid mixture and Bergman [26] – nitration of powdered cellulose. Diels and Orth [27] us spent acid for the first step of nitration followed by the second with fresh mix acid.

Matasa and Matasa [28] described a number of continuous methods of cell lose nitration, among them patents by Hercules Co. [29] and Wasag Chem [30].

So far none of the above methods have received practical application, and appears that only two methods are in use on an industrial scale:

(1) semi-continuous method used by Bofors-Nobel-Chematur in Sweden ar
(2) continuous method used by Hercules Powder Co.

The Semi-continuous Method of Bofors-Nobel-Chematur [31]

The method is depicted by Fig. 48. It was developed in the early 1960s the Nobel Works, Karlskoga, Sweden. The process comprises continuous nit tion, continuous centrifuging and batch stabilization.

Cotton, cotton linters or wood cellulose is made fluffy by a disintegrator ar dried in a continuously working belt drier. Dried cellulose is continuously mix with nitrating acid in a prenitrator. From there the mixture passes into a c fibrator where very close contact is obtained between the cellulose fibres and t acid and all enters into an 'after-nitrator' where the nitration is completed.

The method of continuous centrifuging depends upon whether low or hig

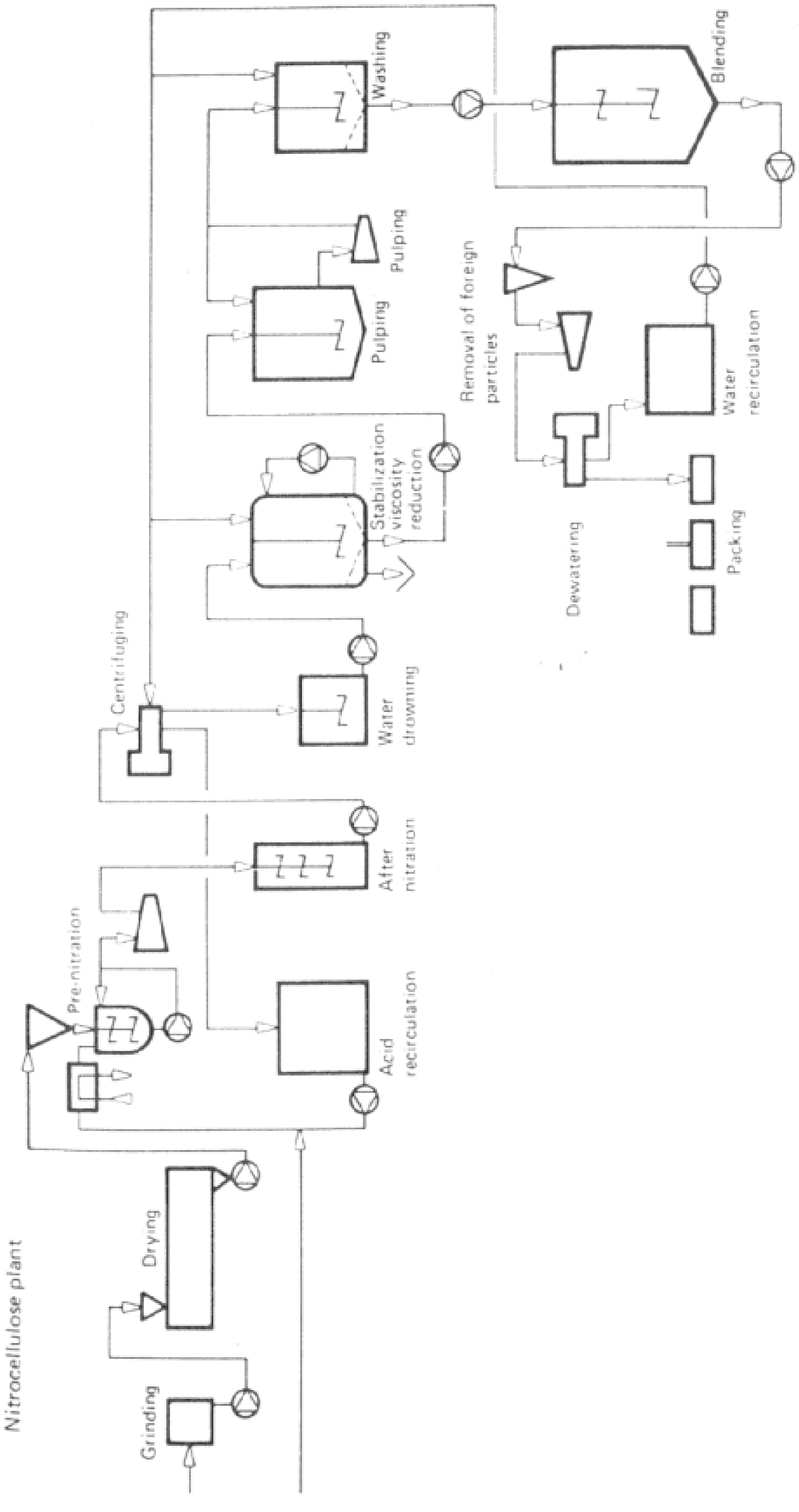

FIG. 48. Semi-continuous making of nitrocellulose of Bofors-Nobel-Chematur (Courtesy Bofors-Nobel-Chematur)

nitrated nitrocellulose should be obtained. Low-nitrated product continuously flows through three stages in the centrifuge. In the first stage the main part of the acid is removed, in the second stage the nitrocellulose is washed with dilute acid and in the third stage the nitrocellulose is washed with water. High-nitrated nitrocellulose is not washed with acid and water.

When leaving the centrifuge the nitrocellulose is mixed with water and pumped to stabilization. The spent acid is partly mixed with nitric acid and oleum for re-use and partly sent for denitration.

The nitrated cellulose is boiled in pressure kiers. The boiling time and temperature depends on the required quality of the product.

Kiered nitrocellulose is pulped in refiners (Fig. 49). The refiners are of the same design as Jordan mills. They contain a conical bar fastened on a movable shaft around the mantle equipped with knives. The inside of the conical shell is also equipped with knives. The nitrocellulose–water slurry is pumped through the gap between the knives. The gap between the knives is adjusted by moving the conical part horizontally.

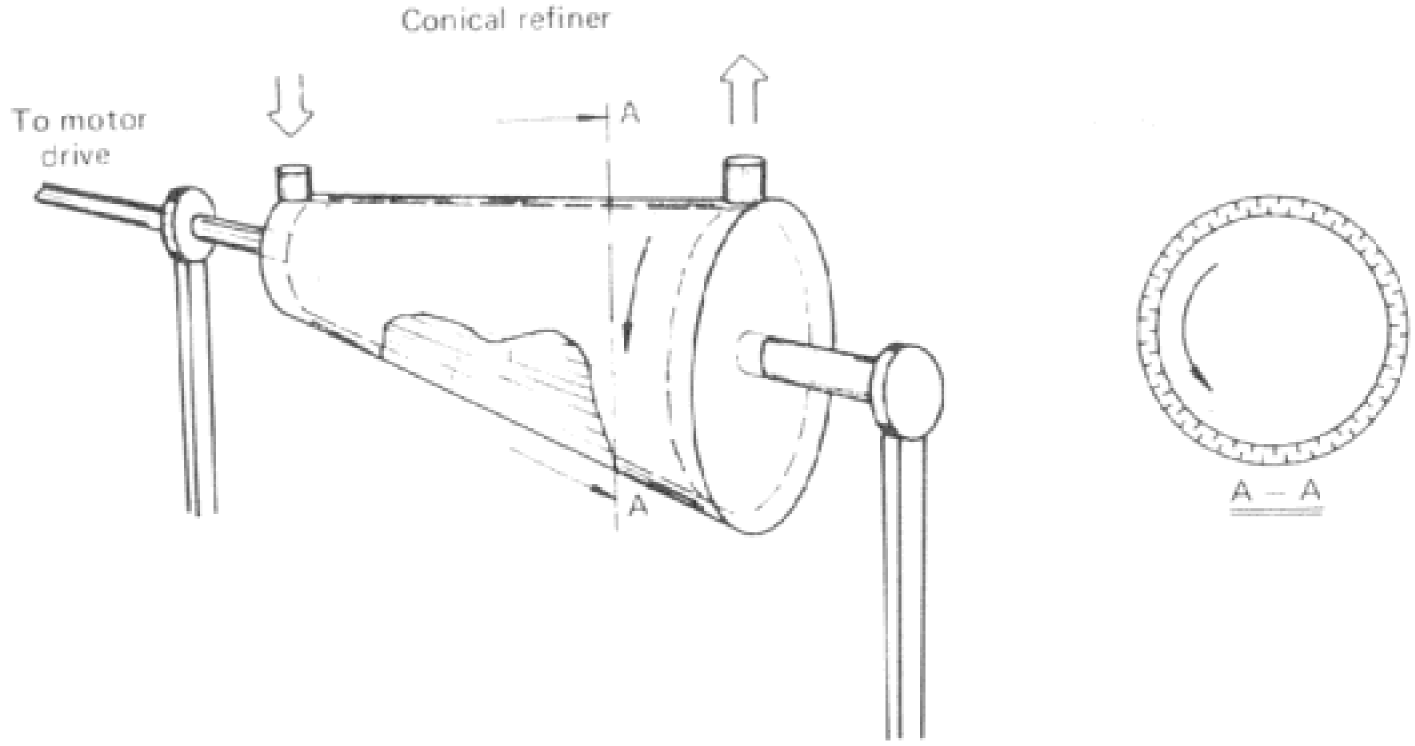

FIG. 49. Conical refiner (Courtesy Bofors-Nobel-Chematur).

Pulped nitrocellulose is subjected to the usual operations: further boiling, washing, blending and the removal of foreign particles. After that the nitrocellulose is dewatered in a centrifuge.

Diagram of Continuous Method of Hercules Powder Co. Ind. [32]. A continuous fully automatic nitrating method is shown in Fig. 50. Dried cellulose and mixed nitrating acid are introduced continuously to a nitration. A suspension of nitrocellulose in the acid enters a centrifuge. The centrifuge is the essential part of the system. It is divided into zones and nitrocellulose is advanced from one zone to another. In the first zone most of the original acid from the nitration is removed. In each of the succeeding zones the acid in nitro-

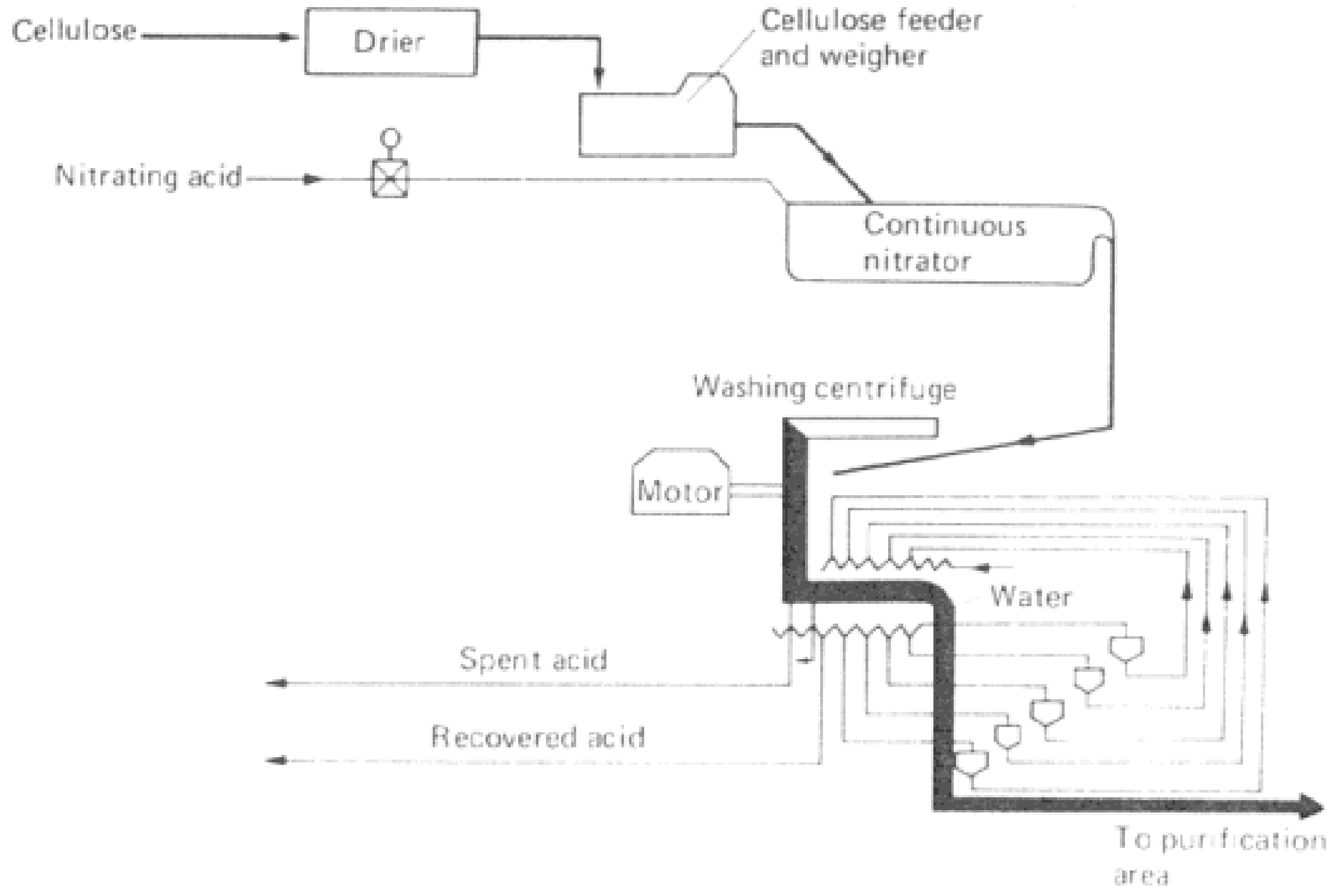

FIG. 50. Diagram of continuous method of making nitrocellulose of Hercules Powder Co.

cellulose is displaced with weaker acid and finally in the last zone with water. In all zones the process occurs simultaneously. The water used for the final displacement is used for the preceding washing and so on, this is done in every step: each effluent is used for the preceding step. Subsequently the displacing acid leaving the system is composed of spent acid of nitration.

Hercules Co. points out that the product of the continuous nitration is more uniform than from the batch processes.

Drying Nitrocellulose

As is known nitrocellulose is stored and transported with 30% water or ethanol. It is also known that for a single base powder (nitrocellulose powder) water in nitrocellulose is replaced by ethanol which remains in it as an ingredient of the solvent (Vol. II, p. 573). However for some types of double base powder (cordite, Vol. III, p. 642) it is necessary to dry the nitrocellulose. Drying nitrocellulose is essential in the manufacture of dynamite (Vol. II, p. 511). However it has so far been considered the most dangerous operation with dry nitrocellulose considering its ease of ignition and burning, and sensitivity to impact and friction. Mario Biazzi S.A. use a Finnish method Finska Forcit [33]. The idea of the system is given in Fig. 51. It consists essentially in drying humid nitrocellulose with dry warm air which passes through the nitrocellulose from the top to the bottom.

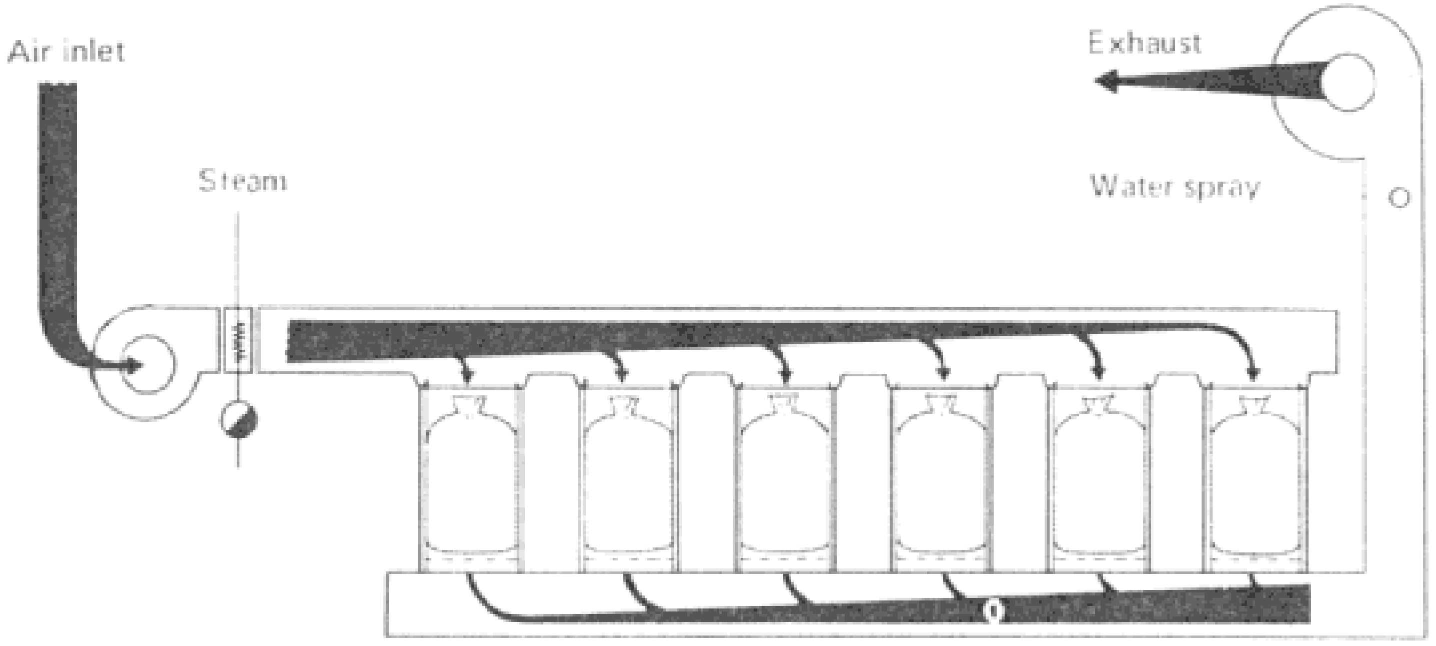

FIG. 51. Finska Forcit method of drying nitrocellulose (Courtesy M. Biazzi S.A.).

Moist nitrocellulose in cotton sacks is put in aluminium cylinders the bottoms of which are made of metal sieves, for example, of phosphorbronze wires. The thickness of the sheet of nitrocellulose should be 25–40 cm the diameter is chosen so that the content of one cylinder is used for one batch of dynamite. Dry air heated to 50°C enters the cylinders under pressure of 700 mm water. The amount of air is 30–50 nm^3 per kg of dry nitrocellulose.

The end of drying is manifested by the increase above 20°C in the temperature of the air leaving the cyclinders. To avoid the danger created by static electricity all cylinders should be earthed. Drying is ended after 1–2 hours. One of the advantages of the method is the fact that no nitrocellulose dust is formed.

Safety in the Manufacture of Nitrocellulose

Generally speaking the manufacture of nitrocellulose should be regarded as a relatively safe process. The most dangerous operation is drying nitrocellulose [34]. It also causes the largest number of accidents [35]. The explosions occurred mainly through the shock, overheating or discharge of static electricity. Another dangerous part of the work is centrifuging – the danger connected with it has been described in Vol. II, pp. 407. 380. Stabilization in autoclaves, that is, boiling nitrocellulose under pressure, also ended with explosions probably due to an insufficient quantity of water in the autoclave. As a consequence decomposition began with the increase of the temperature to 160°C and a violent reaction occurred.

STARCH NITRATES (NITROSTARCH) (Vol. II, p. 418)

Attention should be paid to Abdel-Rahman Shalash [36] who nitrated both amylose and amylopectin and gave an extensive review of the literature on nitrostarch.

Here are the main points of Shalash's work.

Nitration of amylose. This was achieved by using a nitrating mixture of nitric acid and acetic anhydride in volume proportions 50:50 and 60:40. Table 59 gives the main results.

TABLE 59. Nitration of amylose with HNO_3 : acetic anh. 60:40 after 24 hours [36]

Ratio Amylose:Acid	Temperature °C	%N in the product
1:10	10	13.4
	20	13.5
	30	13.66
1:25	10	13.5
	20	13.7
	30	13.76
1:50	10	13.6
	20	13.7
	30	13.8

Nitration of amylopectine. The nitration was carried out with nitric acid in the presence of pyridine. The nitration is extremely fast and the esterification equilibrium is reached at a relatively low degree of nitration as denitration intervenes.

Using nitric acid: pyridine ratio 70:30 and amylopectine: (nitric acid–pyridine) = 1:50 at 10°C, the product contained:

after one hour	11.45%N,
after two hours	12.25%,
after three hours	12.7%,
after four hours	12.1%.

Among other published papers on nitrostarch is that of Vollmert [37]. He nitrated starch with N_2O_5 vapour and obtained the product with 9.7–10.0% N.

X-ray analysis was carried out simultaneously with Kołaczkowska and T. Urbański (Vol. II, pp. 422–423) by Berl and Kunze [38] and by Centola [39]. The former authors examined both: amylose nitrate and amylopectine nitrate.

NITRATES OF VARIOUS CARBOHYDRATES

The thesis of Delpy [40] should be mentioned. He described the nitration products as follows:

hydrocellulose nitrate,	12.61% N
D-glucose nitrate	15.99% N (a sticky, soft substance),
D-mannose nitrate	15.40% N (as above),
D-fructose nitrate	13.56% N, crystals, m.p. 50–60°C,
saccharose nitrate	14.54% N, solid
maltose nitrate	12.03% N,
raffinose nitrate	14.36% N.

The nitration was carried out with a mixture of nitric acid (43.4%), sulphuric acid (44.25%) and water (11.85%).

POLYVINYL NITRATE (Vol. II, p. 173)

Efforts are being made to find an explosive polymer with properties similar to those of nitrocellulose. Naturally attention was directed towards the nitration of polyvinyl alcohol as the most accessible high molecular polyhydroxyl alcohol. It is described in the chapter dedicated to explosive polymers (Chapter XIV).

NITRO-DERIVATIVES OF LIGNIN (Vol. II, p. 433)

Attention is drawn to the monograph by Brauns and Brauns [42]. Although published in 1960 it contains a description of the main work on nitration of lignin.

The diagram suggested by Fraudenberg (Vol. II, p. 435) with the nitration of aromatic ring has generally speaking been confirmed.

The most important seem to be the paper published by Lieser and Schaack [43], Ivanov, Chuksanova and Sergeeva [44].

The form using the nitrating mixture with 7.4% water at 20°C yielded the product containing 12.2% N [43]. The latter nitrated lignin with nitric acid–phosphoric acid and nitric acid–acetic anhydride and obtained the product with 7.5% N [44].

No practical application has been found for the products of nitration.

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CHAPTER 13

N-NITRO COMPOUNDS

(*N*-nitramines and *N*-nitramides (Vol. III, p. 1)

This important group of explosives has recently received particular attention due mainly to heterocyclic nitramines–Cyclonite (RDX) and Octogene (HMX). Interest has also been maintained in Nitroguanidine and EDNA.

Several reviews on nitramines have appeared: by McKay [1], G. F. Wright [2] who reviewed the methods of formation of the nitramino group and its properties, Fridman, Ivshin and Novikov [3] who reviewed chemistry of primary aliphatic nitramines.

Darnez and co-workers [193, 194] revealed the formation of free radicals from secondary nitramines as the result of γ and ultra-violet radiation. Recently Dubovitskii and Korsunskii [4] have reviewed nitramines from the point of view of the kinetic value of their thermal decomposition and came to the conclusion of free radical-chain reaction of breaking the N–NO_2 bond. Also a monograph on octogen has appeared [5].

STRUCTURE AND CHEMICAL PROPERTIES

Very little can be added as regards the electronic spectra of nitramines (Vol. III, p. 3). Among earlier papers were those of Kortüm and Finckh [6], Mehler [7]. The latter author reported two maxima for Cyclonite in ethanol: 202 nm and a shoulder at 236 nm. Piskorz and T. Urbański [8] found the maxima at 232 nm. Two maxima 218–224 and 262–266 nm were present when the molecules contained other chromophores: C=O and C=NH in nitrourea and nitroguanidine (see also Vol. III, p. 25).

Infra red spectra [8, 9] were reported to show the frequencies:

NO_2 ν_{asym}	1630–1550 cm^{-1}
NO_2 ν_{sym}	1354–1262 cm^{-1}
N–N in primary nitramines	1000–948 cm^{-1}

See also the frequencies of *N*-nitrosamines [10].

In primary nitramines the frequency NH can be lowered to 3253–3240 cm^{-1} through hydrogen bonds between NH and NO_2 of neighbouring molecules or neighbouring groups in dinitramines. In deuterated compounds it can be lowered to 2400 cm^{-1} [11].

Primary nitramines are weak acids, for example, methyl nitramine shows $pK_a = 6.0$ [3].

The dissociation constants of *N*-nitro derivatives of α, ω-dinitramines also indicate their weak acid properties [12].

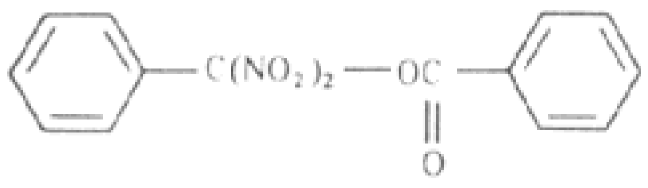
Nitrimino compounds containing =N–NO_2 should also be included in the group of compounds belonging to nitramines and nitramides.

On the contrary a *N*-nitro derivative of hydrazine, the nitroimide (I) (obtained by dehydration of quaternary nitrate of substituted hydrazine) possesses weak basic properties (pK_a = −4.2 ± 0.1) as shown by Epsztajn and Katritzky [13]:

$$(CH_3)\overset{+}{N}{-}NH_2\ NO_3^- \xrightarrow[-H_2O]{Ac_2O} (CH_3)_3\ \overset{+}{N}{-}N{=}NO_2^-$$

I

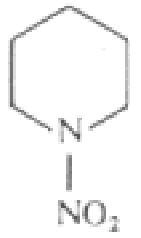
It should be pointed out that considerable effort has been made to obtain *N*-nitrohydrazine from unsubstituted hydrazine. The existing descriptions in the literature [66–69] cannot be considered as conclusive. Thus the nitration of *N,N'*-dibenzoylhydrazine did not yield *N,N'*-dinitrodibenzoylhydrazine [69] but an unsymmetrical αα-dinitrobenzoyl benzoate (II):



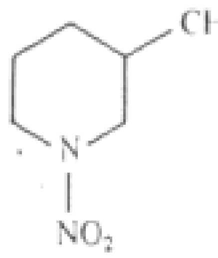
II

This was revealed by Lamberton and Harper [70].

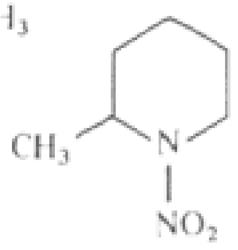
Chiral nitramines – derivatives of piperidine show an optical activity according to Ferber and Richardson [14]. Symmetrical compound III is non-chiral, asymmetrical compounds IV and V are chiral and optically active:



III

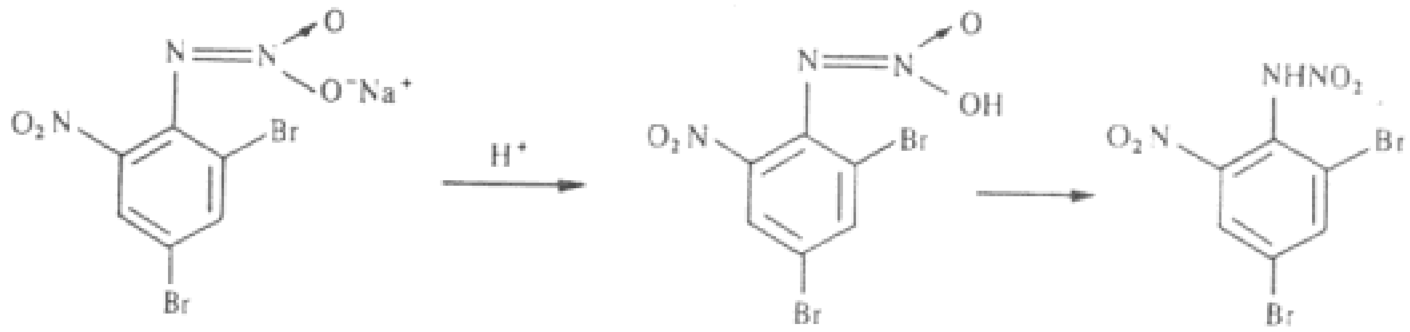


IV



V

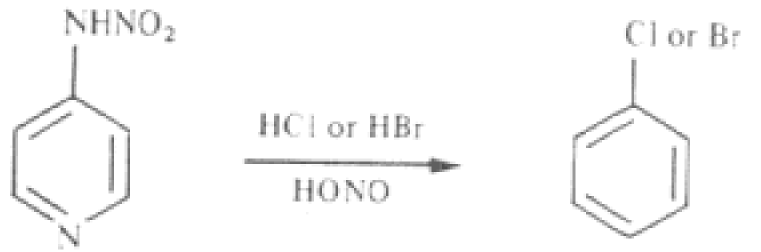
The disputed existence of unstable aci-form of primary nitramines (Vol. II, p. 4) seems to be substantiated by Orton as early as 1902 [15]. Acting with alkalis on 2,4-dibromo-6-nitro-phenyl-1-nitramine he obtained a sodium salt which on acidification yielded a colourless unstable aci-product VI which was quickly transformed into the orange nitramine VII:



VI

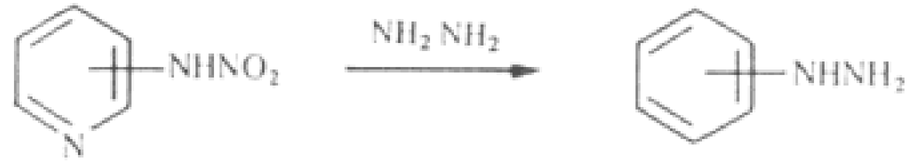
Orange
m.p. 91–92°C
VII

The nitramine group attached to the pyridine ring can readily be replaced by halogen while acting with nitrous acid and hydrochloric or hydrobromic acid [16, 17]:

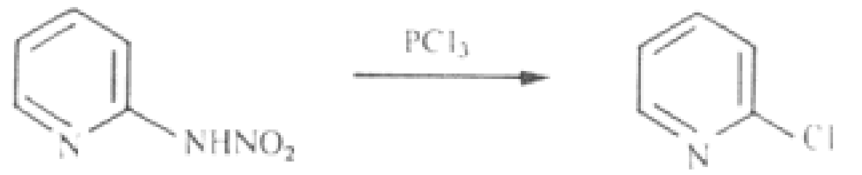


(1)

Talik and his co-workers succeeded in replacing the nitramino group with different nucleophiles (2) and (3) [18, 19]:



(2)



(3)

Nitramines can react with acids (Vol. II, p. 4). With hydrochloric acid the reaction can lead to the formation of chlorides and N_2O according to Lamberton and co-workers [20]:

$$RNHNO_2 + HCl \longrightarrow RCl + N_2O + H_2O. \qquad (4)$$

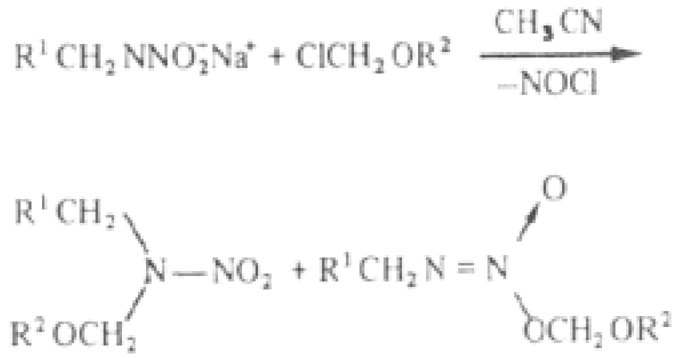
The reaction can be used to reveal the presence of the $NHNO_2$. Nitrous acid can yield diazomethane while reacting with methylnitramine [21].

Nitramines are stable to bases at moderate temperatures, although some of them decompose readily (Vol. II, p. 6).

Primary nitramines can be methylated with diazomethane yielding both *N*-methyl and *O*-methyl derivatives [21] (5):

$$CH_3NHNO_2 \xrightarrow{CH_2N_2} (CH_3)NNO_2 + CH_3N=NOCH_3 \qquad (5)$$

The reaction of nitramines with α-halogenoethers was studied by Thamer and Unterhalt [22] (6):



$$R^1CH_2NNO_2^-Na^+ + ClCH_2OR^2 \xrightarrow[-NOCl]{CH_3CN} \underset{R^2OCH_2}{\overset{R^1CH_2}{\;}}N-NO_2 + R^1CH_2N=N\overset{O}{\;}OCH_2OR^2 \qquad (6)$$

The same authors described a different trend of the reaction with α-halogenothioethers [23].

Primary nitramines react with formaldehyde to yield *N*-hydroxymethyl compounds. The reaction is reversible [24]:

$$\underset{NO_2}{RNH} + CH_2O \rightleftharpoons \underset{NO_2}{RNCH_2OH} \qquad (7)$$

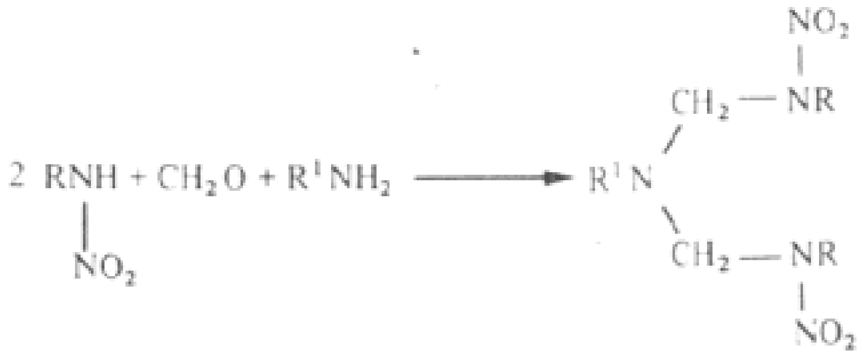
The next step is the Mannich reaction (8) [24] which (as pointed out by Wright [2]) was carried out with nitramines by Franchimont [25] earlier than the work of Mannich:

$$\underset{NO_2}{RNCH_2OH} + R'_2NH \longrightarrow \underset{NO_2}{RNCH_2NR'_2} + H_2O \qquad (8)$$

VIII

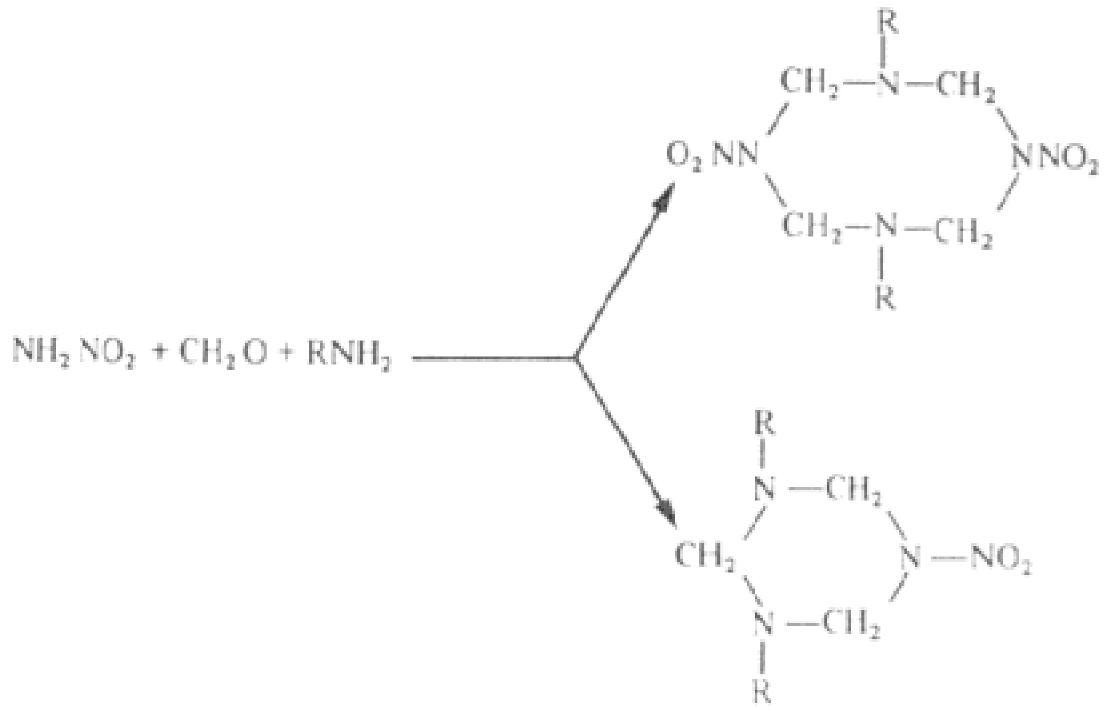
Bases VIII are soluble in water and split CH_2O through the action of alkalis, contrary to Mannich bases which are insoluble in water and stable towards alkalis.

By using primary amines RNH_2 Chapman, Owston and Woodcock [26] obtained nitramines with two nitro groups (9):



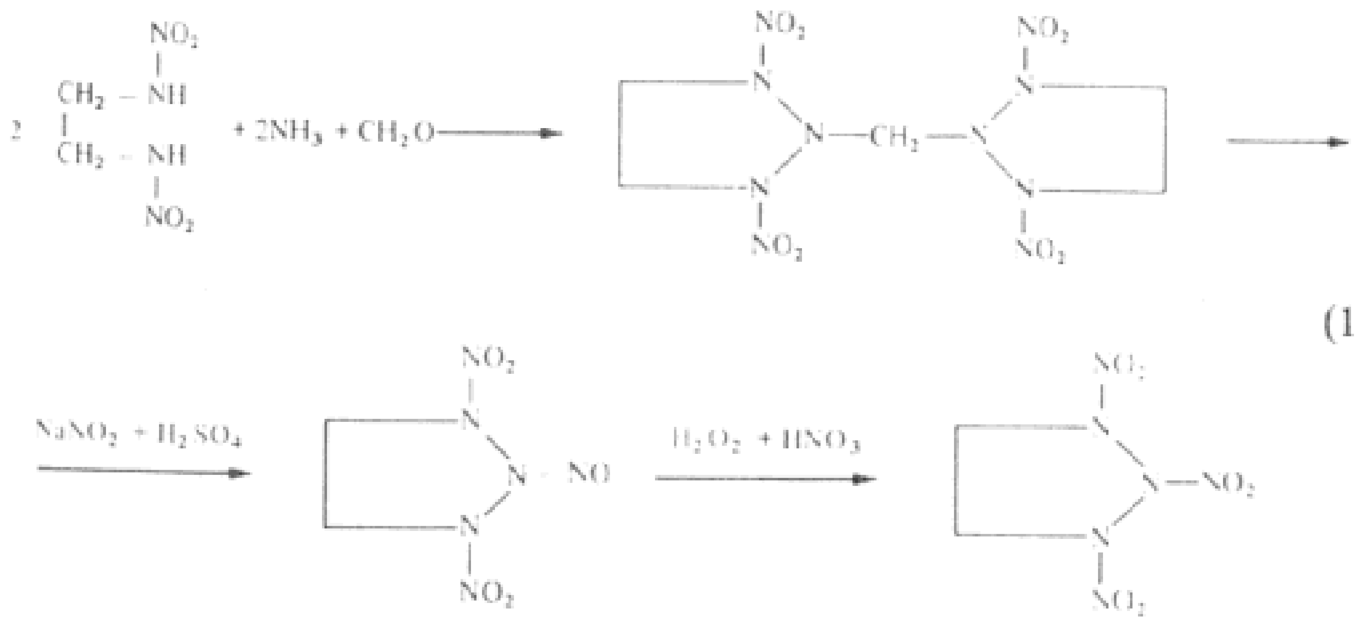
$$2\,\underset{NO_2}{RNH} + CH_2O + R^1NH_2 \longrightarrow R^1N\begin{matrix}CH_2-\overset{NO_2}{NR}\\ CH_2-\underset{NO_2}{NR}\end{matrix} \qquad (9)$$

Also the same authors obtained cyclic nitramines by reacting nitramine (NH_2NO_2) (10) or primary dinitramines with primary amines:

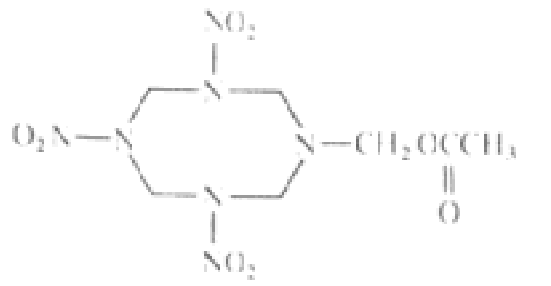


(10)

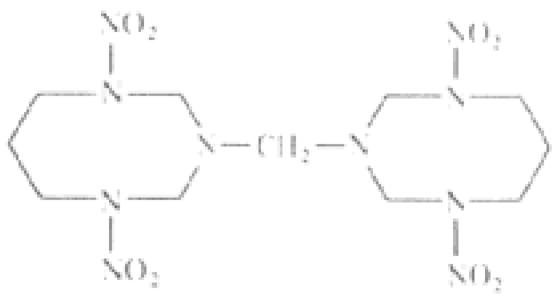
A wide range of cyclic nitramines through the reaction of dinitramines with formaldehyde and diamines were obtained and studied by Bell and Dunstan [27] and Novikov and co-workers [28]. Bell and Dunstan reported reaction (11) and formation of compounds IXa, b, c:



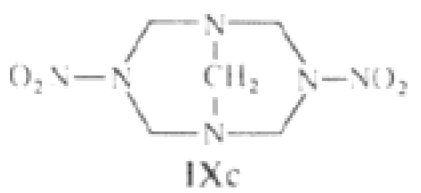
(11)



IXa

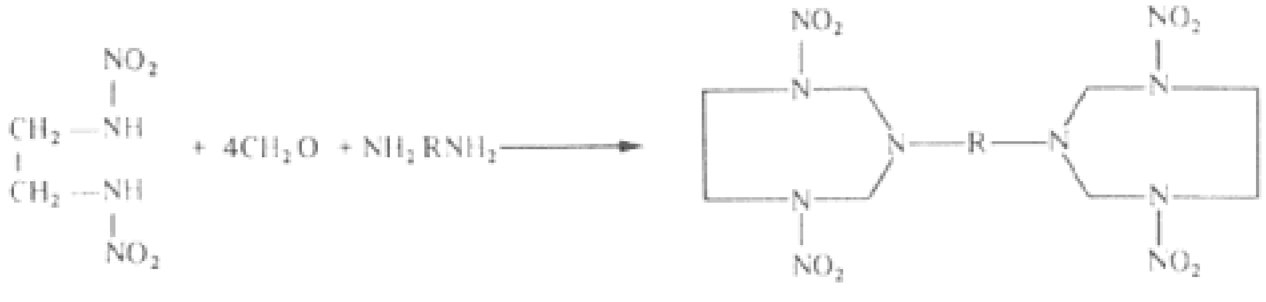


iXb



IXc
DPT
(Vol. III, p. 90, XII)

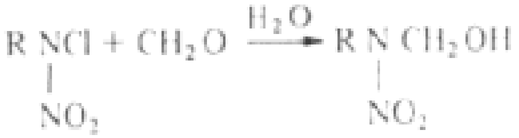
Novikov *et al.* [28] described a number of cyclic products from the reactions:



(12)

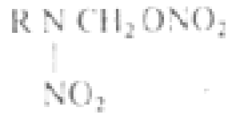
$R = (CH_2)_n$, $n = 2$-$4, 6$

Formaldehyde can replace chlorine in *N*-chloro-*N*-nitramines to form an alcohol [29]:



$$R\underset{NO_2}{N}Cl + CH_2O \xrightarrow{H_2O} R\underset{NO_2}{N}CH_2OH \qquad (13)$$

The alcohols can be nitrated to yield *O*-nitro *N*-nitro compounds (X)



$$R\underset{NO_2}{N}CH_2ONO_2$$

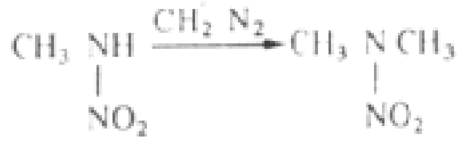
X

According to Majer and Denkstein [30] such esters are unstable, can readily decompose and are dangerous on storage.

Acylation of primary nitramine occurs with great difficulty. Acetyl chloride can acetylate potassium or silver salts of primary nitramines with a yield according to White and Baumgarten [31]. It is rationalized that the difficulty of acetylating metal salts of primary nitramines comes probably from the assumption that the metal salts of nitramines are chelate compounds and not true salts.

Salts of nitramine can react with fluorine to yield fluoronitramine, for example, $C_4H_9\underset{NO_2}{N}F$ [32].

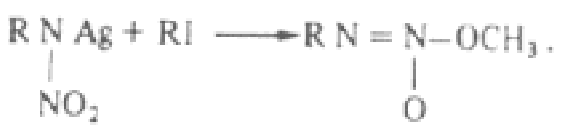
Among other different reactions of primary nitramines alkylation should be mentioned. Methylation can be carried out with diazomethane and can yield methylated products at both: nitrogen (14) and oxygen (15) [33, 132]:



$$CH_3\underset{NO_2}{N}H \xrightarrow{CH_2N_2} CH_3\underset{NO_2}{N}CH_3 \qquad (14)$$

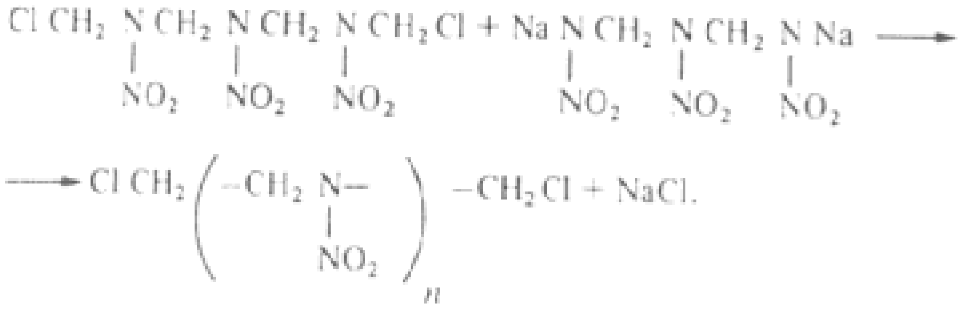
$$C_6H_5NHNO_2 \xrightarrow{CH_2N_2} C_6H_5N=N\left\langle\begin{matrix}O\\OCH_3\end{matrix}\right. \qquad (15)$$

Alkylation can also be carried out with alkyl halides and dimethylsulphate. As a rule *O*-nitro derivatives are being formed [34], viz. (16):



$$\underset{NO_2}{\underset{|}{RNAg}} + RI \longrightarrow RN{=}\underset{O}{\underset{|}{N}}{-}OCH_3. \qquad (16)$$

Potassium and sodium salts of primary nitramines react with compounds containing active chlorine, for example picryl-*N*-chloride and potassium methylnitramine yielded tetryl [35]. An interesting application of this reaction is the formation of a polymer from disodium salts of dinitramines and bis-*N*-chloromethylnitramines [36]:

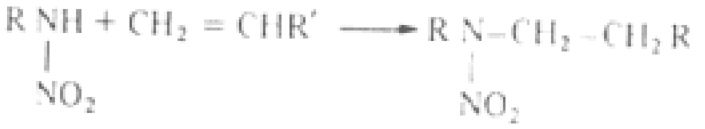


$$ClCH_2\underset{NO_2}{\underset{|}{N}}CH_2\underset{NO_2}{\underset{|}{N}}CH_2\underset{NO_2}{\underset{|}{N}}CH_2Cl + Na\underset{NO_2}{\underset{|}{N}}CH_2\underset{NO_2}{\underset{|}{N}}CH_2\underset{NO_2}{\underset{|}{N}}Na \longrightarrow$$

$$\longrightarrow ClCH_2\left({-}CH_2\underset{NO_2}{\underset{|}{N}}{-}\right)_n{-}CH_2Cl + NaCl. \qquad (17)$$

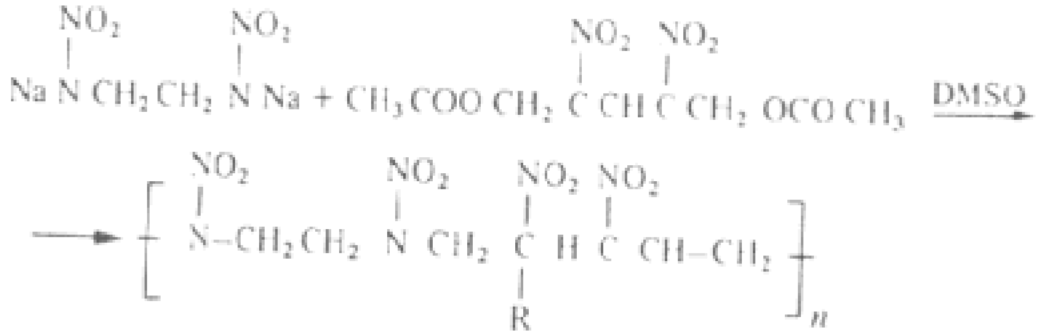
The polymer was suggested as a rocket propellant.

An important reaction is the addition of primary nitramines to an active double bond. This was reported by Kissinger and Schwartz [37] for example (18):



$$R\underset{NO_2}{\underset{|}{N}}H + CH_2{=}CHR' \longrightarrow R\underset{NO_2}{\underset{|}{N}}{-}CH_2{-}CH_2R \qquad (18)$$

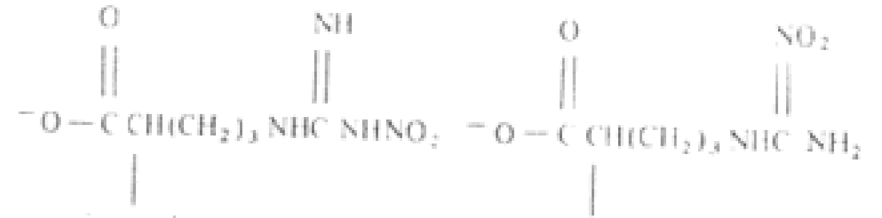
The addition of α, ω-dinitramines to the products of decomposition of nitrodiol acetates was described by Feuer and Miller [38]. The reaction (19) yielded a polymer:



$$Na\overset{NO_2}{\overset{|}{N}}CH_2CH_2\overset{NO_2}{\overset{|}{N}}Na + CH_3COOCH_2\overset{NO_2}{\overset{|}{C}}H\overset{NO_2}{\overset{|}{C}}CH_2OCOCH_3 \xrightarrow{DMSO}$$

$$\longrightarrow \left[\overset{NO_2}{\overset{|}{N}}{-}CH_2CH_2\overset{NO_2}{\overset{|}{N}}CH_2\underset{R}{\underset{|}{\overset{NO_2}{\overset{|}{C}}}}H\overset{NO_2}{\overset{|}{C}}CH{-}CH_2\right]_n \qquad (19)$$

The *N*-nitro protective group of arginine (XIa) was used in synthesis of peptides [39, 40]



$${-}O{-}\overset{O}{\overset{\|}{C}}\underset{NH_3^+}{\underset{|}{C}}H(CH_2)_3NH\overset{NH}{\overset{\|}{C}}NHNO_2 \quad \textbf{XIa} \qquad {-}O{-}\overset{O}{\overset{\|}{C}}\underset{NH_3^+}{\underset{|}{C}}H(CH_2)_3NH\overset{NO_2}{\overset{\|}{C}}NH_2 \quad \textbf{XIb}$$

According to N^{15}-NMR in aqueous solution it has nitrimine structure (XIb).

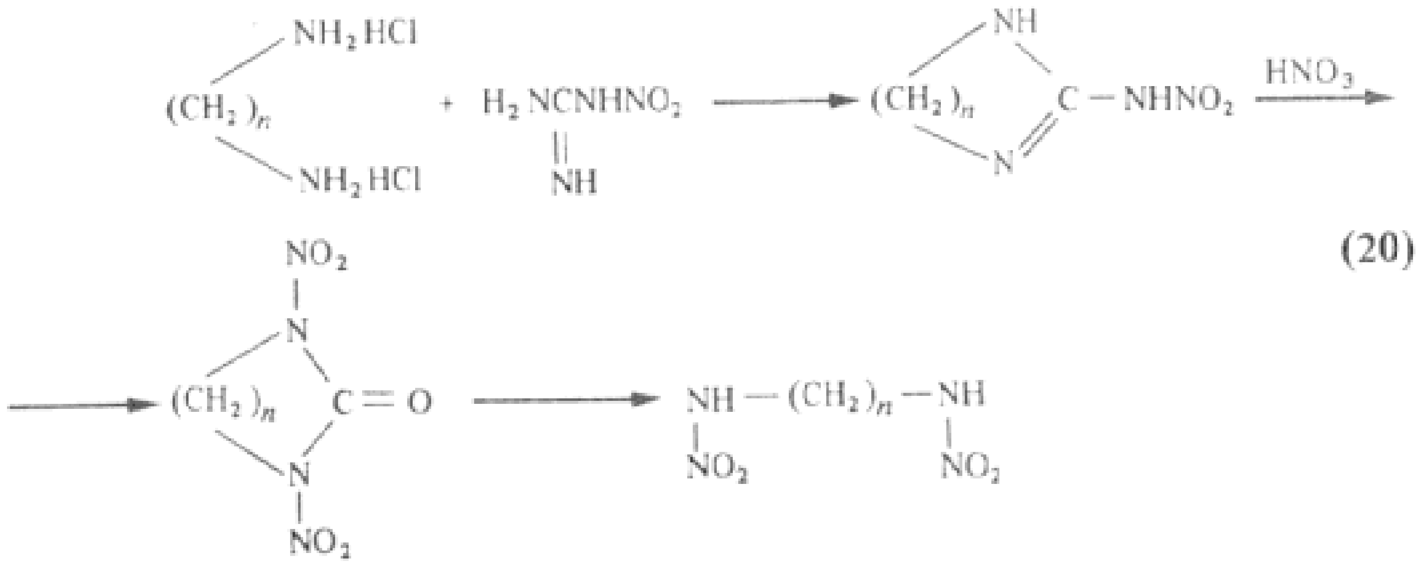
Naturally occurring nitramines have also been described, for example, *N*-nitroglycine [41] and β-nitroaminoalanine [42].

PREPARATION OF NITRAMINES

The methods described in Vol. III, p. 8 remain valid. The only addition related to the formation of dinitramines is given below.

Formation of Dinitramines from Nitroguanidine

This original method was described by McKay and Wright [43] and McKay and Manchester [44]. The method consists in reacting diamines with nitroguanidine to form cyclic products, which after nitration and hydrolysis produced dinitramines (20):



(20)

By this method 1,2-dinitraminopropane, 1,3-dinitraminobutane and 1,3-diamino-2-nitroxypropane were obtained. For more reactions of nitroguanidine see review [3].

N-NITROENAMINES

Some of this group of compounds can be subjected to an interesting 1,3-rearrangement of *N*-nitroenamines to *C*-nitro compounds according to Büchi and Wüest [71].

A simple refluxing of *N*-nitroenamine in xylene under an atmosphere of argon gave the reaction (21):

(21)

ALIPHATIC NITRAMINES AND NITRAMIDES (Vol. III, p.15)

Nitramine (Nitramide)
NH_2NO_2
m.p. 72–73°C

Nitramine offered a considerable interest owing to the simplicity of its molecule (the simplest *N*-nitro compound).

Acid and base catalysed decomposition of NH_2NO_2 has already been described by Hammett [45] who also mentioned earlier works such as that of Brønsted and Pedersen [46]:

$$NH_2NO_2 \xrightarrow{\text{Base}} N_2O + H_2O. \qquad (22)$$

Marlies and La Mer [47] confirmed their results.

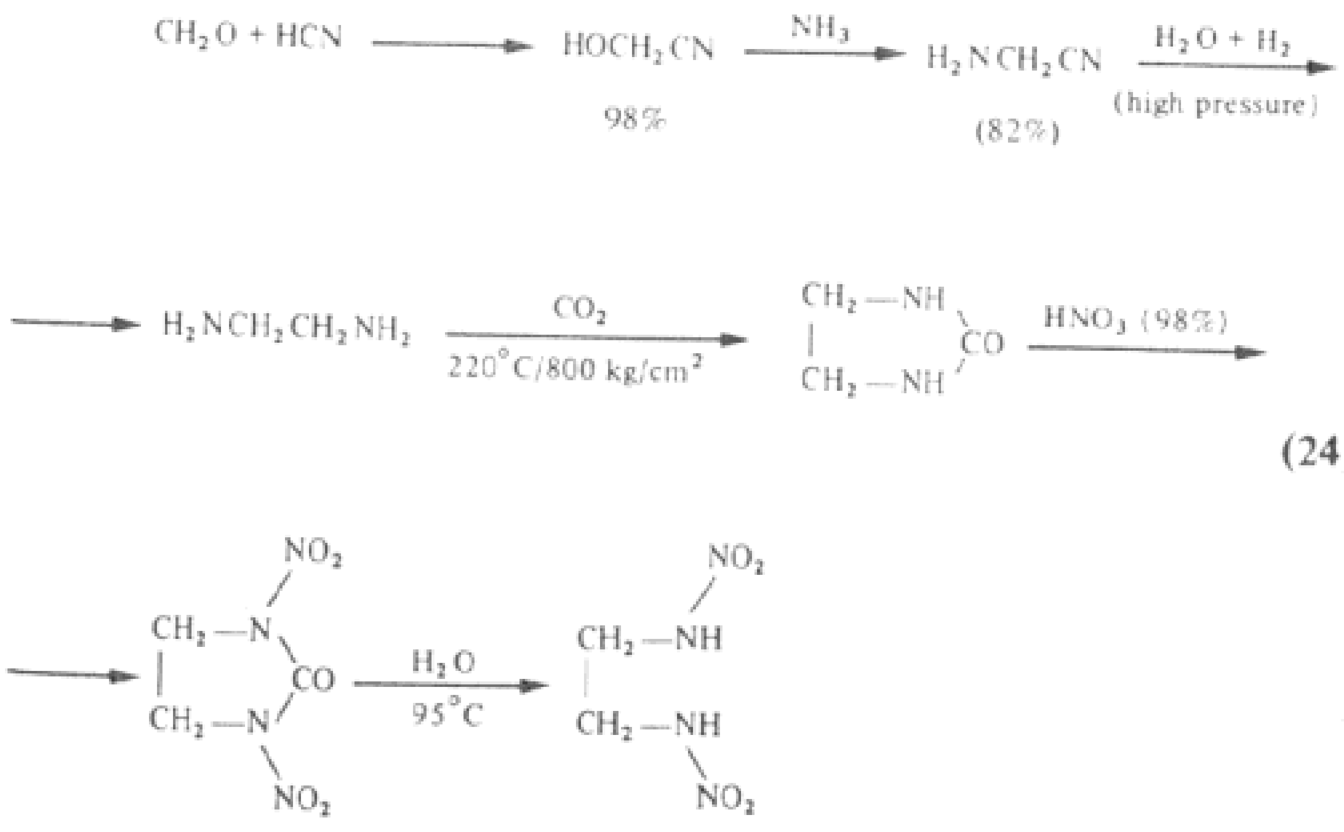
A wide examination of the base-catalysed decomposition of NH_2NO_2 was given by Kresge and co-workers [48, 49]. They suggested two parallel decomposition pathways:

$$B + NH \cdot NO_2H \rightleftharpoons BHN\,NO_2H \rightleftharpoons \overset{+\;-}{BHN}\,NO_2H \rightleftharpoons BH^+ + N_2O + OH^-. \qquad (23)$$

ETHYLENE DINITRAMINE (EDNA, HALEITE) (Vol. III, p. 18)

Preparation. Among different methods of preparing EDNA the method of Franchimont and Klobbie (Vol. III, p. 18) was repeated [50] by boiling dinitroethylenediurethane with alcoholic ammonia followed by acidifying the solution with hydrochloric acid with an overall yield of 60%.

According to American sources issued in 1971 [51] the full method of making EDNA consists in the following steps:



(24)

EDNA

For nitration fuming nitric acid was used and the overall yield was 70% which made the product reasonably cheap.

Physical and Chemical Properties

Pure EDNA has a m.p. of 177–179°C but begins to decompose at 175°C.

Structure by X-raying was determined by Llewellyn and Whitmore [52]. Atomic centres are confined (according to this analysis) to laminae paralleled to (001) approximately of 1.72 Å in thickness. The length of bonds are: NO 1.21 Å (as in nitromethane), C–C 1.52 Å, C–N 1.41 Å, N–N 1.33 Å. The short N–N bond is probably due to positive charges on both N atoms, as has been previously pointed out [11].

Specific gravity of crystals is 1.71 and the density of the pressed substance is:

at 350 kg/cm²	1.28
700	1.38
1000	1.44
1400	1.49
2800	1.56

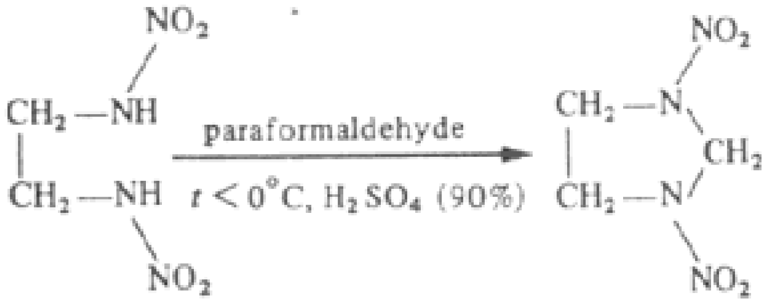
The solubility is given in Table 60.

TABLE 60. Solubility of EDNA

Temperature °C	Solvent	
	Water	Ethanol
20	0.25	1.00
40	0.75	2.46
60	2.13	5.19
78	–	10.4
80	6.38	–
100	20	

The action on metals has also been described [51]: dry EDNA did not attack copper, brass, aluminium, mild steel, stainless steel, nickel, cadmium or zinc, whereas wet EDNA strongly attacked all the above metals with the exclusion of stainless steel.

EDNA is reactive owing to the presence of two primary *N*-nitro groups and according to Goodman [53] can readily form the imidazol ring:



(25)

EDNA is decomposed by hot dilute sulphuric acid (Vol. II, p. 20) and 20% NaOH [51].

Explosive Properties

EDNA is an exceptional, very strong, high explosive which is not very sensitive to impact but has a relatively low ignition temperature.

Thus initiation temperature is:

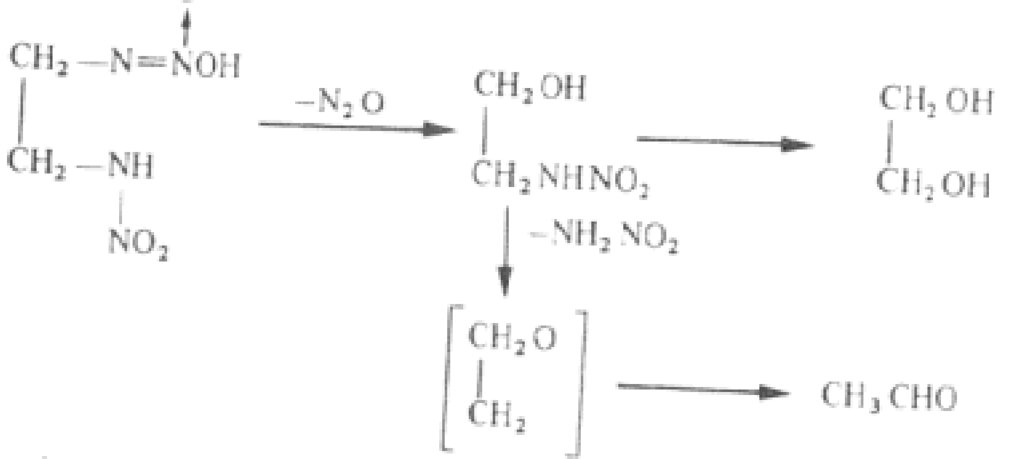
175°C after the induction of 5 sec. [54]
or 189°C after the induction of 5 sec.
216°C after the induction of 1 sec. [51]
265°C after the induction of 0.1 sec.
and 202°C on the basis of the differential thermal analysis [55].

The sensitivity to impact is similar to that of TNT.

Tomlinson [56] examined the decomposition of EDNA in water, dilute sulphuric acid and TNT at different temperatures: 60–120°C and 120°C respectively. EDNA is only sparingly soluble in molten TNT (*ca.* 5% solubility), but the rate of the decomposition much increased in the solution. EDNA in solution decomposed by a second order mechanism with the activation energy E = 20–35 kcal/mol. High acidity favours a low value of E.

In the solid state the decomposition follows a chain mechanism with E = 40–50 kcal/mol.

EDNA decomposes principally through the aci-form to yield glycol, acetaldehyde and nitrous oxide, probably according to the scheme (26):



(26)

Heat of combustion [57] was found to be – −2464.6 kcal/kg.

Heat of formation at C_v is −148 kcal/kg and at C_p −176 kcal/kg [58]. Heat of explosion 1276 kcal/kg and volume of gases 908 l/kg [51].

The explosive properties according to Ficheroulle [50] were: the velocity of detonation at the densities

1.15	6105 m/3
1.25	6800
1.35	7130

and lead block test 129% of picric acid, and Enclycopedia [51] gives for the velocity of detonation 7570 m/s for pressed, unconfined charge of 25.5 mm diameter.

Ficheroulle also described mixtures of EDNA with ammonium nitrate. The stoichiometric mixture of 42.8% EDNA and 57.2% NH_4NO_3 gave the velocity of detonation 6185 m/s at density 1.35 and lead block 113.5% of picric acid.

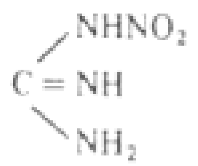
Specificiation of EDNA for US Army of 1943, amended 1947 [51] is as follows:

Moisture:	0.1% max.
Colour:	white or buff
M.P.:	174°C min.
Purity (by dissolving in aqueous NaOH):	99% min.
Insoluble matter (by dissolving in boiling water):	0.1% max.
Granulation:	US Standard Sieve No. 10 100% min US Standard Sieve No. 100 20% max.

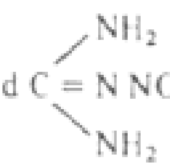
NITROGUANIDINE

Nitroguanidine became an important ingredient of treble base powder containing nitrocellulose–diglycoldinitrate–nitroguanidine (Vol. III, p. 664).

Nitroguanidine was subjected to some theoretical work, such as that dedicated to elucidating the structure:


$C(NHNO_2)(=NH)NH_2$

and


$C(NH_2)(=NNO_2)NH_2$

, i.e. nitramino and nitrimino forms respectively.

X-ray analysis carried out by Bryden and co-workers [59] favoured the nitrimino form. Also NMR analysis of Richards and York [60] showed that the solid nitroguanidine exists in the imino form. Owen [61] calculated the MO of several compounds containing nitrogen and among them nitroguanidine and came to the conclusion that the calculated imino form fits better to the experimental values, as shown in Table 59, with the diagram of bond lengths. The imino structure was also confirmed by Kumler and Sah [62] measurement and calculation of dipole moment.

It is currently accepted that in the solid state nitroguanidine is in the imino-form, but in a solution both forms are present and are in the equilibrium [63]. Kemula and his co-workers [64] examined the change of the ultraviolet absorption spectrum with the change of pH. The spectrum so far published revealed two maxima in aqueous or acid solution: 210 and 265 nm (Vol. II, p. 25, Fig. 4). Kemula *et al.* found 246 and 264 nm. The same frequencies are in the alkaline medium of pH = 2–12, but in the solution of 1.5 M NaOH the longer wave absorption disappeared and the shorter wave band gains intensity (Fig. 52, Vol. III).

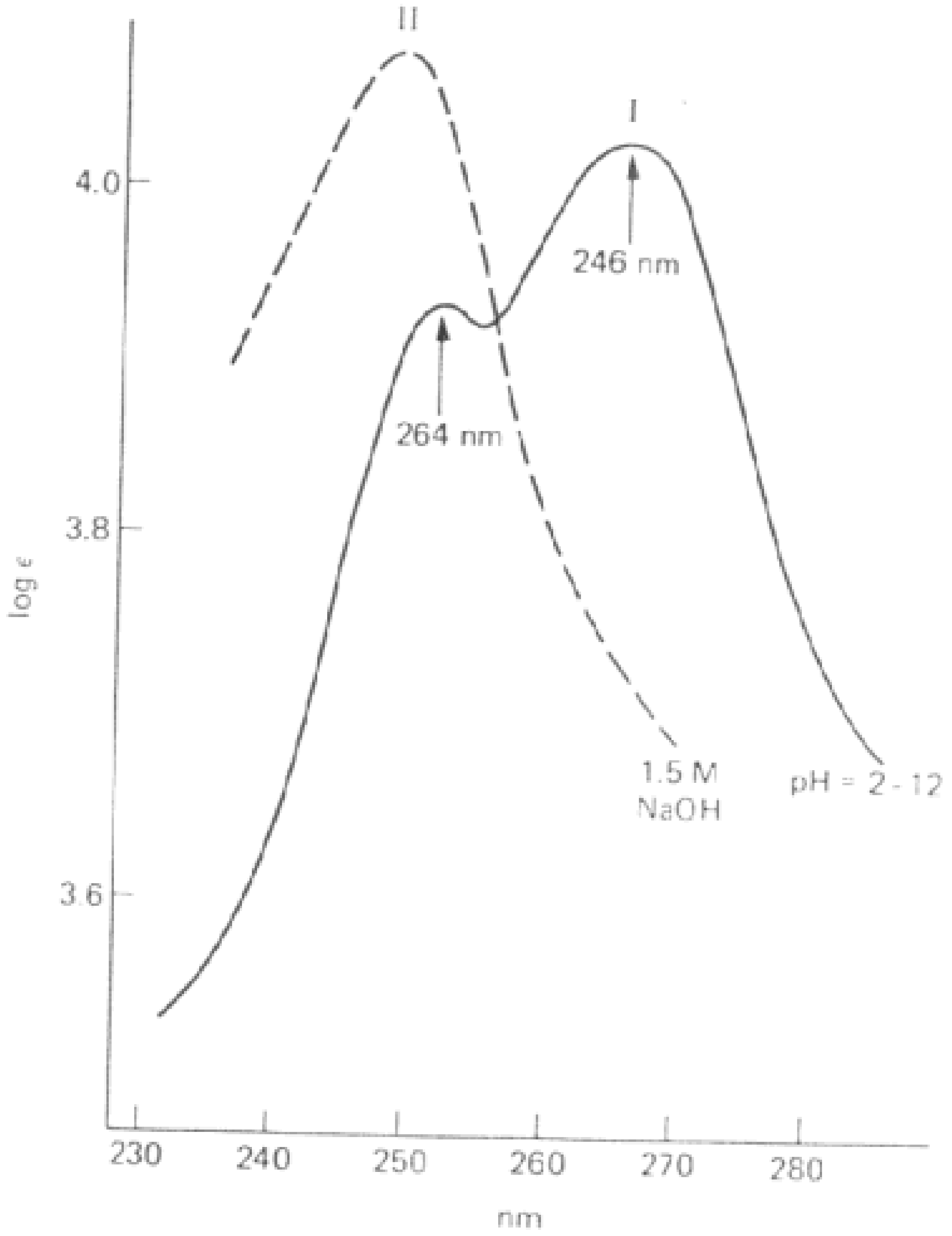
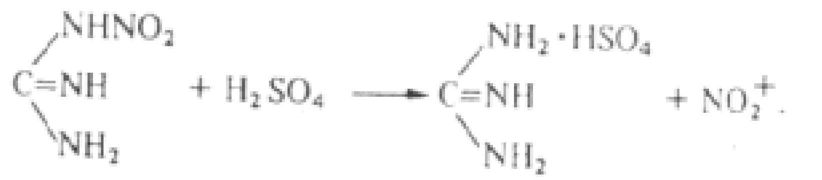


FIG. 52. Ultraviolet spectra of nitroguanidine (see Vol. III, p. 25, Fig. 4).

Reactions of Nitroguanidine

Very little can be added to the description of the chemical properties of nitroguanidine described in Vol. III, p. 25. Some of the reactions with nitroguanidine leading to dinitramine were given on p. 361.

Nitroguanidine in concentrated sulphuric acid can be used as a nitrating agent through the reaction:



$$C(NHNO_2)(=NH)NH_2 + H_2SO_4 \longrightarrow C(NH_2\cdot HSO_4)(=NH)NH_2 + NO_2^+ . \qquad (27)$$

Anthraquinone was nitrated to 1,5-dinitro-anthraquinone by T. Urbański and Zyłowski [65]. The temperature of nitration was 110–120°C for 1 hour and the yield 67%.

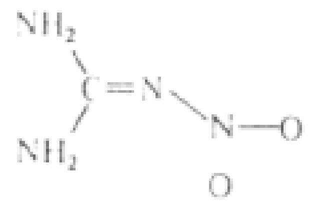
Specification according to Meyer [72]

The existing specifications describe nitroguanidine as a white, free flowing crystalline powder of two types. Both types should correspond to the following requirements:

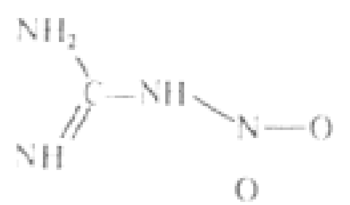
Ash content	0.30% max.
Acid content (as H_2SO_4)	0.06% max.
Volatile matters	0.25% max.
Sulphates	0.20% max.
pH	4.5–7.0
Type I	
grain size	4.3–6.0 μ
net content	min. 98%
Type II	
grain size	3.3 μ max.
net content	min. 99%.

TABLE 61. Nitroguanidine (bond length)

Bond	Nitrimino Form (I)		Nitramino Form (II)	
	Theor.	Exper.	Theor.	Exper.
C–NH_2	1.36	1.36	1.37	1.36
C–N	1.35	1.34	–	
C–NH	–	–	1.32	1.36
C–NH	–	–	1.38	1.34
N–N	1.29	1.35	1.31	1.35
N–O	1.23	1.22	1.22	1.22



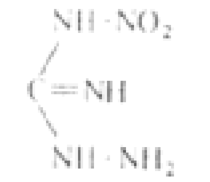
I



II

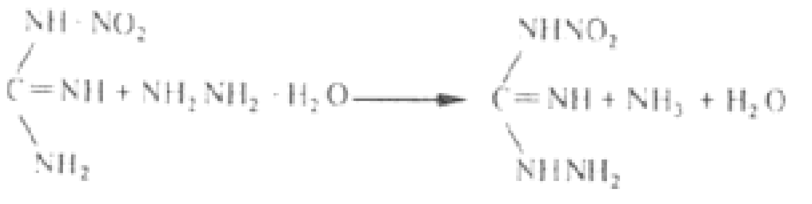
NITROAMINOGUANIDINE

Nitroaminoguanidine can be obtained by acting with hydrazine on nitroguanidine [168, 184]:



$$C(NH\cdot NO_2)(=NH)NH\cdot NH_2$$

m.p. 186–187°C



$$C(NH\cdot NO_2)(=NH)NH_2 + NH_2NH_2\cdot H_2O \longrightarrow C(NHNO_2)(=NH)NHNH_2 + NH_3 + H_2O \qquad (28)$$

By reacting with nitrous acid in acetic acid it yields 5-aminotetrazole [185]. Aminotetrazoles are related to initiating explosives obtained from aminoguanidine (Chapter XVII, and Vol. III, p. 206).

$$\text{Nitrimines}\ \left(\begin{matrix}R^1\\R^2\end{matrix}\!\!>C=N-NO_2\right)$$

The chemistry of nitroguanidine and the work of Büchi are related to the chemistry of nitrimines, that is, compounds containing $>C=N-NO_2$ group. The structure of this group was given by Scholl [75], but was subject to criticism and a few structures were suggested by Fusco and Trisoglio [76] and Freeman [77]. Freeman found the confirmation of the nitrimino structure by ultraviolet, infra red spectra and the transformation of the group into the primary amino group by reducing with potassium borohydride:

$$=N-NO_2 \xrightarrow{KBH_4} -NHNO_2$$

NITRODIETHANOLAMINE DINITRATE (DINA) (Vol. III, p. 36)

This interesting compound was investigated by French chemists who gave thermochemical properties: heat of combustion $-\Delta H_c = 577$ kcal/mol and heat of formation $-\Delta H_f = 70{,}5$ kcal/mol. [89].

Preparation

Desseigne [88] added some information to the method of G. F. Wright *et al.* (Vol. III, p. 36). Here are the main points of the process.

A nitrator was filled with 170 parts of acetic anhydride (99%) and 1.4 parts of hydrochloride of diethanolamine dissolved in 4 parts of acetic acid. Diethanolamine (52.5 parts) and 107 parts of nitric acid (97%) were added keeping the temperature at 10–15°C. After that mixing had been continued for 10–15 min. the product (DINA) began to precipitate. All was poured on ice (200 parts), filtered and washed with water followed by washing with hot 0.25% aqueous solution of sodium carbonate. At the end the solution should be neutralized with acetic acid. The product was finally purified by dissolving in acetone and precipitating with water containing a small amount (*ca.* 0.3%) of ammonia.

The yield was 108 parts, i.e. 90% of theoretical.
The m.p. of the product was 50.15°C.

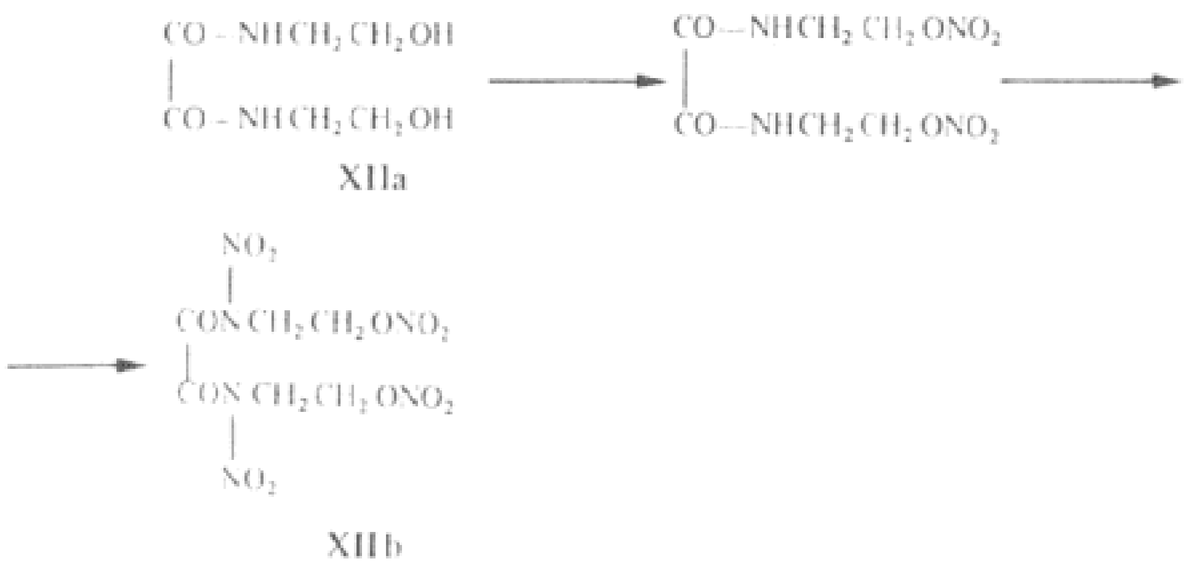
The rate of detonation is 7730 m/s at density 1.60 and 7580 m/s at 1.55. Lead block 146% of picric acid. It shows a lower stability at 100°C and higher sensitivity to impact than tetryl [90].

Glazkova [92] in her monograph described experiments of burning DINA and the influence of various additions. The addition of dichromates of cations (particularly of potassium dichromate) increases the rate of burning.

DINITRODI-(β-HYDROXYETHYL)-OXAMIDE DINITRATE (NENO)

(Vol. III, p. 37)

Desseigne [91] repeated experiments of nitration of the amide (XIIa) in two steps:

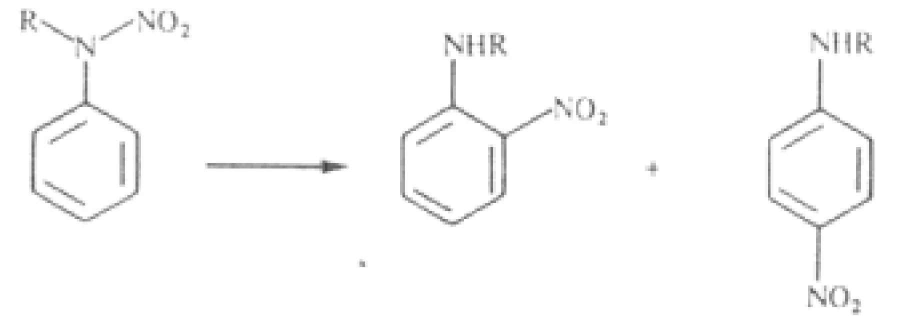


(29)

The nitration was difficult and required the use of nitric acid with 60% oleum at 25°C with an overall yield of 75%. Compound XIIb can dissolve nitrocellulose and could be used according to Desseigne in double base propellants.

AROMATIC NITRAMINES

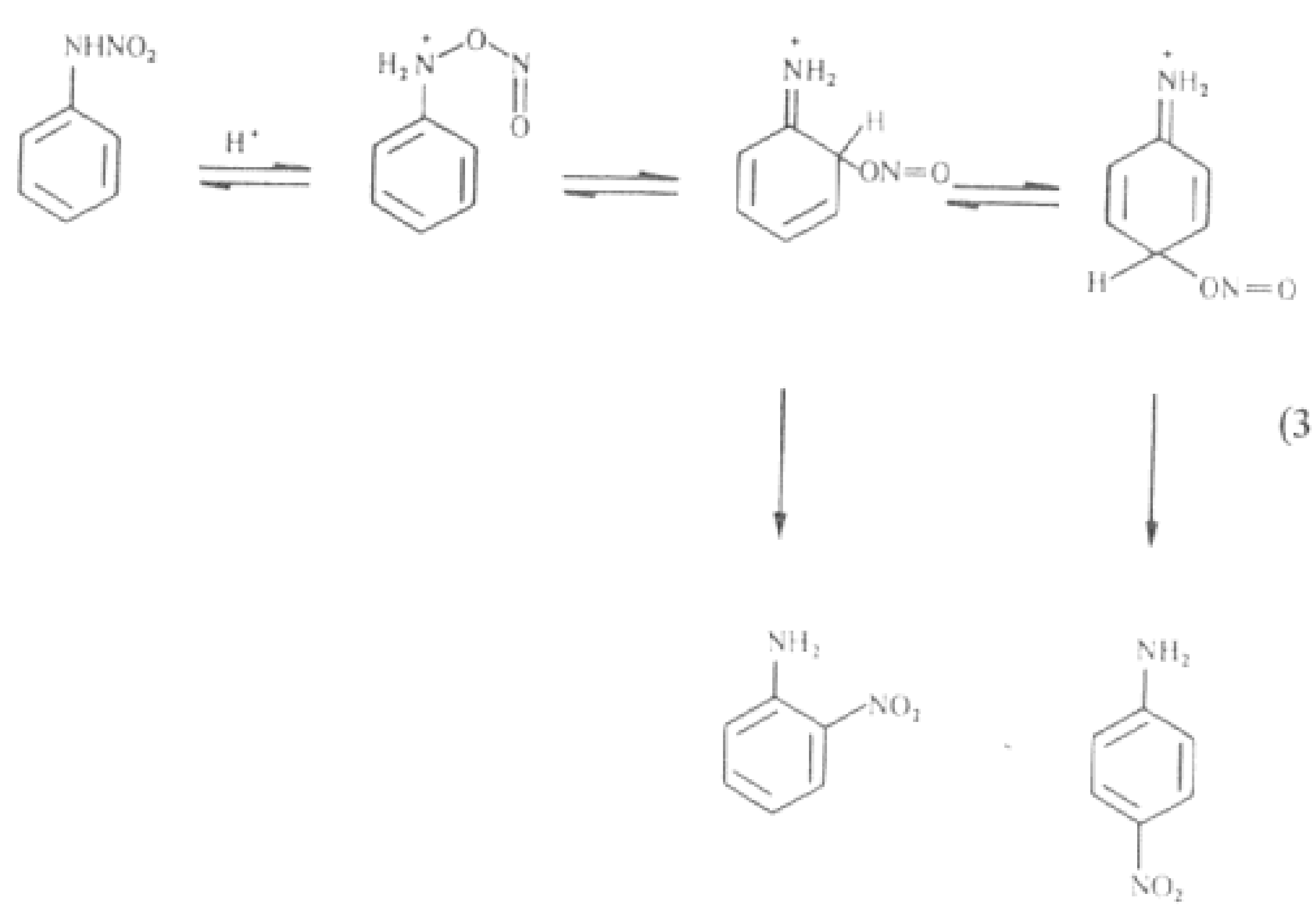
Aromatic nitramines can be subjected to 'Bamberger rearrangement' described for the first time by E. Bamberger in a number of papers since 1893 [78, 79]:



(30)

Bamberger advanced a hypothesis that the nitration of the aromatic ring of aromatic amines begins by *N*-nitration followed by a subsequent rearrangement. The hypothesis was examined by Holleman and co-workers [80] who concluded that ring nitration does not always proceed by way of an initial *N*-nitration. Also Orton with co-workers studied the mechanism of the reaction in a number of papers [81]. He concluded that the Bamberger rearrangement is an acid catalysed reaction.

Hughes and co-workers [82, 83] in a number of papers examined the mechanism of the reaction by using nitrogen isotopic [^{15}N] and [^{2}H] label. They came to the conclusion that the Bamberger rearrangement is an intramolecular mechanism. They rationalized it in terms of the formation of nitrites:



(31)

U.S. chemists [84] examined the action of 0.1 N hydrochloric acid on *N*-methyl-*N*-nitroaniline at 40°C and obtained:

ca. 52% *o*-nitro-*N*-methylaniline
31% *p*-nitro-*N*-methylaniline and
7% *N*-methylaniline.

Nitrous acid (*ca*. 13%) was also formed.

They also came to the conclusion that the rearrangement is an acid catalysed reaction.

TETRYL (Vol. III, p. 40)

In the course of the last few years the significance of tetryl has been considerably reduced. With the advent of Cyclonite (RDX) and PETN, tetryl is losing its significance and in the U.S.A. it was withdrawn from use. Also compounds similar to tetryl with *N*-methyl-*N*-nitro side group have aroused less interest lately.

Nevertheless a few published papers have appeared mainly referred to thermal decomposition of the substance. Former data (Vol. II, pp. 52–53) were confirmed in general, but completed by more detailed experiments. Thus Dubovitskii, Merzhanov and co-workers [85] examined the influence of the density of loading (m/v, where m = the mass of the substance, v = the volume) at 150°C. Some of their results are shown in Fig. 53. It can be seen that the density has little effect on the rate of decomposition. The gases evolved were composed of NO_2, NO and N_2. High (1) and low (3) density.

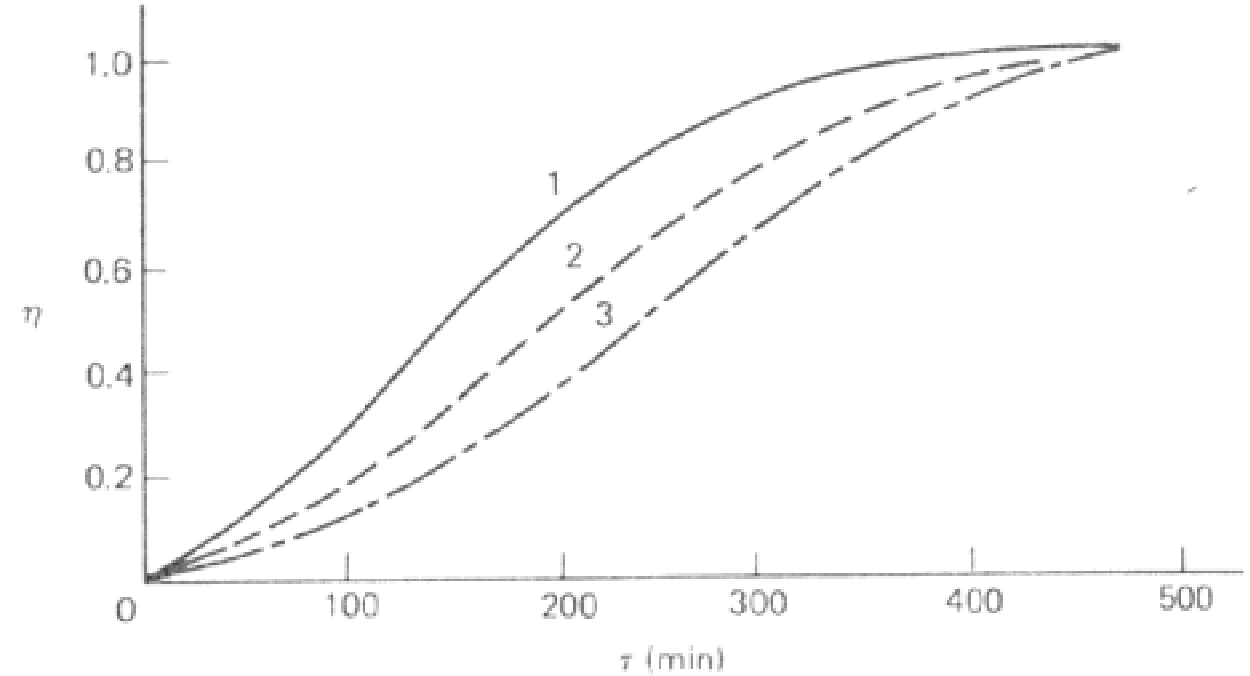


FIG. 53. Thermal decomposition of tetryl [85]. m/v in g/cm^3. 10^{-4}; 1–353.5, 2–49.4, 3–0 (removal of gases); η (degree of decomposition).

Hara, Kamei and Osada [86] obtained similar results. Among the gases from the decomposition of tetryl they also found methane. They carried out the experiments at temperatures from 150 to 175°C. By differential thermal analysis they found the endothermic (negative) peak at 131°C due to the melting of the substance and exothermic decomposition occurred at 160°C. They calculated the activation energy as being 35 kcal/mol. This is in agreement with formerly obtained results (Vol. III, p. 53).

Pre-heating of tetryl increases the rate of burning of the substance. This was already shown by Andreev (Vol. III, Fig. 6), by his later work [94] and substantiated by M. M. Jones and Jackson [87] and Japanese authors [86]. The latter authors found for example that preheating the sample to 180°C lowers its m.p. by 20°C and the decomposition temperature by 12°C. They also examined the samples of tetryl heated at 165°C for 3 hours: by liquid chromatography, by TLC, NMR and mass spectrography. They found that 2,4,6-trinitroanisol and picric acid are formed on the thermal decomposition of tetryl at 160–200°C.

Burning of tetryl is discussed in the monograph by Glazkova [92] and reference is given to the early work of Hinshelwood [93] who pointed out that thermal decomposition of tetryl produces picric acid which plays the part of a catalyst of the decomposition. The rate of burning of tetryl under pressure increases by addition of potassium bichromate, according to Glazkova [92].

Thermal decomposition of tetryl was reviewed by Dubovitskii and Korsunskii [4].

HETEROCYCLIC NITRAMINES (Vol. III, p. 77)

Cyclonite (Hexogen, RDX) (Vol. III, p. 77)

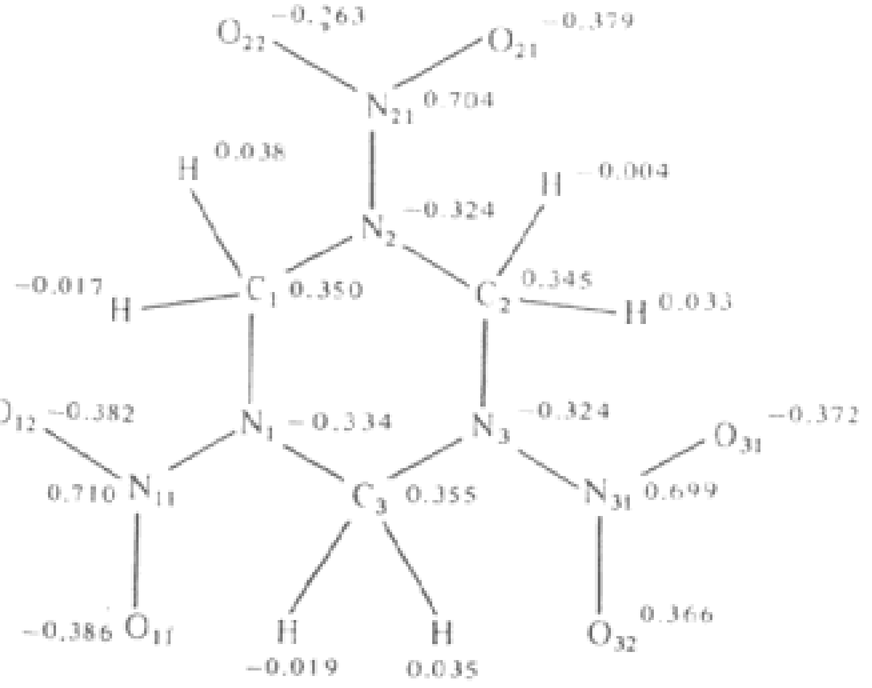
Cyclonite (RDX in Anglo-Saxon literature, that is, Research Department Explosive) 1,3,5-trinitro-1,3,5-triazacyclohexane is at present one of the most important explosives. Over the last two decades extensive literature has been dedicated mainly to its analysis and application.

Structure

The structure of RDX has been characterized by X-ray analysis [95]. Dipole moments measurements to establish stereochemistry of nitramines have been extensively used by a few authors: G. F. Wright [96], Calderbank and Pierens [97].

The latter authors [97] found that the chair calculation 22.27 D corresponded best to experimental value 19.1 D (boat conformation and twist boat conformations gave calculations 5.81 D and 7.04 D respectively). Calderbank and Pierens also measured and calculated the Kerr effect (electric birefringence) and found the calculated value for chair conformation (−2868) fitted best to the experimental figure (−2102). The boat and twist boat conformations gave figures distant from the experiments (+172 and +164 respectively). The conclusion of these authors was that the preferred conformation of cyclonite corresponds in 70% at least of chair.

Delpuech and Cherville [98] calculated electric charges in cyclonite by CNDO method [99]. The results are given in Fig. 54.



Cyclonite (Hexogen, RDX)

FIG. 54. Electron density of cyclonite [98a].

Spectroscopy of Cyclonite

Electronic spectrum of cyclonite has been examined by a number of authors [7, 100, 101] who found a maximum at 202 nm and a shoulder at 236 nm. Later examination of spectra [102] confirmed these results for cyclonite dissolved in ethanol. In methanol they were slightly different: 204 and 234 nm.

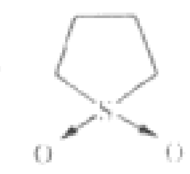
Infra-red spectroscopy was given in the monograph of Bellamy [103].

Chemical Properties

Contrary to aromatic nitro compounds cyclonite does not readily give adducts. No charge–transfer complexes are formed with amines. Selig [104] established the existence of an adduct of cyclonite with hexamethylphosphoric triamide (HMPT). Another complex with tetrahydrothiophene-1,1-dioxide (sulfolane) was described by French authors [105, 106]. Recently Selig [107] reported that a number of heterocyclics with nitrogen or sulphur could form the adducts. Relatively stable equimolar complexes were obtained with:

$O \leftarrow P[N(CH_3)_2]_3$

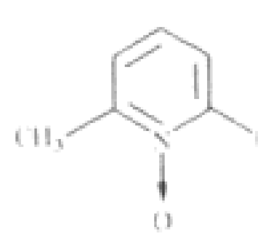
XIII



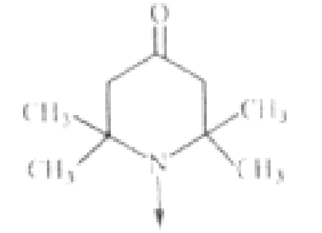
XIV

XV

XVI



XVII



XVIII

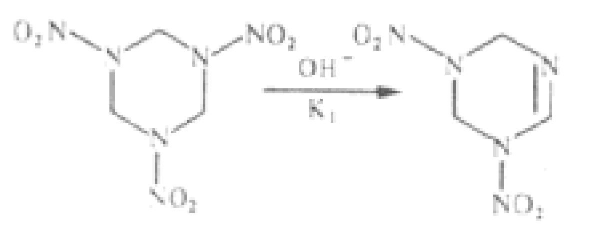
XIII – HMPT, XIV – Sulpholane, XV – Tetrahydrothiophene-1-oxide, XVI – 1,4-Butane sultone, XVII – 2,6-Litidine-*N*-oxide, XVIII – 2,2,6,6-Tetramethyl-4-piperidone-1-oxyd.

Compounds XIV and XVIII are 'selective' to hexogene: they do not form adducts with octogene, whereas all others form adducts with both: hexogene and octogene.

Cyclonite is decomposed in concentrated sulphuric acid and the decomposition yielded most likely nitronium ion (Vol. III, p. 81). This is evidenced by the fact that a solution of cyclonite in sulphuric acid can nitrate aromatic compounds.

Thus Holstead and Lamberton [108] obtained *p*-nitroacetanilide with a 45% yield when acting on acetanilide with a solution of cyclonite in 95% sulphuric acid. T. Urbański and Zyłowski [65] nitrated anthraquinone with the same solution at room temperature for 24 hours. The yield of 1,5-dinitroanthraquinone was 36%.

Croce and Okamoto [109] described a cationic micellar catalysis (Chapter IV) of aqueous alkaline hydrolysis of cyclonite (and octogene). Denitration occurred in the presence of ethylhexadecyldimethylammonium bromide. Liquid chromatography was used as the analytical method (32):



(32)

1,3,5-Triaza-3,5-dinitrocyclohexene-1-ene resulted.

Thermal Decomposition

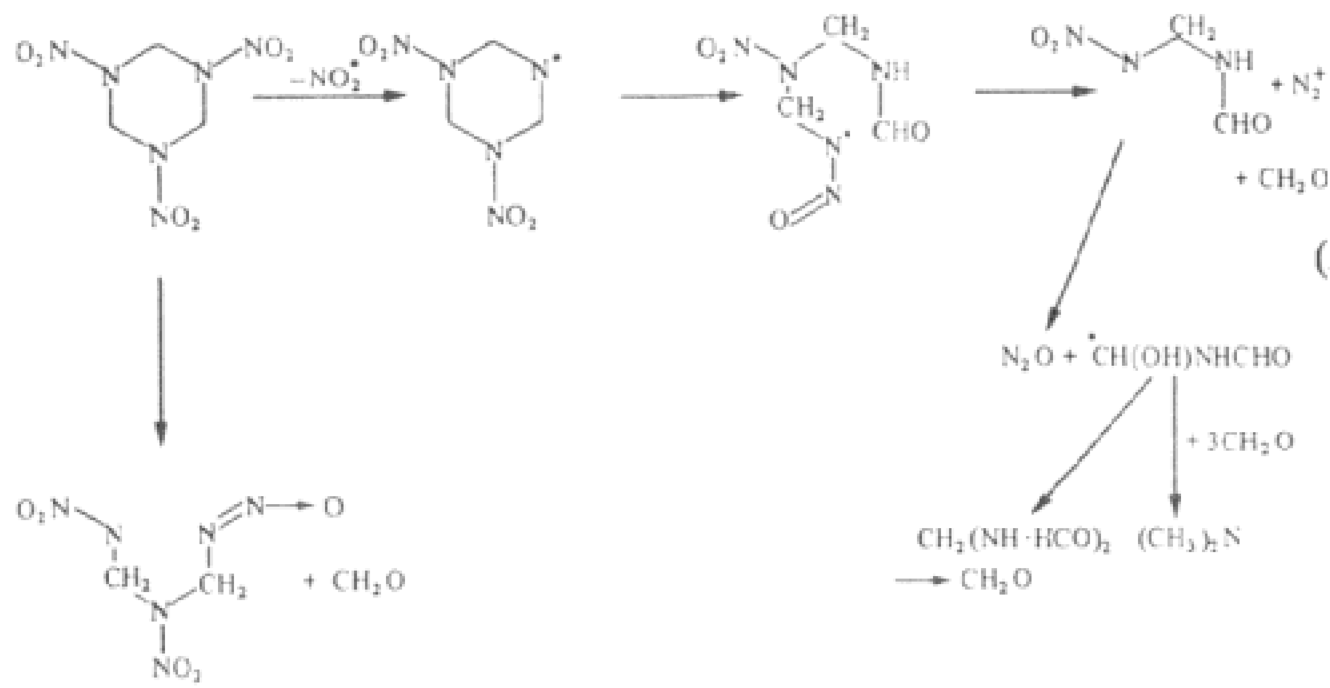
Thermal decomposition of cyclonite was investigated by numerous authors (also Vol. III, p. 83): [110–115]. Maksimov [111] described several experiments of decomposition of cyclonite and octogene as solid substances and in solution. The energy of activation was calculated as $E = 52.0$ kcal/mol. $\log_{10} B = 19.1$.

Figure 55 shows the decomposition of cyclonite in solution in *m*-dinitrobenzene at 160–200°C. A concentration of 4% was used with the exception of the sample examined at 190°C where the concentration was 13%. The energy of activation was $E = 39.7$ kcal/mol, $\log_{10} B = 14.3$. One of the conclusions of the authors was that cyclonite decomposes faster in solution than as a solid. This is in an agreement with existing views that explosives in a liquid form decompose faster than solid due to the transition of the solid to a higher energy liquid state (experiments by T. Urbański *et al.*, Vol. II, pp. 181–183). According to Maksimov the decomposition of hexogene at 180°C in solution is 16 times faster than in the solid state.

Cosgrave and Owen [115] and Debenham and Owen [170] studied the decomposition of cyclonite at 195°C and 173–184°C respectively. They came to the conclusion that the initial decomposition takes place in the vapour phase and is followed by a more rapid decomposition in the liquid phase (e.g. a solution of cyclonite in 1,3,5-trinitrobenzene [170]).

Major products were: hydroxymethyl formamide and its polymers. The following is a list of products of the decomposition: N_2, N_2O, NO, CO_2, CO, CH_2O, H_2, H_2O, HCN, HCOOH, NH_3, NO_3^-, NO_2^- and the polymer mentioned above.

They gave a simplified presentation of the thermal decomposition of hexogene (33):



(33)

Other work on thermal decomposition of cyclonite was done by Wilby [171], Rosen and Dacons [172], Rauch and Fanelli [173] and Batten [174].

Recently Kishore and Laye [116] examined thermal decomposition of cyclonite by differential scanning calorimetry. The curves of the decomposition are of an 'S' shape (similar to those of tetryl – Fig. 53). Isothermal curves are similar to Figs 55 and 56. The author calculated the *E* value of decomposition of cyclonite in an open vessel as being 41 ± 2 kcal/mol. They also reported the values of *E* obtained by other authors. In addition to those given in Vol. III, p. 83 (by Robertson), they are those of:

Rogers and Morris [117] 67.5 kcal/mol
Adams [118] 45.5 kcal/mol (203.5–261°C)
Batten and Murdie [119] 67.0 kcal/mol (179–200°C)
Hall [120] 45.2 kcal/mol (210–261°C).

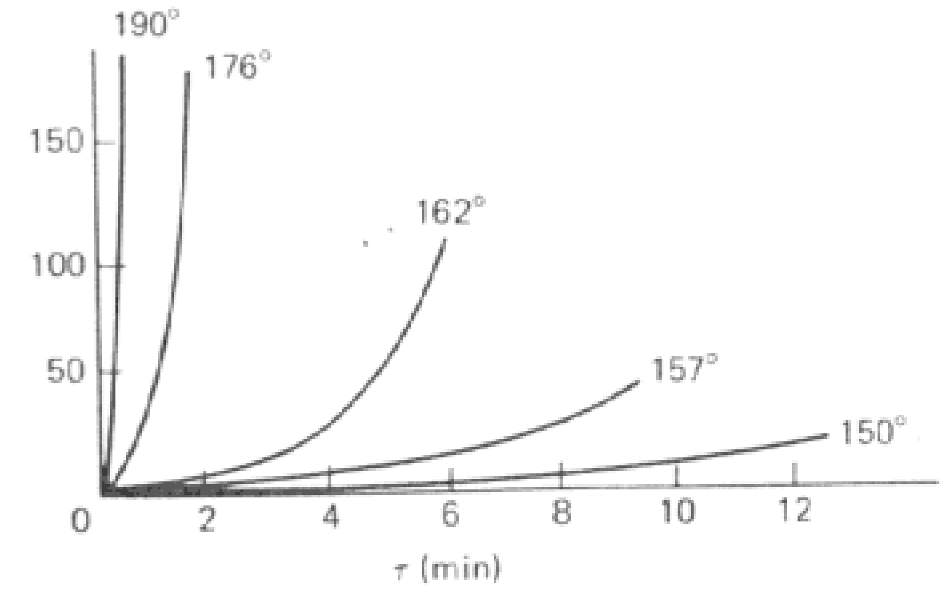


FIG. 55. Thermal decomposition of solid cyclonite [111].

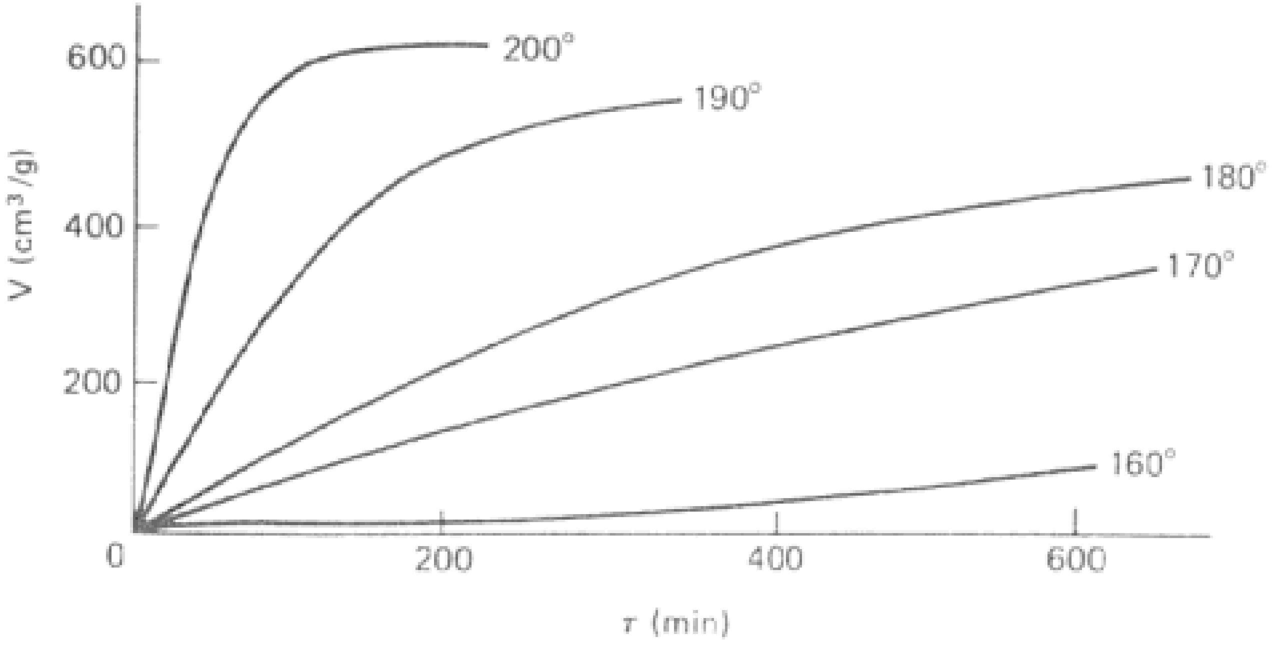


FIG. 56. Thermal decomposition of cyclonite in solution [111].

Kishore concluded that the figure closest to 45 kcal/mol was the most reliable. The order of the reaction is 0.6 according to the same author. See also the review article of Dubovitskii and Korsunskii [4].

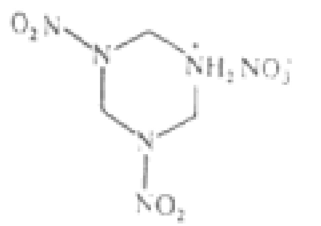
Preparation of Cyclonite (Vol. III, p. 87)

Nitration of hexamine. Very little can be added to the mechanism of the reactions leading to cyclonite, as given in Vol. III.

With regard to the nitration of hexamine with nitric acid Singh [121] brought a small change to the charge distribution in compound (VIb – Vol. III, p. 89), and Lamberton *et al.* [122] added some more information on compound XIX (the same as Ia, Vol. III, p. 91).

Bell and Dunstan [123] subjected reactions of hexamethylenetetramine with nitric acid, at various temperatures, to a detailed examination. Addition of water to nitrolysis solution obtained by the action of nitric acid (98%) on hexamine at –30°C yielded P.C.X., that is 3,5-dinitro-3,5-diaza-1-azoniacyclohexane or 3,5-dinitro-3,5-diazapiperidinium nitrate (XIX) (Vol. III, p. 91, Ia). The nitrolysis mixture kept at 0°C for 2 hours yielded 83% RDX and traces of the linear compound: derivative of tetra-azanonane (IX of p. 89, 91, Vol. III).

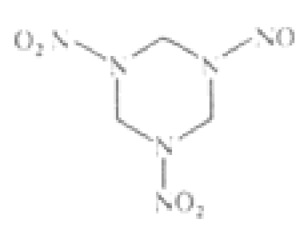
Acetic anhydride reacted with hexamine by nitrolysis to yield RDX, and linear derivatives of 2,4,6-trinitro-2,4,6-triazaheptane: diacetoxy compound (Vol. III, p. 91, XV and dinitroxy (XX):



XIX

$$O_2NOCH_2-\overset{\overset{\displaystyle NO_2}{|}}{N}-CH_2-\overset{\overset{\displaystyle NO_2}{|}}{N}-CH_2-\overset{\overset{\displaystyle NO_2}{|}}{N}-CH_2ONO_2$$

XX



XXI

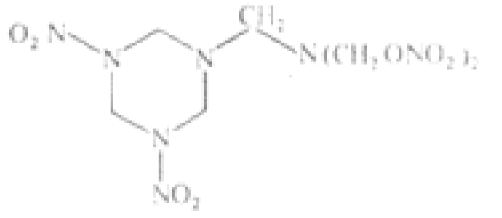
A small quantity of linear dinitroxytetra-azanonan (IX, Vol. III, pp. 89, 91) was also formed.

By adding aqueous sodium nitrite to the nitrolysis mixture at –30°C, 75% yield of 1,3-dinitro-5-nitroso-1,3,5-triazacyclohexane (XXI) was obtained.

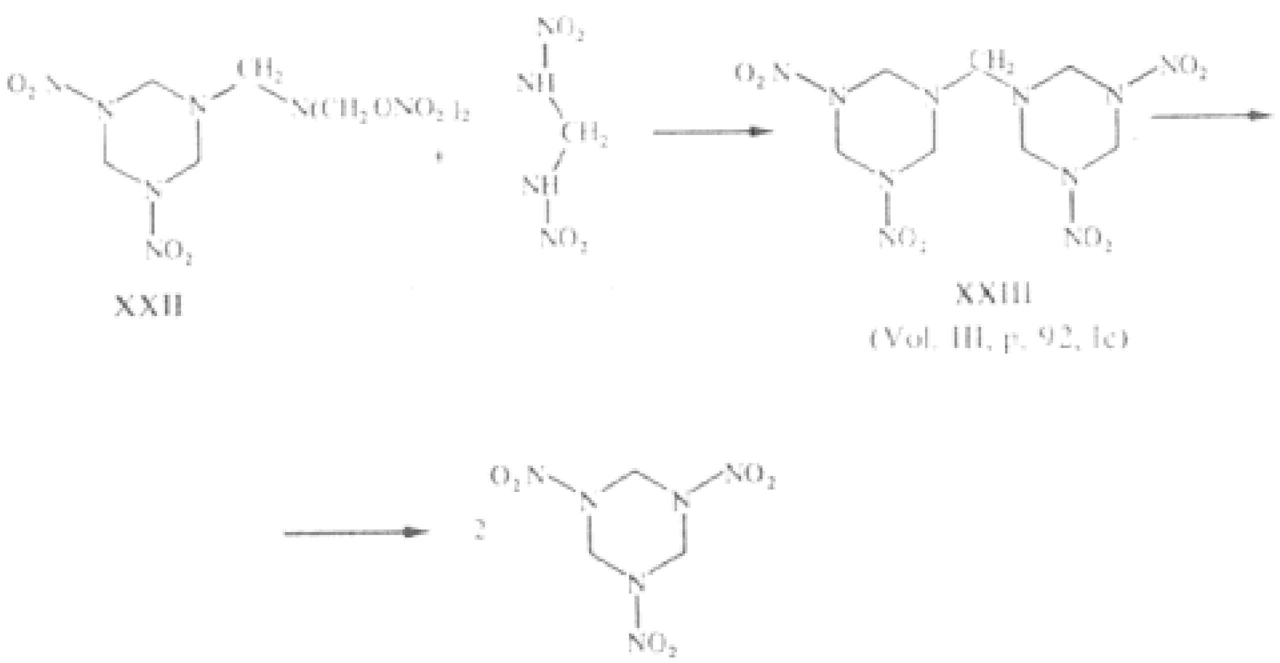
An interesting reaction was found when cold (–30°C) nitrolysis mixture was treated with methylenedinitramine $CH_2(ONO_2)_2$ and after that kept at 30°C for 15 min. The yield of RDX was almost doubled – from 82 to 145% calculated on the basis of hexamine ⟶ one mole of RDX.

Larger ring nitramines – homologues of RDX – were obtained by adding dinitramines such as ethylene and trimethylenedinitramine. Homologues of RDX with cycloheptane and cyclooctane ring resulted.

These experiments suggested that bis(nitroxymethyl)aminomethyl intermediate (XIII, Vol. III, p. 91) can be a probable precursor which upon nitrating to dinitrate and reacting with methylenedinitramine eventually yielded RDX according to scheme (34).



XXII (Vol. III, p. 91, XIII)



XXII

XXIII
(Vol. III, p. 92, Ic)

(34)

Preparation of Cyclonite from Hexamine Dinitrate Acetic Anhydride

The methods by W. E. Bachmann (in the U.S.A.) and Köffler (in Germany) – Vol. III, p. 111 have now received particular attention in view of the fact that the route with acetic anhydride can lead to the formation of Octogene (HMX).

Reed [124] described the reaction of hexamine, nitric acid, trifluoroacetic anhydride in the presence of liquid SO_2 which is a very good solvent for hexamine. The reaction yielded (85%) 1-trifluoroacetyl-3,5-dinitro-1,3,5-triazacyclohexane, m.p. 131–132°C.

Explosive Properties of Cyclonite (Vol. III, p. 84)

Little can be added to the information given in Vol. III as regards explosive properties of Cyclonite. Interesting information was recently given by Institut Franco-Allemand de Recherches de Saint-Louis, France [186]. The rate of detonation of single crystals of cyclonite was found to be different along different crystal axis:

(001)	8700 m/s
(110)	8587 m/s
(111)	8437 m/s

T. Urbański and Galas [187, 188] examined the influence of non-explosive liquids on the velocity of detonation of cyclonite. The results with two liquids: water and glycerol are collected in Table 62. The shape of the curve: velocity of detonation against the proportion of liquids is much the same as for PETN and liquids as depicted in Fig. 42.

TABLE 62. Detonation of cyclonite with water and glycerol [187, 188] in steel tubes 20/26 mm diameter, detonator No. 8 with 10 g PETN

Proportion of liquid %	Density Total ρ	Density Real ρr	Rate of detonation m/s Observed V_0	Rate of detonation m/s at density ρr V_r	Difference V_0-V_r
Water					
0	1.45	1.45	7705	7705	0
10	1.45	1.31	7235	7280	-45
20	1.45	1.16	7775	6820	935
30	1.45	1.02	7070	6365	705
Glycerol					
10	1.40	1.26	7360	7125	235
20	1.40	1.12	7505	6685	820
30	1.40	0.98	7875	5240	1635
35	1.40	0.91	7740	6015	1725
40	1.40	0.84	7555	5790	1765

Apin and Velina [189] also examined the velocity of detonation and the pressure of detonation of explosives with water. Apin, Pepekin *et al.* [190] subjected the cyclonite–water system to a detailed thermochemical examination.

They found a straight line increase of the heat of detonation against water content from 0 to 24% of water: 1380 cal/g of dry substance and 1187 cal/g of a mixture of 76% cyclonite and 24% water. This gives a calculated value for the dry substance 1565 cal/g. It corresponds also to the maximum of the increase of the velocity of the detonation V_0-V_r (Table 62) [187, 188]. Further addition of water (above 24%) does not increase the heat of detonation [190] and the increase of the velocity of detonation V_0-V_r drops [187, 188].

Apin, Pepekin *et al.* [190] explain the phenomenon of the increase in the rate of detonation by adding water in the following way. The liquid plays the part of a confinement which prevents the dispersion of the products of detonation and prolongs the time necessary to complete the reaction in a similar way to the action of a confinement. This is certainly true but according to T. Urbański [187–188] the importance of the covolume [191] should also be taken into consideration. Another factor which should be considered is the increase of entropy (S) and Gibbs free energy (G = H–TS) which is higher in a mixture than in the individual ingredients and T. Urbański [192] advanced an hypothesis that the high entropy and free energy play an important part in properties of explosives such as their rate of detonation and sensitivity to impact. According to T. Urbański the high entropy and free energy of mixtures is one of the factors which increases the rate of detonation of a solid explosive by adding a non-explosive liquid.

Manufacture of Cyclonite (RDX) according to Mario Biazzi S.A. (Vevey) [125]

This process consists of continuous nitration of hexamine with nitric acid (98.5%), continuous 'decomposition' of the secondary products formed during nitration and continuous filtration of RDX from its spent acid.

The hexamine, dried and sifted is fed into the first nitrator with a constant feeding rate. The nitric acid is fed from a constant level overhead tank. The feeding rate is regulated by the remote control of a pneumatic valve. The contents of the first nitrator continuously overflow into the second and then to the third (last) nitrator.

From the last nitrator all overflows to the decomposing vessels. Decomposition is initiated by filling the first decomposer with some of the nitric acid (50%) obtained from the absorption of the nitrous gases evolved during decomposition. The RDX crystallizes out and is continuously separated by vacuum filters. The RDX cake is flushed on the filter with cold water. The dilute nitric acid goes through the filter into an intermediate vacuum tank equipped with a strainer retaining all the RDX which may escape from the filter. From the tank the acid is pumped into storage. The acid washing water is collected in a separate tank from where it is evacuated by pumping.

The RDX cake washed from the filter cloth is continuously evacuated into a slurrying tank where it is mixed with water and transferred by means of water injector to another building. Reactors are cooled with Freon 12.

During nitration gases are evolved. They are drawn from the equipment vessels by means of a fan to a tower where they are met with water in a countercurrent.

The acid RDX/water slurry flows into a continuous vacuum filter, the transport water is drawn through the filter into an intermediate tank with a strainer to retain traces of RDX. From the filter RDX falls into a suspension funnel with aqueous sodium bicarbonate. The suspension flows into the stabilization battery made of a series of steam injectors separated by cooling elements. The injector stabilization battery removes the occluded acid. The injection of steam reduces the size of crystals and removes the acid.

From the stabilization battery, the RDX/water mixture flows to the phlegmatizer or to a continuous filter. If RDX is phlegmatized, this is done in three jacketed and stirred vessels where crystals are coated with wax. The molten wax is added to the first phlegmatizer and is hardened by cooling in the second and third vessels and finally filtered. Moisture content (both unphlegmatized and phlegmatized) – 10%.

Specification for Hexamine 'Nitration Grade'
Moisture max. 0.2%
Crystal size: over 500 μ max. 30%
300–500 μ 70–85%
less than 200 μ max. 10%
Dust, sulphates, chlorides, heavy metals – absent
Water insoluble max. 0.10%
Ash max. 0.03%

Consumption for 1000 kg RDX
Hexamine 866 kg
Nitric Acid (calculated as 100%) 8530 kg
Process water 21000 kg

Phlegmatizing agent – according to requirements (see below)
Neutralizing agent ($NaHCO_3$) 3–5 kg.

Steam 4500 kg
Electric energy 1440 kWh
Compressed air 100 Nm^3

Specification for RDX is according to U.S. Standards for type A product.

Specification for Cyclonite (Hexogen)

According to the Encyclopedia of Fedoroff and Sheffield [126] the specifications for Cyclonite in Germany and in the U.S.A. are as follows.

Germany (Vol. III, p. 105). Hexogen should be crystalline, dry, colourless and screened. Hexogen intended for use in detonators and percussion caps should be purified by crystallization (e.g. from nitrobenzene). Hexogen intended for phlegmatization and used in boosters should contain water.

Melting point: (a) for W-, K- and SH-Salz (Vol. III, p. 104) m.p. should be above 200°C, (b) for E-Salz above 190°C.

Granulation. For boosters hexogen should pass through a 0.75 mm sieve (DIN 8), for ignition charges through a 0.60 mm sieve (DIN 10).

Loss of Weight: should not exceed 0.1% of 10 g sample for 5 hr at 100°C. Sulphate and Chlorine should be absent.

pH should be below 7.5. Formaldehyde – only trace. Acidity: 10 g sample should not use N/20 NaOH more than 3.0 cm^3 for E-Salz, 2.0 cm^3 for SH- and K-Salz, 0.3 cm^3 for recrystallized W- and K-Salz and any other kind of Hexogen for detonators and percussion caps.

Aceton insoluble – max. 0.1%. 120°C KI test – no discoloration after 10 min and only slight discoloration after 20 min.

U.S.A. Specification of 1963 covers two types of RDX and light classes based on uses and granulation.

Type A – made by the nitric acid method.
Type B – made by the acetic anhydride process.

Properties:	Type A	Type B
m.p.	200°C	190°C
Aceton insoluble max.	0.05	0.05
Inorganic insoluble max.	0.03	0.03
Particles retained on US Std. Sieve No. 60 max.	5	5 particles
Acidity max.	0.05% as HNO_3	max. 0.02% as CH_3COOH.

For the use of various classes of the fineness – see Encyclopedia [126].

Disposal of Waste Cyclonite [126]

A five per cent solution of NaOH should be brought to boiling point by injecting steam. Cyclonite should be added in small portions. After adding all the cyclonite boiling should be continued to be discharged into a sump.

Toxic Properties of Cyclonite (Vol. III, p. 86)

More information was collected on toxicity of Cyclonite. Experiments with animals confirmed earlier findings of convulsions caused by Cyclonite. The important observations on humans were: the same effects were caused by inhaling the dust of Cyclonite and one fatal accident has been recorded [195].

EXPLOSIVES WITH CYCLONITE AS A MAIN COMPONENT

The *Encyclopedia of Explosives* [169] classifies the explosives with cyclonite into three groups: A, B and C.

Group A consists of cyclonite desensitized with waxes, this was originally used during World War II. In Great Britain cyclonite was desensitized with 9% beeswax. In Germany Montan was used (Vol. III, pp. 105, 113) in quantity 5–10%. In the U.S. synthetic waxes are used: compositions A3 and A4 are composed of 91% RDX/9% wax and 97% RDX/3% wax respectively. The composition A3 was made by heating a water slurry of RDX to 100°C and adding the wax with a wetting agent. After the wax melted, all was cooled, filtered and dried at 75°C. Composition A5 contained 1.0–1.5 stearic acid (Type I) or 1.6% stearic acid and 0.4% graphite (Type II).

Aluminized composition A of 92% RDX and 8% aluminium was originally intended for an armour piercing shell, but was found to be too sensitive to shock.

Group B are castable mixtures of RDX, TNT and some of them were known as Cyclitols. Various proportions of RDX and TNT were used, for example in Germany during World War II: Cyclitols 50/50, 53/47 for bombs and demolition charges, cyclitol 60/40 for some shells, cyclitol 20/80 containing 20% cyclonite, 80% TNT and the addition of 1% Montan wax.

The U.S.A. used mixture cyclonite/TNT in proportion 60/40 with 1% of synthetic wax added (composition B) or without wax (composition B-2). Other compositions of cyclonite/TNT were: 75/25, 70/30 and 65/35. The rates of detonation varied from 7840 m/s (composition B) to 8060 m/s (composition 70/30), the densities were: 1.68–1.71.

Group C are plastic explosives (Plastic explosives in Great Britain, Explosifs plastiques in France, Plastit in Germany).

U.S. Composition C contained after several modifications, such as Composition C-3: cyclonite 77%, DNT 10%, MNT 5%, TNT 4%, Tetryl 3% and Nitrocellulose 1%. The last five ingredients served as a plasticizer. It gave lead block test 117% of TNT. It could withstand being plastic between −29° and +77°C.

Composition C-4 developed by Ottoson and Lerner (according to [169]) contains 91% cyclonite and 9% of the plasticizer composed of 5.3% di-(2-ethylhexyl) sebacate, 2.1% polyisobutylene and 1.6% motor oil. It remains plastic between −57° +77°C.

A considerable number of explosives existed in different countries during World War II. Most of them contained Cyclonite, TNT and aluminium with desensitizing waxes. Their compositions are given in the Encyclopedia [175]. An interesting substitute for TNT in Germany was a castable explosive composed of 50% methylamine nitrate, 35% sodium nitrate, 15% Cyclonite. A German Full-pulver Nr 86 consisted of ethylenediamine dinitrate 46%, RDX 18% and wax 36%. German plastic explosives contained liquid or semi-liquid nitroaromatics with nitrocellulose.

OCTOGEN (HMX) (Vol. III, p. 117)

There is a growing interest in Octogen (HMX in Anglo-Saxon literature, High-Melting-Explosive), 1,3,5,7-tetranitro-1,3,5,7-tetrazacyclo-octane. This is due to remarkable explosive properties manifested by a very high velocity of detonation – over 9000 m/s (see explosive properties, p. 390). Also in some countries it is regarded as a heat resistant explosive because of its high melting point – 276–280°C d (Chapter VII).

The fact that a monograph has recently appeared [5], indicates the great interest being shown in Octogen.

Structure and Physical Properties

Octogen exists in four polymorphic modifications: I–IV or α, β, γ, δ which are most likely conformational modifications. Each of the four can be obtained by crystallization from a different solvent keeping a different rate of cooling of the solution.

TABLE 63. (see also Table 21, Vol. III, p. 118)
Some properties of octogen modifications*

	β	α	γ	δ
Region of stability	room temperature to 115°C	115–156°C	156°C	156-m.p.
Melting points (on rapid heating)	246–247°C	256–257°C	278–280°C	280–281.5°C
Molar refraction				
R calculated 58.0	56.1	55.7	55.4	55.9
Sensitiveness to impact				
mass in kg/height	5/15	1/20	1/20	1/10
energy of impact kg/cm^2	0.75	0.2	2.2	0.1

* Compiled from [5].

Here is the description according to Fedoroff and Sheffield [127]:

The common modification, stable at room temperature β-HMX is obtained by very slow cooling of HMX dissolved in acetic acid, acetone, cyclohexanone, acelonitrile, nitric acid or nitromethane. The crystals are monoclinic.

α-HMX can be formed from the same solution as above under condition of rapid cooling. The crystals are orthorhombic.

γ-HMX are also formed from the same solution but under a very rapid cooling. The crystals are monoclinic.

δ-HMX are formed from solvents in which the substance is only slightly soluble, such as acetic acid in small amounts and by rapid cooling by pouring over ice. Selig [128] obtained δ modification by crystallizing β from *N,N*-dimethyl-*p*-toluidine. The crystals belong to hexagonal system.

As regards to crystal shape and more information on crystallographic systems – see [5].

The change of modifications at different temperatures and their relative stability is given in Fig. 57 based on the literature [129, 130].

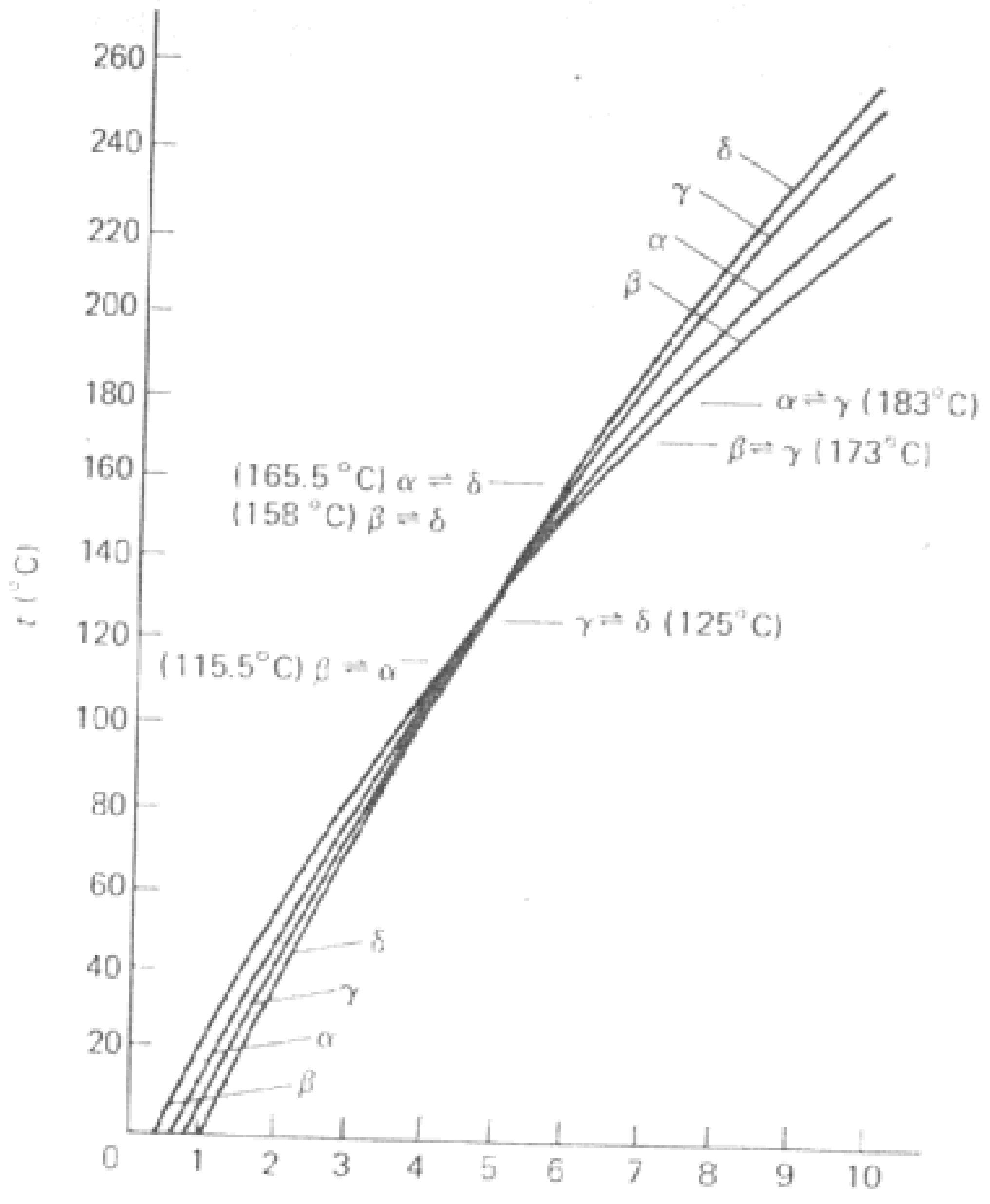


FIG. 57. Transition of octogen modifications [128, 129].

On the abscissae is given a relative value of free energy. The most stable modifications of octogene are above the point of crossing the curves.

X-ray and ESR analysis of β-octogen gave the structure presented in Fig. 58 according to Cady, Larsen and Cromer [131].

They found that the nitro groups in octogen are in both equatorial and axial positions. The presence of axial groups was explained by Stals [133] as being due to mutual electrostatic actions of nitramino groups. The conformation of α, β and γ-octogen based on dipole moments measurement was given by G. F. Wright [96] and depicted in Fig. 59.

Charge distribution in β-octogen [98a] is presented in Fig. 60.

According to data given in the monograph by Orlova *et al.* [5] the following were enthalpies – ΔH of the change of modifications:

	temperatures t°C	– ΔH cal/g
α → δ	193–201	5.97 ± 0.18
β → δ	167–183	7.91 ± 0.11
γ → δ	175–182	2.25 ± 0.08

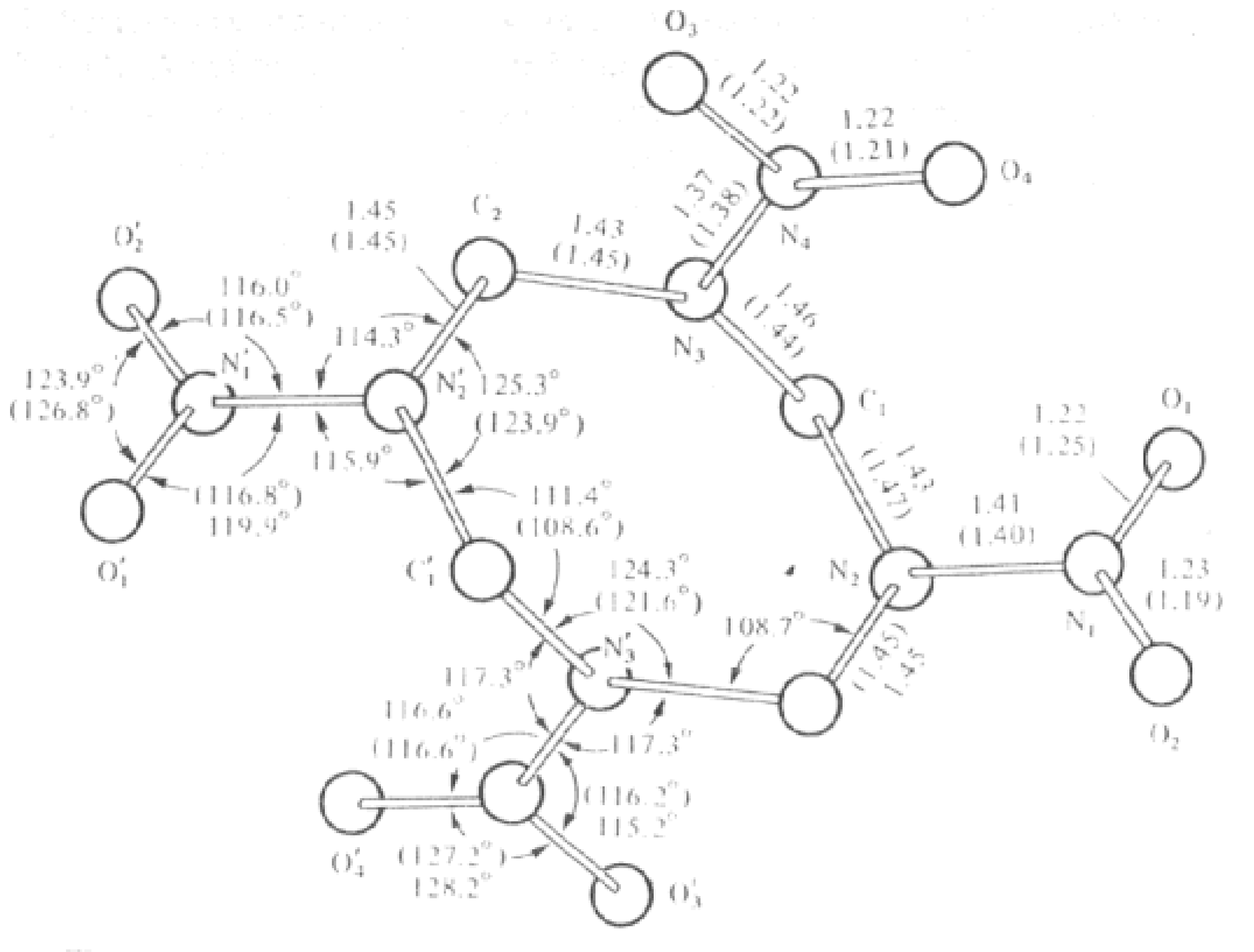


FIG. 58. Structure of β-octogen [130, 131]. Data from ESR are given in brackets.

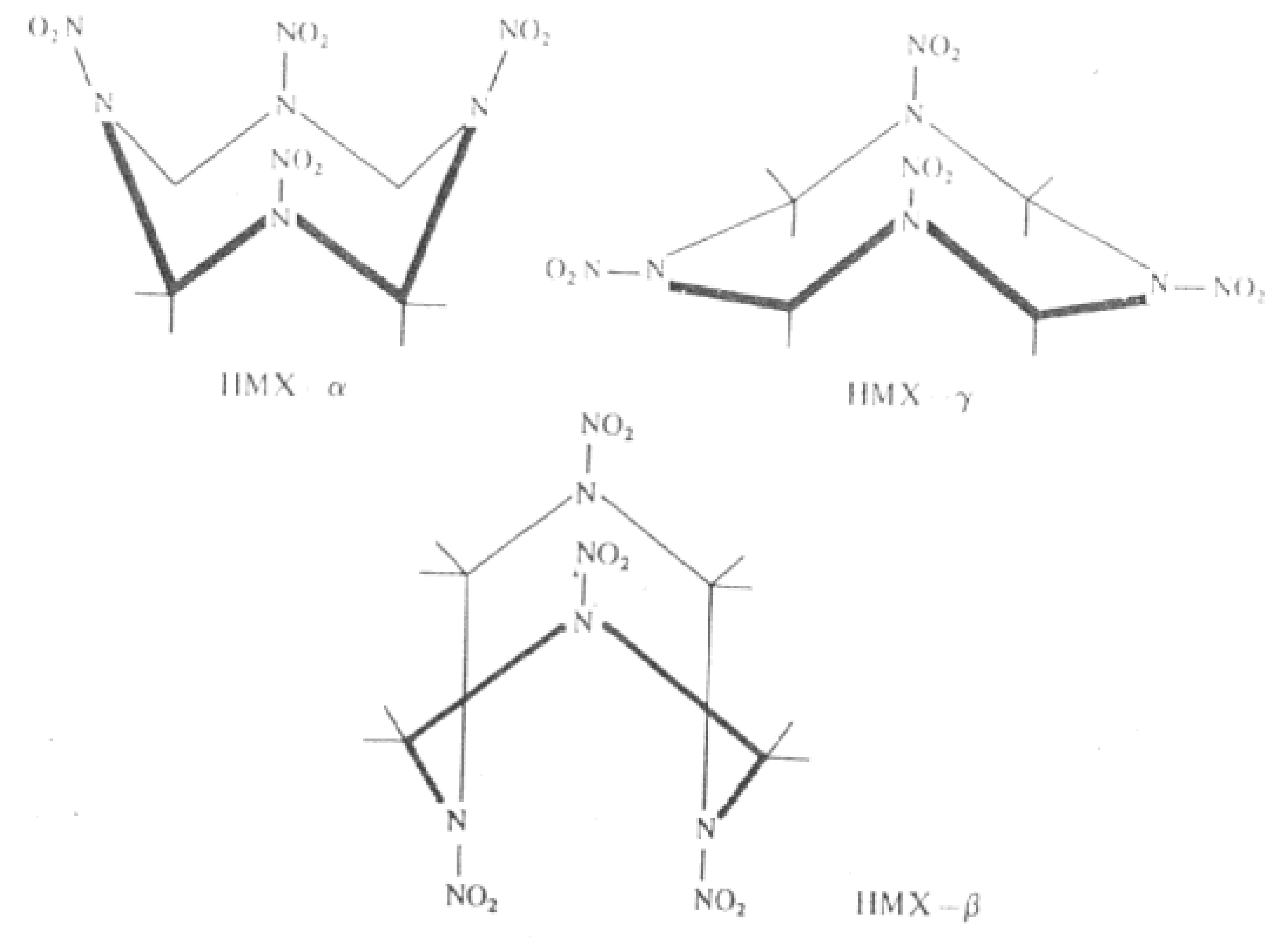
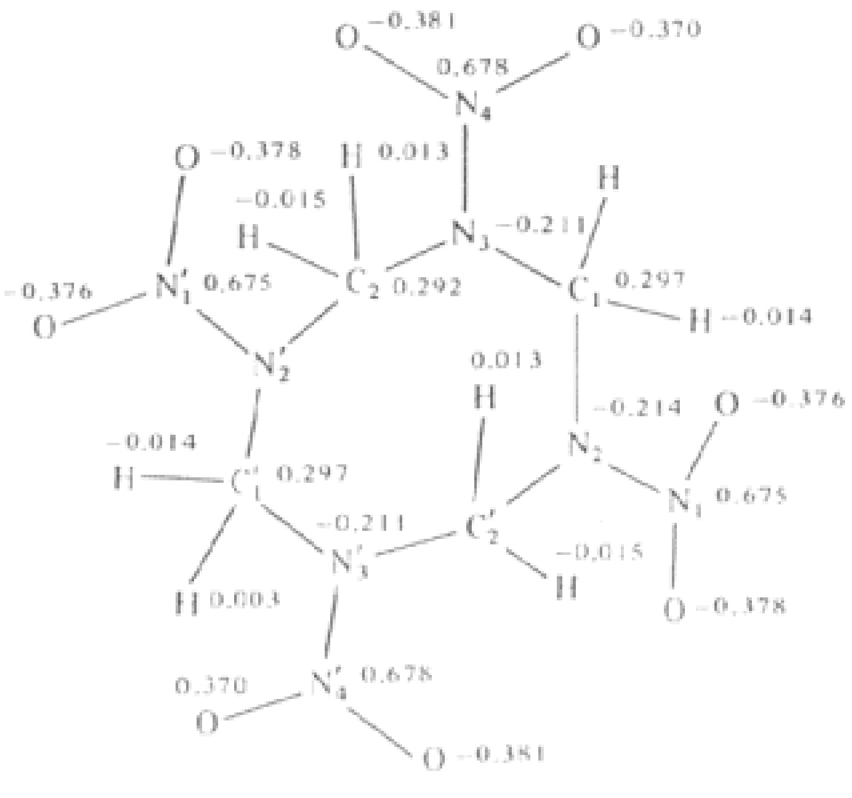
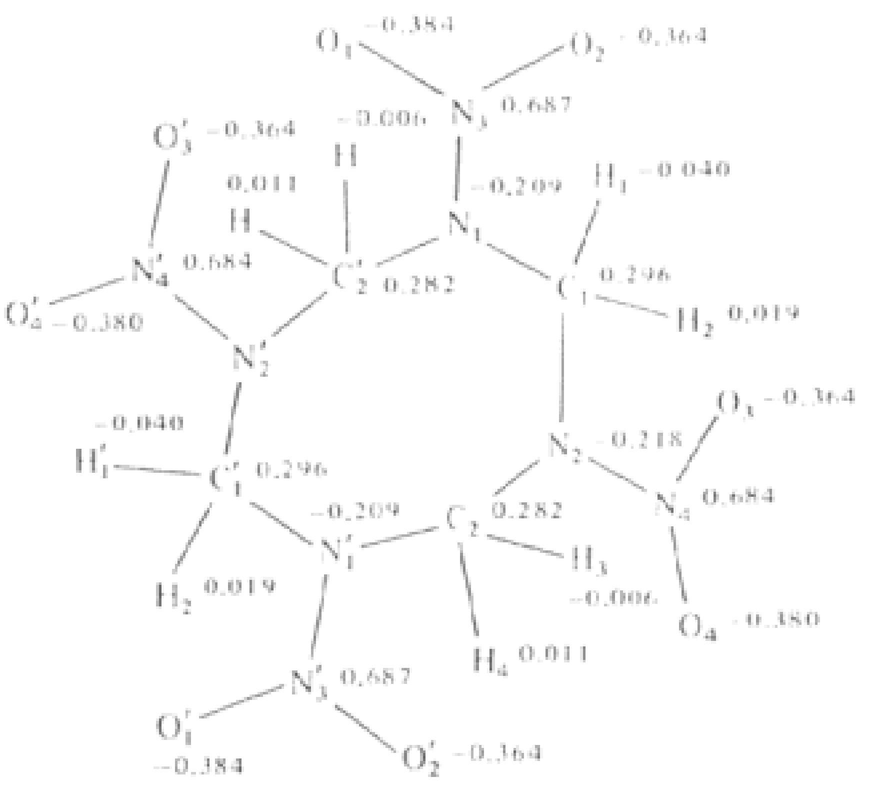


FIG. 59. Conformation of α-, β- and γ-octogen [96].



Octogen, HMX – β



Octogen, HMX – α

FIG. 60. Charge distribution in octogen (α- and β-), according to Delpuech and Cherville [98a].

Ultraviolet spectra of octogen were examined by a number of authors [134, 135, 102]. All of them found two maxima in ethanol: 201 and 206 nm.

Infra red spectra were also examined and gave clear differences between crystalline modifications [95, 96, 136]. According to G. F. Wright [96] this could serve as an analytical tool for distinguishing the modifications when crystalline was solid. Raman spectra were taken for β-HMX and isotopes: ^{15}–NO_2, ^{15}–N–NO_2, ^{13}–C and d_8 HMX [137]. One of the conclusions was the presence of hydrogen bonds between NO_2 and CH_2 groups.

Volk and Schubert [138] described mass-spectrography and Lamberton and co-workers [139] NMR spectroscopy of HMX and other nitramines.

Solubility of Octogen

According to the *Encyclopedia of Explosives* [127] the solubility of octogen is as follows in grams of HMX, in 100 g of the solution, at 25°C:

In acetic acid	0.0375 g
acetone	0.96
acetonitrile	1.98
cyclohexanone	2.11
dimethylformamide	4.4
ethyl acetate	0.02

In 1,2-dichloroethane: 0.02 at 24°C and 0.125 at 70°C.

In general, octogen is less soluble than cyclonite (Vol. III, pp. 79–80).

Specific heat of octogen at −75°C in 0.153 cal/g/°C,

0	0.228
25	0.248
50	0.266
75	0.288
100	0.295

The figures are taken from the Encyclopedia [127].

Chemical Properties

One of the characteristic features of octogen which distinguishes that compound from hexogen is that octogen readily forms additional complexes – probably charge–transfer complexes. They have been described by a number of authors [140, 136] but mainly by Selig [141]. He described complexes of octogen in molecular ratio 1:1 with amines, for example

aniline	m.p. 172°C

o-, *m*- and *p*-toluidine, m.ps 166°, 134° and 139°C respectively 1- and 2-naphthylemine; m.ps 203° and 148°C respectively, with some substituted phenols:

o-cresol	m.p. 108°C
1-naphthol	m.p. 182°C

With some compounds, for example *N*-methyl-2-pyridon, *N*-methyl-*p*-toluidine, *o*-nitroaniline, hexamethylphosphotriamide the molecular ratio octogen: second compound is 2:1.

The X-ray analysis of octogen showed a 'sandwich' structure very common in CT-complexes.

The difference between hexogen and octogen as regards the formation of complexes can be used for the separation of octogen from hexogen.

Enthalpy of decomposition of complexes on melting is of the order of 2–3 kcal/mol.

Octogen did not decompose when boiled with 2% nitric and sulphuric acid, but concentrated sulphuric acid decomposed in a way similar to the decomposition of hexogen but slower than that of the latter [142]. Ion NO_2^+ is probably present in the octogen–sulphuric acid solution.

On the other hand, octogen is more reactive with alkali than hexogen. A solution of 1% Na_2CO_3 decomposed octogen completely after prolonged boiling. A solution of sodium carbonate or sodium hydroxide can be used to decompose the residual octogen. The irradiation of octogen with ultraviolet light [154] liberated stable free radicals $\cdot NO_2$.

Thermal Decomposition

Octogen is probably more stable than Cyclonite and is comparable with TNT at 150°C in the vacuum stability test [127].

A scanning calorimeter can give information on the decomposition of various forms of octogen in the temperature range 180–210°C [13]. Maksimov [111] examined the behaviour of octogen at high temperatures. The decomposition of solid samples at temperatures from 183° to 230°C was measured by determining the volume of gaseous products, some of the curves are given in Fig. 61. The energy of activation was calculated: 37.9 kcal/mol and $\log_{10} B = 11.2$. The decomposition of a 2% solution in *m*-dinitrobenzene was examined at temperatures [171] up to 215°C. Some of the curves are presented in Fig. 62. The energy of activation was found to be $E = 44.9$ kcal/mol and $\log_{10} B = 16.0$. In solution the decomposition was faster than that of the solid substance. Octogen is decomposed much slower than hexogen, in other words exhibits much better stability than hexogen.

The problem of octogen stability was tackled in similar ways by a number of authors: Baum and Shipitsin [143], Maycock *et al.* [144, 145], Rogers and Morris [146], Hall [147], Kimura and Kubota [148].

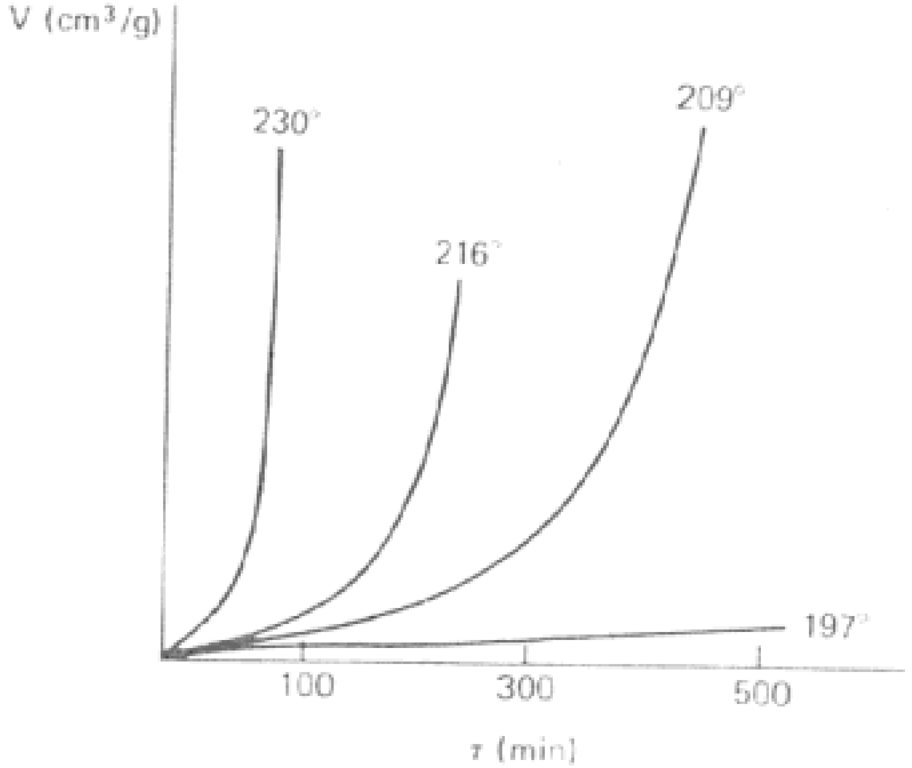


FIG. 61. Thermal decomposition of solid octogen [111].

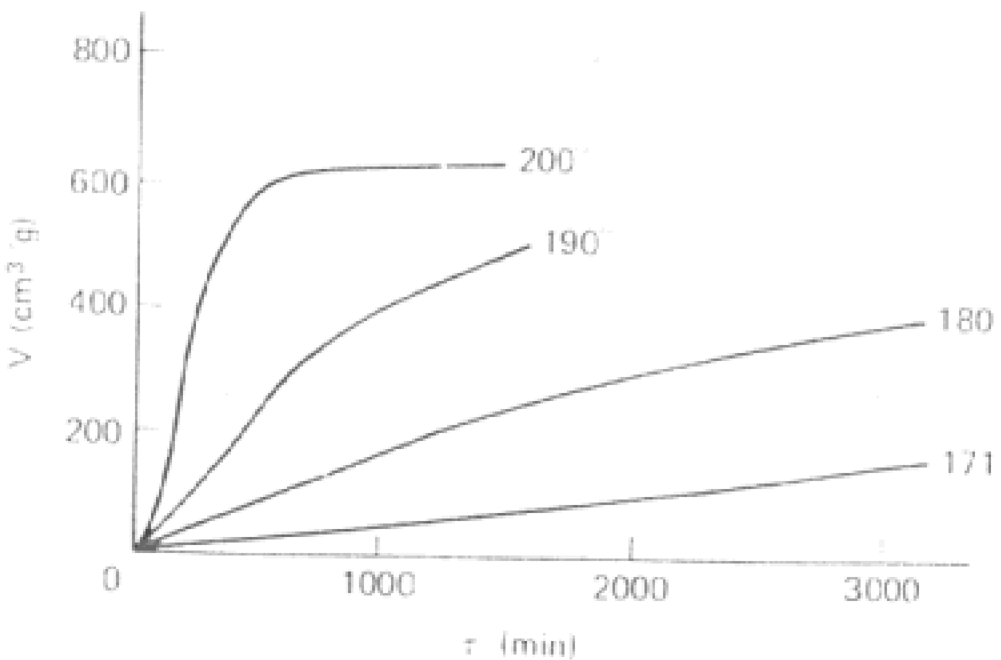


FIG. 62. Thermal decomposition of octogen in solution [111].

The induction period on a heated surface for octogen was found to be [149]:

at	350°	300°	280°	275°C
	1.7	5.3	10.0	12.3

The statement by Henkin and McGill [150] is interesting in that octogen, placed on a copper surface of 360°C, does not decompose. There is no doubt that octogen is a heat resistant explosive.

Robertson [151] and Suryanarayana and co-workers [152] have reported that formaldehyde is one of the major products of the decomposition of HMX. Suryanarayanan *et al.* concluded from studies on isotopically labelled HMS that the thermal degradation of HMX is mainly accompanied by C–N rather than N–N rupture. Amongst other decomposition products, hydroxymethyl formamide was found [153]. When kept at a temperature of 200°C β-form passes into a less stable δ-form. This explains an interesting fact described by Haeuseler [167] that is, β-octogen in a hermetic container exploded after being kept for 30 min at 200°C.

It should be pointed out that the behaviour of octogen at high temperature offers some other less expected features. Thus the very high figures of the activation energy of α- and β-octogen were found to be of the order of 150–230 kcal/mol for the decomposition temperatures from *ca.* 190°C to m.p. (*ca.* 280°C) [146–148].

Kimura and Kubota [148] tried to find a tentative explanation for such high figures in terms of autocatalytic reactions. See also the review of Dubovitskii and Korsunskii [4].

Thermochemical and Explosive Properties

The following data were given in [5] and [127]:

Heat of explosion of octogen is 1356 kcal/kg (water–liquid)
and 1222 kcal/kg (water–gas)
Heat of combustion 2255–2362 kcal/kg, 667.4 kcal/mol
Enthalpy of formation $-\Delta H_f = 17.93$ kcal/mol
(or 25.0 kcal/mol).

The strength of the explosive in ballistic mortar and in lead block was: 150% and 145% respectively, velocity of detonation 9124 m/s at the density 1.84. The detonation pressure determined by the depth of the impression in a steel plate [155] was found 0.397 mm, that is 150% of that of TNT.

The rate of burning of octogen [156] depends on the pressure, but is independent of the density:

Pressure	12.5	52.0	154.0	205.0 kg/cm^2
Rate of burning				
at $\rho = 1.66$	0.489	1.48	3.91	5.20 g/cm^{2}s
$\rho = 1.02$	0.480	1.43	3.31	5.13 g/cm^{2}s

Burning can pass to the explosion. This was studied extensively by Andreev and Gorbunov [157]. Octogen of the density 0.85 and 0.93 can explode after 0.06 and 0.54 s respectively. At a density 0.94 no explosion occurred. The authors introduced the term a 'critical density' which forms a threshold of the possible passing burning to explosion.

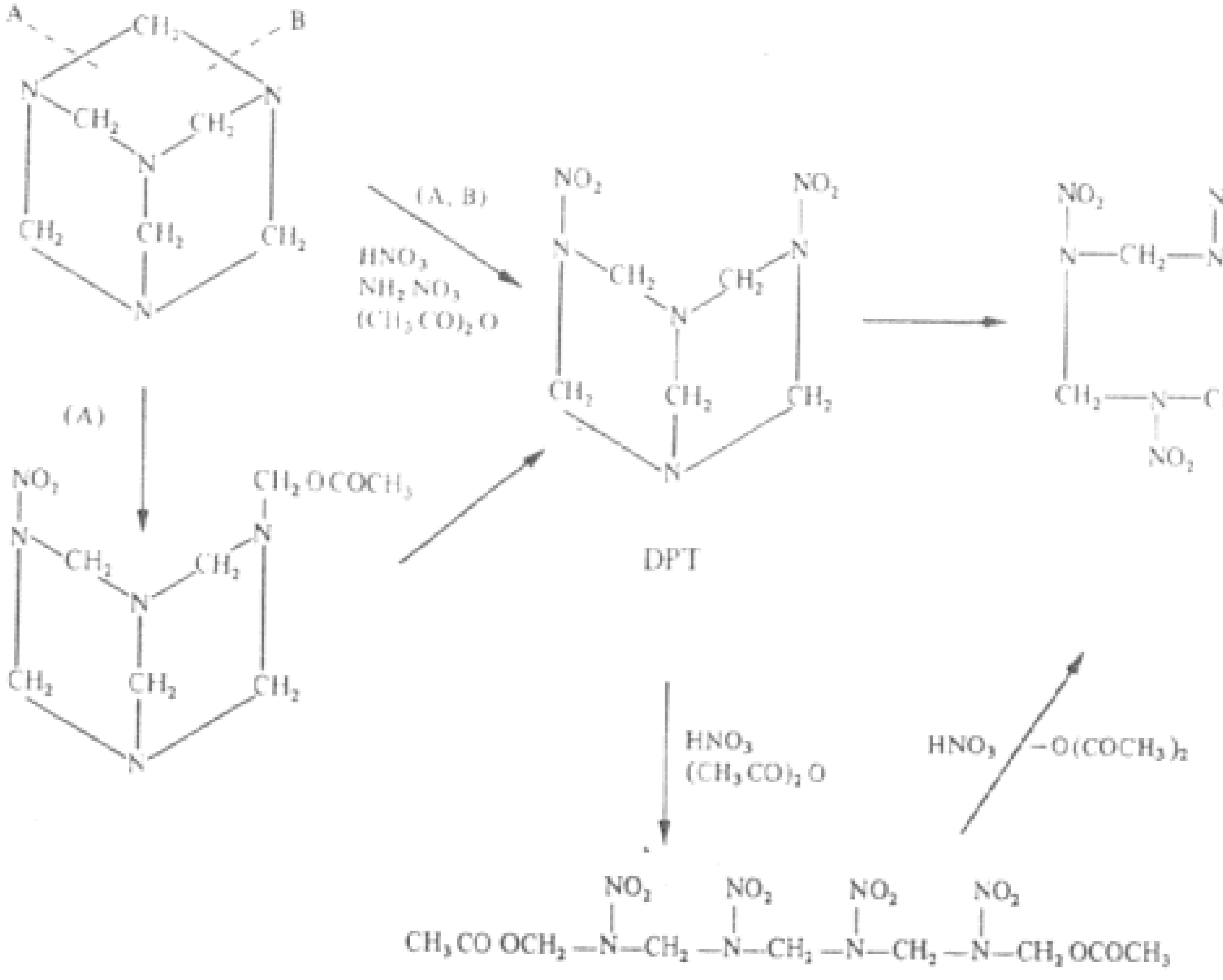
The problem of burning HMX seems to gain some importance as HMX became a common component of propellants. Particularly important is HMX with aluminium described below (p. 394).

Preparation of Octogen

Octogen (HMX) is formed in the nitration of hexamethylenetetramine ('hexamine') and is a by-product of production of cyclonite (RDX) as it was pointed out in Vol. III, p. 90. However, the statement given in Vol. III needs to be corrected. On the basis of our present knowledge, octogen which accompanies cyclonite does not reduce the power of cyclonite. On the contrary, owing to a higher velocity of detonation octogen can increase the strength of cyclonite.

W. E. Bachmann and Sheehan [158] developed a method of preparing RDX containing a small quantity of HMX. The method involved nitrolysis of hexamine with ammonium nitrate–nitric acid solution and acetic anhydride. By varying parameters of temperature and acid concentration, ammonium nitrate and acetic anhydride it was shown that the ratio RDX/HMX can be altered. These results led Bachmann and co-workers to prepare mixture rich in HMX. The optimum yield obtained was 82% conversion of hexamine to HMX/RDX mixture containing up to 73% HMX.

The mechanism of the formation of octogen can be presented by scheme (35):



(35)

Low acidity and the presence of NH_4NO_3 (and paraformaldehyde – [162]) favours the formation of octogen. Without ammonium nitrate the linear compound was formed. Higher acidity helps to obtain RDX [159].

Bell and Dunstan [162] nitrated DPT at –20°C. After warming the solution to 30°C HMX resulted in a low yield.

By using $^{15}NH_4NO_3$ W. E. Bachmann and co-workers [159] established that only 15% of nitrogen from NH_4 enters octogen, and much more (*ca.* 37%) enters hexogen. Castorina and co-workers [160, 161] used C labelled hexamine, DPT and paraformaldehyde, and found that all these compounds contribute to the formation of octogen. They obtained HMX with 15% of RDX. They isolated pure HMX by dissolving all in acetone, evaporating to form a precipitate and cooling to 25°C. The crystalline solid is HMX. The presence of RDX in the substance can be detected by acting with sodium nitroso ferricyanide on the acetone solution. A blue colour reveals the presence of RDX (reaction of S. B. Wright according to [161]).

It has been found by Picard [162] that the addition of paraformaldehyde to the mixture of ammonium nitrate–nitric acid–acetic acid–acetic anhydride increases the yield of octogen.

The following is the method described by Fedoroff and Sheffield [127] as apparently used in U.S.A.

To a 6–10 l. flask equipped with a stirrer and three dropping funnels add 785 g acetic acid, 13 g acetic anhydride and 17 g of paraformaldehyde keeping the temperature at 44 ± 1°C. Add over 15 min a solution of 101 g of hexamine in 165 g acetic acid, 320 g of acetic anhydride and 180 g of ammonium nitrate–nitric acid solution prepared by dissolving 840 g of ammonium nitrate in 900 g of nitric acid (99% concentration). The hexamine and nitric acid are added continuously in correct proportions. The mixture is stirred for 15 min. After that are added: 320 g of acetic anhydride and 271 g of nitric acid–ammonium nitrate solution in that proportion and then 160 g of acetic anhydride are added in bulk. The mixture is stirred for 60 min., 350 g of hot water are added and refluxed for 30 min. The content is cooled to 20°C by adding ice, the precipitate is collected and washed with three portions of cold water.

The yield of β-HMX is 95% of the theoretical and the purity 90%.

A similar method of obtaining β-HMX was given by Robbins and Boswell [163]. The composition of the product was 77.5% HMX and 22.5% RDX. The yield of HMX was 87.5%. A method was also described for nitrating hexamine with nitric acid in the presence of BF_3. A yield of 96% was claimed [164].

Preparation of Octogen from DPT (3,7-dinitro-1,3,5 7-tetraazabicyclo [3, 3, 1] nonane) (Vol. III, p. 90, formula XII)

There are methods of obtaining octogen in two steps by forming DPT as the first step, followed by acting on DPT with nitric acid or nitric acid with ammonium nitrate or nitric acid, ammonium nitrate and acetic anhydride. However the yield of DPT is not very high.

The best method of obtaining DPT consists in introducing hexamine dinitrate to 90% sulphuric acid at 8–15°C. After 45 min. all is poured on ice and the solution is filtrated. The filtrate is neutralized with 28% ammonia to pH = 5.5–6.5 DPT precipitated [165].

Another method of making octogen from DPT (1 mole) consists in acting with NH_4NO_3 (1.6 mole) and nitric acid (3.2 mole) at 60–65°C for one hour. Water is then added and all is heated for 12 hours in a steam-bath. The yield was 75% of the theoretical (according to [5]).

The description of the industrial manufacture of octogen in Hungary has been given [166]. In the first step DPT was obtained from hexamine, acetic anhydride, paraformaldehyde and a solution of ammonium nitrate in nitric acid. After that the rest of the reagents were added.

Altogether for 1 mole of hexamine, the following reagents were added:

5–7 moles of nitric acid (min. 98%),
3–5 moles ammonium nitrate,
10–11 moles acetic anhydride and
0.27–0.54 moles of paraformaldehyde.

The reaction was carried out at 44°C.

After that water was added and the temperature was raised to 98°C by injecting live steam. All was cooled and the product filtered. It contained 60–70% octogen and 30–40% hexogen.

To obtain pure β-form the product is dissolved in acetone and refluxed for 45 min. All forms of octogen pass into the solution. Also unstable products decompose on boiling.

If pure octogen free of cyclonite is required, octogen can be obtained due to lower solubility in acetone. By warming the product with a three times larger quantity of acetone at 40–50°C, all cyclonite passes into the solution.

The commercial grade of HMX produced in France seems to contain *ca.* 2.25% RDX [179].

Specification for Octogen

The U.S. specification describes two grades of octogen:

Grade 1, min. 93%,
Grade 2, min. 98%.

The quantity of octogen is determined by treating an 0.2 g sample with 100 ml of 1,2-dichloroethane saturated with HMX. The insoluble matter is pure octogen.

The octogen should consist of β-polymorph by examination of a 5% mull of the sample in hexachlorobutadiene or tetrachloroethylene in a sodium chloride cell. Another sample of pure β-polymorph is placed in a compensating cell. The absorption is observed between 14.0 and 14.3 μ.

M.p. should be min. 270°C
Insoluble in acetone max. 0.05%

Inorganic insoluble max. 0.03%
Acidity max. 0.02% (as acetic acid)
Granulation is different in 5 classes.

For transportation it is kept in water-tight bags with a minimum 10% solution of 40% isopropyl alcohol and 60% water.

In the presence of RDX the quantitative determination of HMX is by the formation of the stable complex: of HMX with dimethylformamide insoluble in CCl_4. Another method consists in the separation of HMX by low solubility in 1,2-dichloroethane. For detailed description of the methods see the Encyclopedia [127].

The Soviet Union specification for octogen used for detonating fuses includes the items as follows (according to [5]):

m.p. min 278°C
critical and limiting diameters at density 1.65

should be 1 mm and 4 mm respectively.

The velocity of detonation is

8400 m/s at $\rho = 1.65$ and
8800 m/s at $\rho = 1.75$.

When heated at 335°C the induction period should be 5 s.

For other requirements referred to charges for deep bore-holes see [5].

EXPLOSIVES WITH OCTOGEN AS A MAIN COMPONENT

Price [176] gave a description of the explosive properties of octogen (91%) desensitized with wax (9%): at density 1.71 it shows the rate of detonation 8680 m/s. Octol – a castable mixture of octogen (77%) and TNT (23%) gave the rate of detonation 8540 m/s (density 1.80). They are stronger than analogous compositions with cyclonite.

Kegeler [177] described the composition of 65% octogen with 35% TNT. It shows the rate of detonation

8254 m/s at $\rho = 1.80$, and
8156 m/s at $\rho = 1.77$.

There are also compositions described, for example of 94% octogen, 3% nitrocellulose and 3% (β-chloroethyl) phosphate [178].

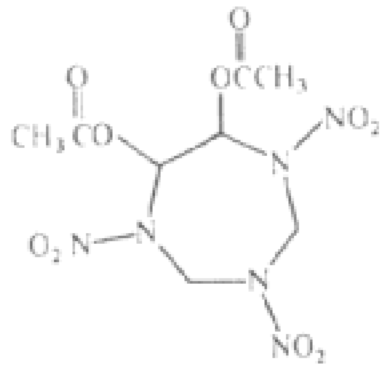
Of considerable importance now are mixtures of octogen with aluminium powder. Two papers have appeared recently on the ability of aluminized HMX to pass from burning to detonation. Langen and Barth [179] described the properties of Octal 70/30, that is, HMX (with wax) 70% and aluminium 30%. HMX with wax was composed of 95% of Höchst waxes 'S' and 'KP' in equal proportions, that is 2.5% of each. The authors of the paper described the method of mixing the ingredients as follows: 100 parts of HMX desensitized with waxes were pre-heated to 90°C, 42.9 parts of aluminium degreased with carbon tetrachloride and preheated to 90°C were mixed in a vessel connected to ground potential. After that the mixture was sieved through 1 mm mesh size. The performance of Octal 70/30 was better than that of RDX/Al 70/30. This can be seen from Table 64.

TABLE 64. Comparison of octal 70/30 with RDX/Al

	Heat of explosion kcal/kg	Lead block test cm^3
Octal 70/30	1650	555
RDX/Al 70/30	1635	470

Price and Clairmont [180] examined fine (5 μm) and coarse (95 μm) aluminium on the deflagration to detonation transition of HMX/Al pressed charges. They found that Al, particularly fine grain, increases the length of the predetonation column. However wax is more effective than Al: it is more efficient in delaying the detonation.

BSX (1,7-DIACETOXY-2,4,6-TRINITRO-2,4,6-TRIAZAHEPTANE)



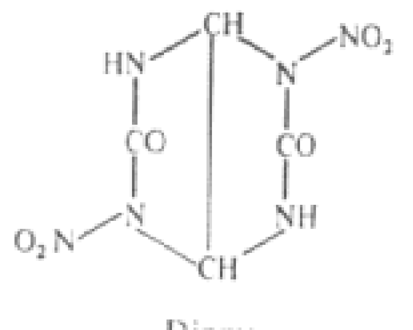
"BSX"

The compound is formed as a by-product of cyclonite when made by the method of W. E. Bachmann [158–159] and Köffler (Vol. III, p. 111).

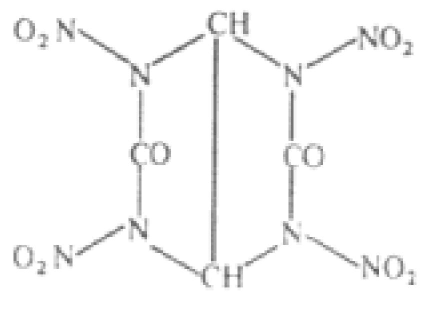
This was described by G. F. Wright [2].

The remarkable property of the compound shown by Hall [181] is its ability to form complexes: with dioxane, cyclohexanone, tetrachloroethane, formamide. All in the proportion 1:1. The complex with acetophenone is in the proportion 2:1.

DINGU AND SORGUYL



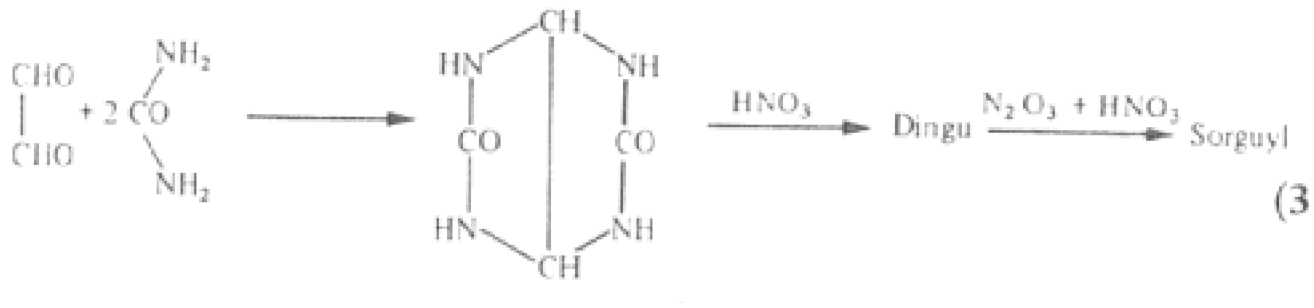
Dingu
(Dinitroglycolurile)



Sorguyl
(Tetranitroglycolurile)

French authors obtained a patent [182] for two explosive compounds: Dingu and Sorguyl.

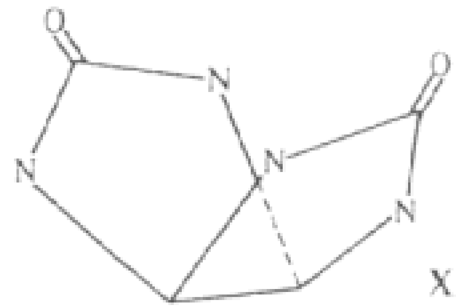
Both are obtained by the nitration of glycolurile which is formed through the action of urea on glyoxal (36).



Glycolurile

(36)

The stereochemical structure of glycolurile can be depicted by formula (XXII)



XXII

The following are data on Dingu and Sorguyl (Table 65) according to Meyer [183].

TABLE 65. Properties of Dingu and Sorguyl

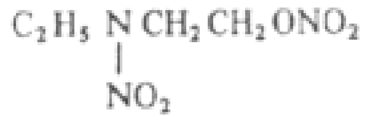
	Dingu	Sorguyl
Decomposition temperature	225–250°C (beginning 130°C)	237°C
Density	1.94	2.01
Rate of detonation	7580 m/s at = 1.75	9150 m/s at = 1.95
Oxygen balance	−27.6%	+5.0%

Dingu is relatively readily decomposed by alkaline hydrolysis, but is stable in an acid medium. It is insoluble in molten TNT, soluble in dimethylsulphoxide.

Sorguyl is remarkable by its high density, extremely high velocity of detonation, and positive oxygen balance. It is not hygroscopic but decomposes by hydrolysis. It decomposes in molten TNT.

N-NITRO-*O*-NITRO COMPOUNDS

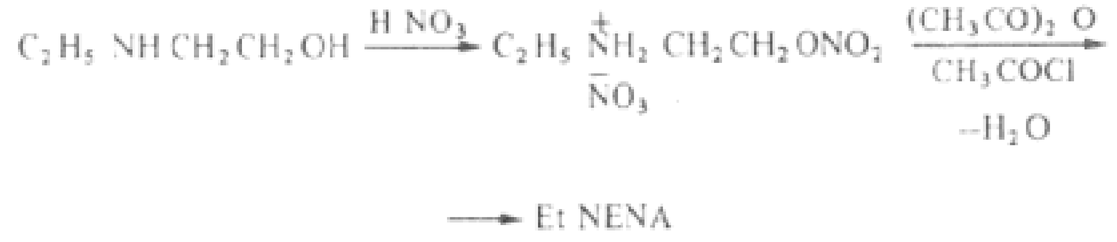
One representative of this group of compounds merits attention. This is 1-(*N*-Ethyl)-nitramino-2-ethanol Nitrate, code name Et-NENA [73]



$$\mathrm{C_2H_5\underset{\underset{NO_2}{|}}{N}CH_2CH_2ONO_2}$$

m.p. 4.0–5.5°C

This is an oil, d = 1.32 at 25°/4°C, n_D = 1.479/25°C. It was prepared by Blomquist and Fiedorek [73, 74] from ethylaminoethanol. The latter was added dropwise to 98% nitric acid at 10°C. The resulting mixture was added dropwise to 95% acetic anhydride with some acetyl chloride to transform the nitrate salt into nitramine:



$$\mathrm{C_2H_5\,NH\,CH_2CH_2OH \xrightarrow{H\,NO_3} C_2H_5\,\overset{+}{N}H_2\,CH_2CH_2ONO_2\;\bar{N}O_3 \xrightarrow[CH_3COCl\;\;-H_2O]{(CH_3CO)_2\,O} Et\,NENA}$$

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APPENDIX

Thermal Decomposition

Thermal decomposition of dimethyl nitramine was studied by Flournoy [1]. Korsunskii, Dubovitskii and co-workers [2, 3].

The decomposition occurred in two steps:

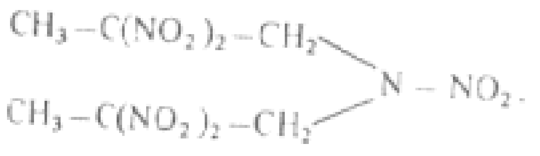
$$(CH_3)_2N{-}NO_2 \rightleftharpoons (CH_3)_2N\cdot + \cdot NO_2 \qquad (1)$$

$$(CH_3)_2N{-}NO_2 + NO_2 \longrightarrow \text{products of oxidation} \qquad (2)$$

Similar results were described by Korsunskii, Dubovitskii and Shurygin [4] on the decomposition of higher nitramines.

The activation energy of the decomposition of dimethylnitramine was found to be 40.8 kcal/mol and the log of frequency factor log B = 14.1.

Korsunskii, Dubovitskii and co-workers [5] studied the thermal decomposition of an interesting compound: bis-(2,2-dinitropropyl)-*N*-nitramine:

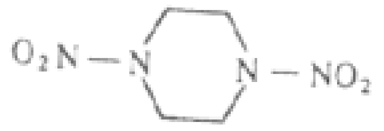


They examined the decomposition of 5% solution of the compound in *m*-dinitrobenzene at temperatures 145–196°C and found energy of activation 39.7 kcal/mol and log B = 15.7.

Thermochemistry

Pepekin and co-workers [6] examined thermochemistry of cyclic *N*-nitro compounds: dinitropiperazine and cyclonite (RDX).

The data are as below:



Cyclonite

	H_f cryst. kcal/mol	H_f gas
Dinitropiperazine	−12.7	13.9
Cyclonite	14.7	45.8

Mechanism of the Nitration of Hexamine to Cyclonite (RDX) and Octogen (HMX).

The above mechanism was described in Vol. III (pp. 87–98, 113–117). It was also investigated by nuclear tracer technique with:

Hexamine	^{14}C
Paraformaldehyde	^{14}C
$^{15}NH_4NO_3$ [7].	

The result of these experiments confirmed in general the diagrams of the reactions given before.

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CHAPTER 14

EXPLOSIVE POLYMERS

With the present advent of polymer chemistry numerous efforts have been made on synthetic polymers containing nitro groups (whether *C*-, *O*- or *N*-nitro groups) with the aim of possibly replacing (or imitating) nitrocellulose and (to a much smaller extent) nitrostarch. To date it has been difficult to obtain a synthetic polymer which would possess the same mechanical properties as that of nitrocellulose.

C-NITRO POLYMERS

Nitropolystyrene and its Derivatives

In Vol. I, pp. 418–419 nitropolystyrene was described and its possible practical application is mainly in low power mining explosives and in pyrotechnic mixtures. According to [3], molecular weight is over *ca*. 38000.

An interesting polymer 'Peptidyl' was obtained by E. Katchalski and co-workers [1] which is poly-4-hydroxy-3-nitrostyrene, an improved version of the polymer used by Merrifield [2] for the formation of peptides. Peptidyl was obtained by nitrating a co-polymer of acetoxystyrene with divinylbenzene in proportion 100:4. Divinylbenzene is used as a cross-linking agent.

Nitroindene Polymer (p. 410)

Nitroindene polymer was obtained by the nitration of polyindene [3]. It is an amorphous solid of m.p. 230°C, and is insoluble in most solvents. Decomposition (explosion) temperature is above 360°C. It is slightly hygroscopic, taking 1.61% water from the atmosphere of 100% relative humidity. The International heat test at 75°C showed 1.1% loss of weight. A sample of 5 g evolved *in vacuo* 12 cm^3 of gas in 48 hours. It was considered for use in U.S. Army as a time fuse but was found to be too sensitive to impact.

POLYNITRO ALKANES

Nitroethylene Polymer (Vol. I, p. 596) $(CH_2 = CH\,NO_2)_n$

Nitroethylene was mentioned in Chapter VIII. Here the polymer will be described, according to Noma and co-workers [4], Perekalin and Sopova [5], Encyclopedia of Fedoroff and Sheffield [6], Novikov and co-workers [7].

Nitroethylene polymer is a white amorphous solid which does not melt but decomposes on heating above 75°C.

During World War II in the U.S.A. [6] a method of preparing nitroethylene was developed consisting of the action of sodium bicarbonate on 1-chloro-2-nitroethane. The yield of nitroethylene was 76%.

Polymerization was carried out in aqueous medium in the presence of an emulsifier and ascaridole (a terpene peroxide) as a catalyst. Air over the liquid was replaced by nitrogen and nitroethylene was introduced gradually to the water. The reaction ended after 2 hours of mixing.

Perekalin and his co-workers [8] have done pioneering work on the polymerization of nitroethylene under γ-radiation from Co^{60}. Perekalin *et al*. pointed out that the methods so far used to polymerize nitroethylene gave a low molecular weight of *ca*. 2000. When the polymerization was carried out in a solvent, for example, dimethylformamide or tetrahydrofurane, the molecular weight was higher but the product was still a powder, although the γ-radiation yielded a transparent product. The part which was not polymerized was subjected to further irradiation etc. and eventually a transparent block was obtained. Perekalin also found that polymerization continues after irradiation. On the basis of the latter fact he concluded that the polymer contains free radical of long life and the reaction of polymerization is a free-radical reaction. The molecular weight of polynitroethylene obtained by Perekalin *et al*. was of the order of 38000 (through measurement of viscosity) and density was 1.535. It decomposed when heated to 150°C.

In a number of papers Yamaoka and co-workers [9–14] examined polymerization. Their main conclusion was that radiation induced polymerization through the anionic mechanism involving free ions and induced post-polymerization at temperatures below −150°C.

Nitroethylene polymer is a white amorphous solid which does not melt. According to [6] it decomposed slowly at 75°C. After 2 hours of maintaining this temperature it ignited. When heated to 100°C it deflagrated with a sooty smoke in 23 min. On a hot plate of 200°C it decomposed without explosion. The sensitivity to impact is of the order of TNT. The strength (in ballistic mortar) constitutes only 29% of that of TNT. Hungarian authors [15] reported the data for polynitroethylene as follows:

heat of detonation	720 kcal/kg
lead block expansion	114 cm^3
impact sensitivity (2 kg)	70–90 cm (TNT 50–60 cm).

POLYURETHANES WITH ALIPHATIC *C*- AND *N*-NITRO GROUPS

A large number of polyurethanes were made of nitro aliphatic polymers consisting in co-polymerization of nitro aliphatic diisocyanate with nitro aliphatic diols. They were made by Aerojet General Corp., by Blatz, Gold and co-workers [16].

Two main lines were taken:

(1) to polymerize isocyanates to polyurethanes with diols (in mol. proportion 1:1) both containing *C*-nitro groups, and some of diols with *N*-nitro groups,

(2) to nitrate the above polymers ('the postnitration') to increase the number of the nitro group.

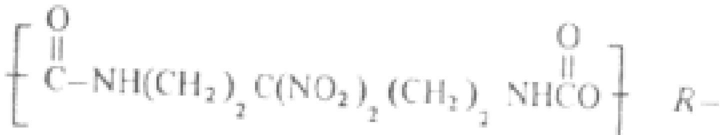
Most of the compounds are described below.

1. Co-polymers from 3,3-Dinitro-1,5-pentane Diisocyanate (I) and Nitrodiols.

$$O{=}C{=}N{-}CH_2\,CH_2C(NO_2)_2\,(CH_2)_2{-}N{=}C{=}O$$

I

The general formula (II) gives the structure with variable *R* which depends on the used nitrodiol



$$\left[\overset{\displaystyle O}{\overset{\|}{C}}{-}NH(CH_2)_2C(NO_2)_2(CH_2)_2\,NH\overset{\displaystyle O}{\overset{\|}{C}}O\right]_n R-$$

II

The following were compounds IIa–IIe made of I and different diols listed below (Table 66).

TABLE 66. Co-polymers of I with diols: polymer II

Compound	Name of diol	Formulae of polymers II $R=$
IIa	2,2-Dinitro-1,3-propanediol	$-CH_2-C(NO_2)_2-CH_2O-$
IIb	5,5,5-Trinitro-1,2-pentanediol	$-OCH_2-\overset{\displaystyle O-}{\overset{\vert}{C}}H(CH_2)_2-C(NO_2)_3$
IIc	2,2,4,4-Tetranitro-1,5-pentanediol	$-CH_2-C(NO_2)_2-CH_2-C(NO_2)_2-CH_2O-$
IId	4,4,6,8,8-Pentanenitro-1,11-undecanediol	$-(CH_2)_3-C(NO_2)_2-CH_2-CH(NO_2)-CH_2-C(NO_2)_2-(CH_2)_3O-$
IIe	4,4,6,6,8,8-Hexanitro-1,11-undecanediol	$-(CH_2)_3-C(NO_2)_2-CH_2-C(NO_2)_2-CH_2-C(NO_2)_2-(CH_2)_3O-$
IIf	5,7,9-Trinitro-5,7,9-triaza-3,11-dioxa-1,13-tridecanediol	$-(CH_2)_2OCH_2N(NO_2)CH_2N(NO_2)CH_2N(NO_2)-CH_2-O(CH_2)_2O-$

Another group of polymers with the same diisocyanate (I) was reacted with diamine (III) to form polymer (IIIa) which is a urea derivative:

$$NH_2(CH_2)_2C(NO_2)_2(CH_2)_2NH_2$$

III

$$\left[\overset{\displaystyle O}{\overset{\|}{C}}\,NH(CH_2)_2C(NO_2)_2(CH_2)_2NH\overset{\displaystyle O}{\overset{\|}{C}}\,NH(CH_2)_2\,C(NO_2)_2(CH_2)_2\,NH\right]_n$$

IIIa

Another series of polymers were made from 3,3,5,7,7-Pentanitro-5-aza-1,9-nonane Diisocyanate (IV) and diols. The general formula of polymers is V and the compounds are listed in Table 67.

$$O{=}C{=}N{-}(CH_2)_2C(NO_2)_2CH_2\,N(NO_2)CH_2C(NO_2)_2\,(CH_2)_2{-}N{=}C{=}O$$

IV

$$\left[\overset{\displaystyle O}{\overset{\|}{C}}{-}NH{-}(CH_2)_2\,C(NO_2)_2CH_2N(NO_2)CH_2C(NO_2)_2(CH_2)_2{-}NH\overset{\displaystyle O}{\overset{\|}{C}}O\right]_n R$$

V

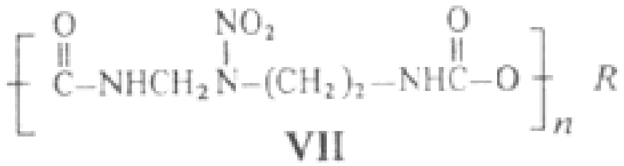
TABLE 67. Co-polymers of IV with diols: polymers V

Compound	Name of diol	Formulae of Polymers V $R=$
Va	2,2-Dinitro-1,3-propanediol	$-CH_2-C(NO_2)_2-CH_2O-$
Vb	5,5,5-Trinitro-1,2-pentanediol	$-CH_2-\underset{\begin{array}{c}\vert\\(CH_2)_2\\\vert\\CH(NO_2)_3\end{array}}{CH}-O-$

Three co-polymers were made from 2-Nitraza-1,4-butane Diisocyanate (VI) with diols to form polymers VII:

$$O{=}C{=}N{-}CH_2\overset{\displaystyle NO_2}{\overset{|}{N}}{-}(CH_2)_2{-}N{=}C{=}O$$

VI



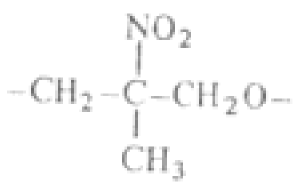
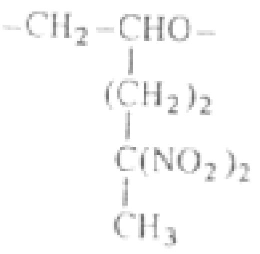
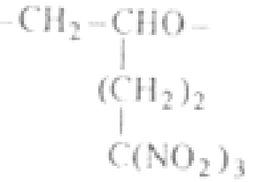
$$\left[\overset{\displaystyle O}{\overset{\|}{C}}{-}NHCH_2\overset{\displaystyle NO_2}{\overset{|}{N}}{-}(CH_2)_2{-}NH\overset{\displaystyle O}{\overset{\|}{C}}{-}O\right]_n R$$

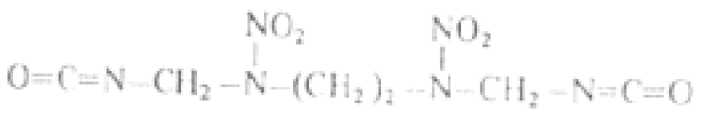
VII

Their formulae are given in Table 68.

Two co-polymers were made of 2,5-dinitraza-1,6-hexane diisocyanate (VIII) and diols which led to polymers (IX):

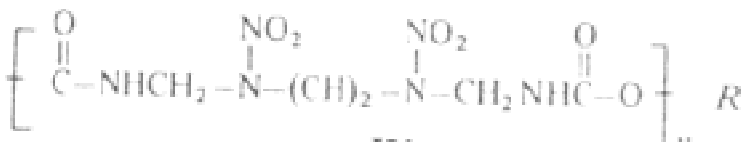
TABLE 68. Co-polymers of VI with diols: polymers VII

Compound	Name of diol	Formulae of Polymers VII *R*=
VIIa	2-Nitro-2-methyl-1,3-propanediol	 $-CH_2-\underset{\underset{\displaystyle CH_3}{\vert}}{\overset{\overset{\displaystyle NO_2}{\vert}}{C}}-CH_2O-$
VIIb	5,5-Dinitro-1,2-hexanediol	 $-CH_2-\underset{\underset{\underset{\underset{\underset{\underset{\displaystyle CH_3}{\vert}}{\displaystyle C(NO_2)_2}}{\vert}}{\displaystyle (CH_2)_2}}{\vert}}{C}HO-$
VIIc	5,5,5-Trinitro-1,2-pentanediol	 $-CH_2-\underset{\underset{\underset{\underset{\displaystyle C(NO_2)_3}{\vert}}{\displaystyle (CH_2)_2}}{\vert}}{C}HO-$



$$O{=}C{=}N{-}CH_2{-}\overset{\displaystyle NO_2}{\overset{\vert}{N}}{-}(CH_2)_2{-}\overset{\displaystyle NO_2}{\overset{\vert}{N}}{-}CH_2{-}N{=}C{=}O$$

VIII

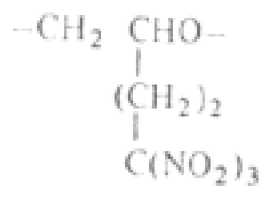


$$\left[\overset{\displaystyle O}{\overset{\Vert}{C}}{-}NHCH_2{-}\overset{\displaystyle NO_2}{\overset{\vert}{N}}{-}(CH)_2{-}\overset{\displaystyle NO_2}{\overset{\vert}{N}}{-}CH_2NH\overset{\displaystyle O}{\overset{\Vert}{C}}{-}O\right]_n \quad R$$

IX

The formulae of IX are given in Table 69.

TABLE 69. Co-polymers of VIII with diols: polymers IX

Compound	Name of diol	Formulae of Polymers IX *R*=
IXa	2,2-Dinitro-1,3-propanediol	$-CH_2-C(NO_2)_2-CH_2O-$
IXb	5,5,5-Trinitro-1,2-pentanediol	 $-CH_2-\underset{\underset{\underset{\underset{\displaystyle C(NO_2)_3}{\vert}}{\displaystyle (CH_2)_2}}{\vert}}{C}HO-$

All polymers show the relative viscosity of 1% acetone solution between 1.1 and 1.8 cp. Partial compatibility with nitrocellulose and rubber has been described for polymers IIc and IId. The densities of samples II were 1.50–1.64. Polymer IIa showed explosive properties; it detonated with the rate of 6200 m/s at d = 1.57.

The sensitivity of the melting points to impact and stability are given in Table 70.

TABLE 70. Some properties of co-polymers: diisocyanates–diols

Compound	m.p. °C	Impact sensitivity* RDX = 28 cm cm	Stability	
			134.5°C methyl violet min	65.5 KI-starch, min
IIa	75–78	100	195	300
IIb	85–95	85	78	10
IIc	70–80	80–85	13	12
IId	*ca.* 40	100	10, Expl. 22	11
IIe	40	100	Expl. 8	8
IIf	55–60	80–85	300	300
IIIa	110–115	80–85	75	300
Va	75–85	40		13
Vb	65–75	65		20
VIIa	90–100	100		300
VIIb	70–80	100		390
VIIc	80–90	55		38
IXa	85–95	100		90
IXb	90–100	60		10

* Impact sensitivity is expressed in the height of 2 kg weight giving 50% probability of explosions comparing with the standard-Cyclonite (RDX) which requires 28–35 cm height.

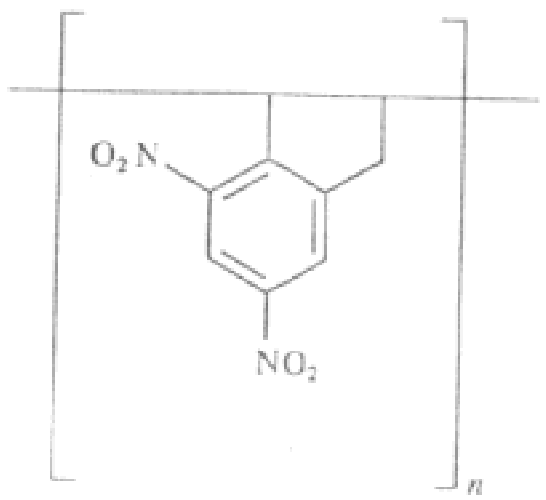
Preparation

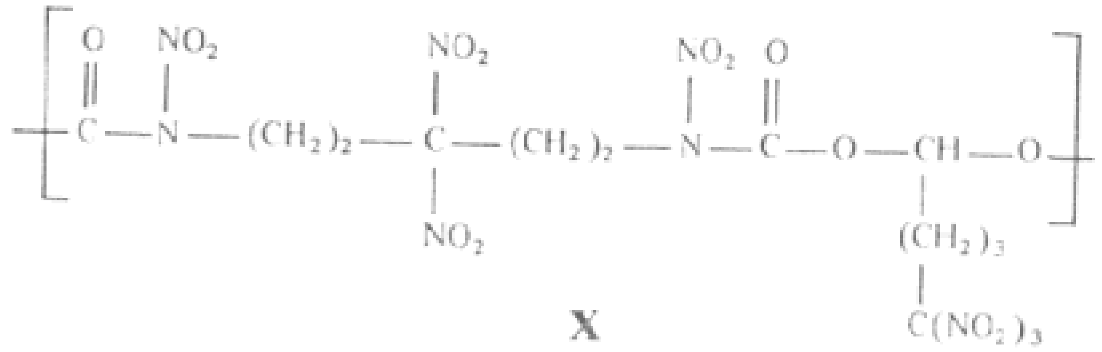
Polymers were prepared by adding dropwise a solution of a diol and a catalyst in absolute dioxane to an equivalent amount of a diisocyanate at 20 to 50°C depending on the substances used. The catalyst in all instances (with the exception of IId and e) was ferric acetylacetonate in quantity of 0.05–0.15% in relation to the diol. With IId and IIe it was boron trifluoride–ether complex in proportion of *ca.* 1.5 mol %. The temperature was kept at 20–40°C for a longer time: from 2 days to several weeks. At the end the temperature should be raised to 50°C. The product was precipitated by adding water. The solvent was removed by steam distillation or by vacuum drying. The yield in most instances was of the order of 95% (with IIf it was *ca.* 44%).

It can be seen from Table 70 that some of the polymers possess poor stability but show low sensitivity to impact. Some of them are remarkably stable at 134.5°C.

2. Nitration of polyurethanes containing nitro groups [16]. Several polyurethanes described above have been subjected to nitration. However, most of the products show poor stability. The previously described IIb was nitrated with 100% nitric acid at room temperature followed by gradually raising the temperature to 50°C and keeping it for 20 min. The product (X) was obtained by pouring on ice and vacuum drying the precipitated product. The impact sensitivity was 30 cm (RDX 28 cm), heat test (with KI) 5 min at 65.5°C and the relative viscosity was 1.6 cp at 25°C for 2% solution in acetone.

Nitroindene polymer (p.404)





$$\left[-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\overset{\mathrm{NO_2}}{\overset{|}{\mathrm{N}}}-(\mathrm{CH_2})_2-\underset{\mathrm{NO_2}}{\underset{|}{\overset{\mathrm{NO_2}}{\overset{|}{\mathrm{C}}}}}-(\mathrm{CH_2})_2-\overset{\mathrm{NO_2}}{\overset{|}{\mathrm{N}}}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{O}-\underset{\mathrm{C(NO_2)_3}}{\underset{|}{\underset{(\mathrm{CH_2})_3}{\underset{|}{\mathrm{CH}}}}}-\mathrm{O}-\right]_n$$

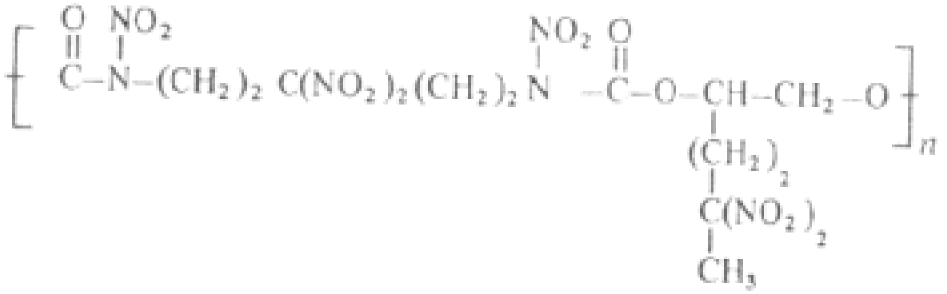
X

Some co-polymers of urethanes with diols after the nitration could also not stand the test at 134.5°C. One of them exploded after 11 min of heating.

The exception from the point of view of stability shows the nitrated polymer made of I and 5,5-dinitro-1,2-hexanediol. It is an amorphous powder, m.p. 55–65°C (XI) and is soluble in acetone. The polymer was prepared in two steps:

(a) the monomers were dissolved in dioxane and kept at 50°C for *ca.* 24 days. The product was precipitated with water.

(b) The polymer was nitrated with 100% nitric acid at 0°C. It was precipitated with water. The yield was 97%.

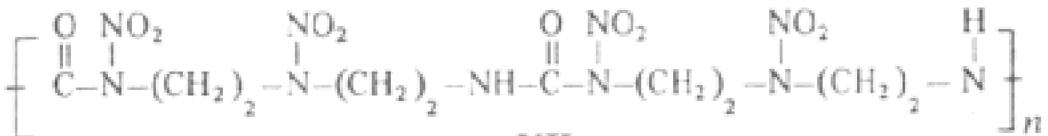


$$\left[-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\overset{\mathrm{NO_2}}{\overset{|}{\mathrm{N}}}-(\mathrm{CH_2})_2\,\mathrm{C(NO_2)_2}(\mathrm{CH_2})_2\,\overset{\mathrm{NO_2}}{\overset{|}{\mathrm{N}}}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{O}-\underset{\mathrm{CH_3}}{\underset{|}{\underset{\mathrm{C(NO_2)_2}}{\underset{|}{\underset{(\mathrm{CH_2})_2}{\underset{|}{\mathrm{CH}}}}}}}-\mathrm{CH_2}-\mathrm{O}-\right]_n$$

XI

Impact sensitivity was 100 cm (RDX 28 cm). Thermal stability: at 65.5°C (KI paper) 23 min, at 134.5°C no decomposition (methyl violet paper) in 5 hours.

Another product which may show some promise with regard to stability is nitrated urea derivative (XIV)



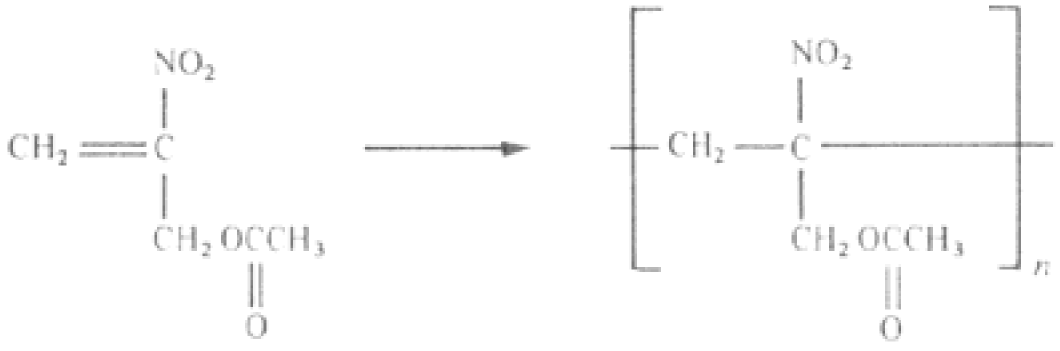
$$\left[-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\overset{\mathrm{NO_2}}{\overset{|}{\mathrm{N}}}-(\mathrm{CH_2})_2-\overset{\mathrm{NO_2}}{\overset{|}{\mathrm{N}}}-(\mathrm{CH_2})_2-\mathrm{NH}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\overset{\mathrm{NO_2}}{\overset{|}{\mathrm{N}}}-(\mathrm{CH_2})_2-\overset{\mathrm{NO_2}}{\overset{|}{\mathrm{N}}}-(\mathrm{CH_2})_2-\overset{\mathrm{H}}{\overset{|}{\mathrm{N}}}-\right]_n$$

XII

It is an amorphous solid, m.p. 80–90°C which was obtained by hydrolysing 3-nitro-3-aza-1,5-pentane diisocyanate with water followed by nitration.

C-NITRO POLYMERS FROM MONOMERS WITH A VINYL GROUP

Nitroallyl Acetate Polymer [3]



$$\mathrm{CH_2}{=}\underset{\mathrm{CH_2OCCH_3}\atop{\|\atop \mathrm{O}}}{\underset{|}{\overset{\mathrm{NO_2}}{\overset{|}{\mathrm{C}}}}}\longrightarrow\left[-\mathrm{CH_2}-\underset{\mathrm{CH_2OCCH_3}\atop{\|\atop \mathrm{O}}}{\underset{|}{\overset{\mathrm{NO_2}}{\overset{|}{\mathrm{C}}}}}-\right]_n$$

XIII

The monomer – nitroallyl acetate can be obtained from methyl nitrate and formaldehyde, followed by esterification and oxidation (1):

$$\mathrm{CH_3ONO_2} + 2\mathrm{CH_2O}\xrightarrow{\text{(gas phase)}}\mathrm{CHNO_2(CH_2OH)_2}\xrightarrow{\mathrm{CH_3COOH}}$$

$$\mathrm{CHNO_2(CH_2OOCCH_3)_2}\xrightarrow{[\mathrm{O}]}\mathrm{CH_2{=}C(NO_2){-}CH_2COOCH_3} \qquad (1)$$

XIII

The monomer has m.p. 17.5°C, b.p. (at 2 mmHg) 68°C.

It polymerizes on exposure to air at room temperature. The stability does not seem to be satisfactory – an explosion occurred after 10 min of keeping at 134.5°C.

Ethyl Nitroacrylate

$$\mathrm{NO_2\ CH = CH\ COOC_2H_5}$$

The compound was obtained by Yanovskaya, Stepanova and Kucherov [17] from formylacrylic acid ester and nitromethane. No information was given on the possible polymerization of the compound.

Nitroethyl acrylate

$$CH_2 = CH–COO\ CH_2CH_2NO_2$$

b.p. 100°C (5 mmHg)

This was one of the most simple acrylates obtained by Marans and Zelinski [18] (see also Chapter VIII). It can polymerize under the action of benzoyl peroxide at 100°C in the atmosphere of nitrogen. The polymer is a soft, viscous resin (contrary to the polymer of methacrylate which is hard).

Nitroethyl Methacrylate [18]

$$CH_2{=}\underset{\displaystyle CH_3}{C}–COO\ CH_2CH_2NO_2$$

b.p. 115°C (10 mmHg)

The compound gives a polymer when catalysed by benzoyl peroxide at 100°C in the atmosphere of nitrogen. The polymer is a hard resin.

Trinitroethyl acrylate

$$CH_2{=}CH–COOCH_2C(NO_2)_3$$

b.p. 80°C (2 mm)

This was obtained by Ville [19] by acting with acrylyl chloride on 2-trinitroethanol (Chapter VIII). No information was given on the possible polymerization.

Dinitropropyl Acrylate (DNPA) [3]

$$CH_2{=}CH\ COO\ CH_2C(NO_2)_2CH_3$$

m.p. 175°C, b.p. 96°C (0.2 mmHg)

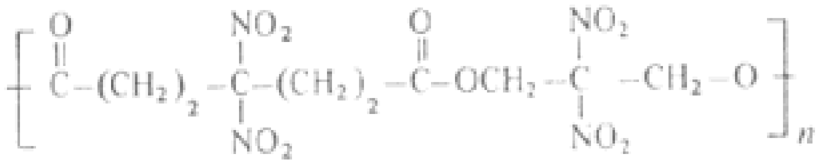
The monomer was prepared by dissolving 2,2-dinitropropanol and acrylic chloride in carbon tetrachloride and heating for 12 hours at 55°C. The dried product was mixed with powdered silver and vacuum distilled. It can be used as a binder in propellants burning readily at a pressure of *ca.* 70 kg/cm². It can be polymerized in toluene in the presence of azobisisobutyronitrile as a free radical catalyst, under dry nitrogen at 80°C for 45 min. The conversion of 25% was obtained to yield the polymer:

$$\left[CH_2–\underset{\displaystyle COOCH_2C(NO_2)_2CH_3}{CH}\right]_n$$

Poly-DNPA has an explosion temperature at 250°C, the detonation rate of 6100 m/s [19].

POLYESTERS OF DINITROCARBOXYLIC ACIDS AND DINITRODIOLS

The polymer of 4,4-Dinitro-1,7-Heptanediol Chloride and 2,2-Dinitro-1,3-Propanediol was described [20]:



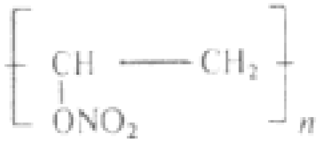
$$\left[\overset{\displaystyle O}{\overset{\|}{C}}–(CH_2)_2–\underset{\displaystyle NO_2}{\overset{\displaystyle NO_2}{C}}–(CH_2)_2–\overset{\displaystyle O}{\overset{\|}{C}}–OCH_2–\underset{\displaystyle NO_2}{\overset{\displaystyle NO_2}{C}}–CH_2–O\right]_n$$

The molecular weight of the polymer was 4000–9000, i.e. $n = 11–24$. It is a yellow coloured powder of m.p. 180–185°C.

It was prepared by dissolving equivalent amounts of the monomers in dioxane followed by maintaining the temperature of 30°C for 3 days. The solution was filtered, poured into water with ice and vacuum steam distilled to obtain the product. It shows a low sensitivity to impact: 2 kg at 85–95 cm (RDX 28 cm), and a good stability: at 65.5°C (KI paper) is 100 min, at 134.5°C (Methyl violet paper) – 80 min.

POLYMER WITH *O*-NITRO GROUPS

Polyvinyl Nitrate (PVN) (Vol. II, p. 173)



$$\left[\underset{\displaystyle ONO_2}{CH}–CH_2\right]_n$$

The polymer originally created certain hopes that it could replace (partly at least) nitrocellulose. The problem remains unsolved although a considerable amount of information on PVN was collected.

The following are references which should be added to those mentioned in Vol. II: Frank and Krüger [21], Chédin and Tribot [22], Auberstein and Laford [23], Akopyan and co-workers [24].

Properties of PVN

Chemical and physical properties. A rather detailed description of PVN can be found in the paper by Diepold [25]. Here are the data on properties of PVN according to this author:

Nitrogen content N 15.15% (which indicates the degree of esterification 92.8%). The other sources [29] gave 15.7% which is practically 100% nitration (99.8%).

Molecular weight M_w	200 000,
Viscosity of 0.5% solution in acetone at 25°C	0.45 cP
Included (or adsorbed) acidity	less than 0.005% HNO_3
Insoluble (in acetone)	max. *ca.* 1%
Colour	yellowish white
Size of grains	less than 1 mm
Density	1.6
Free flowing density	0.3

Hygroscopicity at 30%/90% relative humidity was 0.62% [27]

Softening temperature	30–40°C
Freezing temperature	30°C

Strength:

Temperature °C	On stretching	Breaking elongation
–40°	500 bar	0.4%
+20°	450 bar	0.8%
+40°	20 bar	400%

The plastic properties of PVN plastified with dibutyl phthalate or bis(2-fluoro-2,2-dinitroethyl) formal was examined by Michaud and co-workers [26] through pulsed NMR analysis. The purpose of this study was to find the different phases and to examine them in a function of concentration and temperature. The following were the phases found in the plasticized PVN: (1) a rigid polymer, (2) a mobile polymer, (3) a rigid plasticizer and (4) a mobile plasticizer. The work has a general significance on the insight of the nature of plastification and mobility of macromolecular chains and on the nature of the plastic flow and exudation.

Explosive Properties (according to [25])

PVN (15.15% N) shows the temperature of decomposition:

195°C when heated at the rate of 20°C/min,
177°C when heated at the rate of 5°C/min.

The induction period is 7 min and over 18 hours at 175° and 165°C respectively. According to Picatinny Arsenal [27] PVN (14.86% N) gives an explosion after 5 sec at 265°C.

The sensitivity to impact was 95 cm from a weight of 1 kg.

It is easily ignited and burns readily at the rate of 3 mm/s under pressure of *ca.* 6 kg/cm². The velocity of detonation slightly differs from those given in Vol. II, p. 173 [28] and according to [25] is:

density 0.3	*ca.* 3200 m/s
0.8	*ca.* 3500 m/s
1.5 (pressed)	*ca.* 6500 m/s
1.5 (cast)	*ca.* 7000 m/s.

Lead block of Trauzl 330 cm³.

The thermochemical data are as below:

Heat of explosion 960 kcal/kg [25] and 900 kcal/kg [27]
Heat of combustion 3016 kcal/kg [25] and 2960 kcal/kg [27]
Temperature of explosion 2560°C
Volume of gases 930/kg.

Stability was determined as the loss of weight of 0.3–0.4% at 75°C for 48 hours.

Picatinny Arsenal gave the following information on stability:

Heat test (KI) at 65.5°C was over 60 min., at 134.5°C (Methyl violet) 20 min., red fumes after 25 min., explosion after more than 5 hours.

The solubility of PVN largely depends on the degree of polymerization and hence on the viscosity. The larger the viscosity the lower the solubility.

The chemical stability of PVN was extensively studied by Poulain, Michaud and Poulard [29]. They examined polymers with the molecular weight M_w and molecular number M_n of the order of 150,000–320,000 and 120,000–140,000 respectively. They aged PVN at 90° and 65°C. They followed: (1) the decomposition of the nitrate groups, (2) the degradation of the chains followed by chromatography.

As much as (1) follows the usual trend of decomposition of nitrate esters including nitrocellulose, (2) offers a much more complicated picture which differs from that of nitrocellulose. This is the observation that during heating the length of chain of PVN decreases followed by a cross-linking. (Neither length of chains or cross-linking occurs during the ageing of nitrocellulose). This is depicted in Fig. 63 referred to PVN.

The French authors [29] also examined the stabilizing action of 2-nitrodiphenylamine upon PVN. The character of ageing at 90°C was not changed by the presence of the stabilizer.

Preparation of Polyvinyl Nitrate

Le Roux and Sartorius [28] (Vol. II, p. 173) gave the following method of nitrating polyvinyl alcohol.

Five parts of polyvinyl alcohol (containing 10% of moisture) were introduced during *ca.* one hour into 100 parts of nitric acid (99–100%) at –8°C. The result-

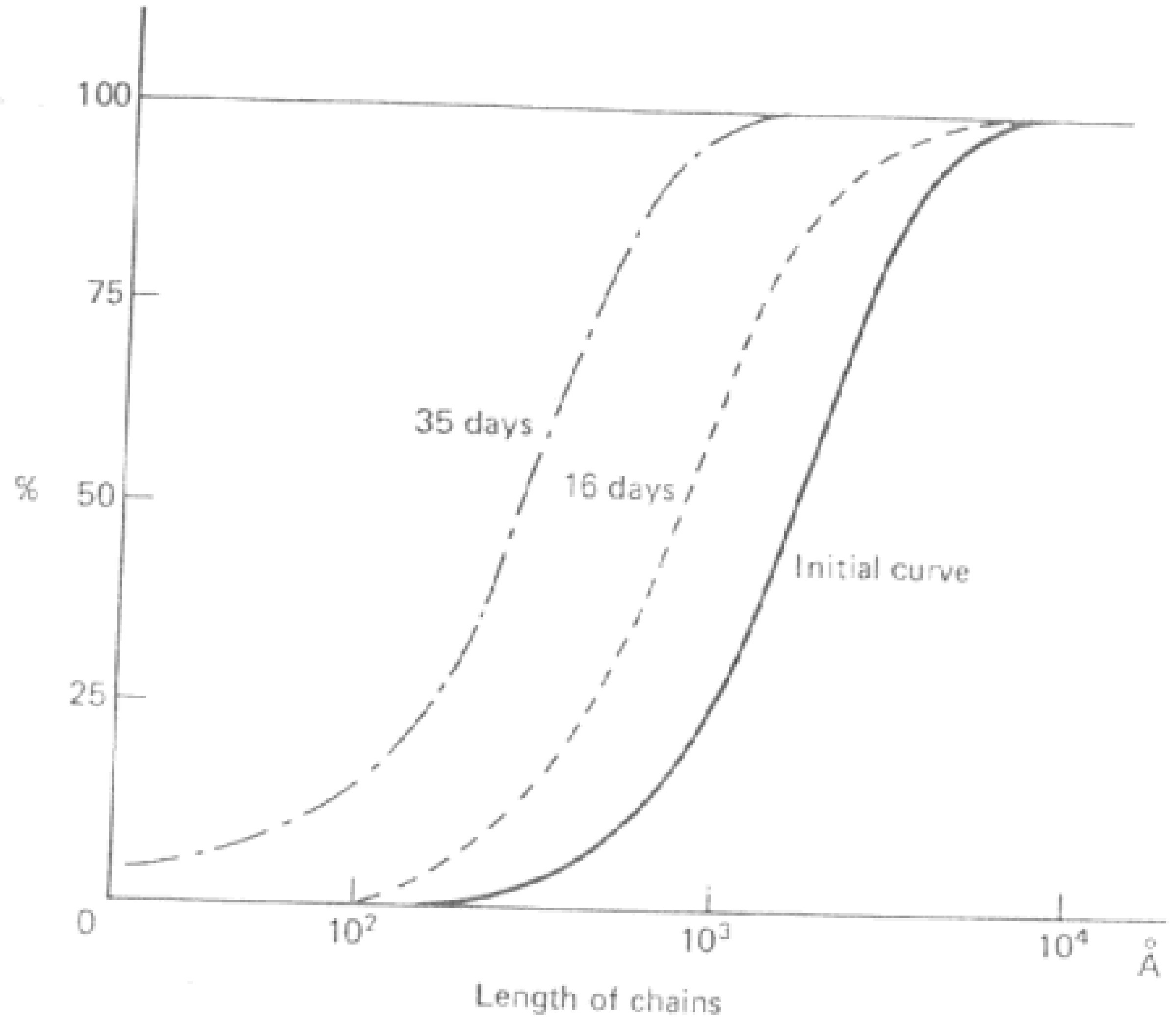


FIG. 63. Ageing of solutions of Polyvinyl Nitrate (PVN).

ing slurry was mixed for two hours and all was drowned into water with ice. The PVN white powder was washed with water to neutrality and left under water for 12 hours. The operation and standing for 12 hours was repeated with ethanol and eventually with 12% sodium bicarbonate solution. Final washing with water and drying yielded 96% of PVN.

The authors found that the determination of nitrogen in PVN in a nitrometer or by the Kjeldahl method did not give reliable results. It was necessary to use the Dumas method. According to Diepold [25] the method of titration with Fe II also gives reliable results.

The method of nitrating PVA at Picatinny Arsenal, U.S.A. [27] was as follows:

PVA was mixed with acetic anhydride, the mixture cooled to −5°C, a large excess of nitric acid was added keeping the temperature below 20°C. All was poured into cold water. The product was collected and purified by boiling in frequently changed water.

Diepold [25] described two methods of nitrating PVA: with nitric acid alone and with nitric acid/sulphuric acid mixtures.

Nitration with nitric acid. PVA was dissolved in nitric acid in proportion: Acid/PVA more than 20:1, otherwise the viscosity of the solution in nitric acid is too large to have an efficient mixing. The concentration of nitric acid should not be lower than 95%. The temperature should be kept near 0°C and the time: 15 min for introducing PVA into the acid, 30 min for the nitration and 15 min after the nitration at 20°C. The product was precipitated by pouring into water with ice. The yield was 90% of PVN with 14.8% N (the degree of nitration 88.7%), and the spent acid contained 50% HNO_3. This method does not seem to be sufficiently economic.

Nitration with nitric acid–sulphuric acid. The addition of a small proportion of sulphuric acid to nitric acid prevents dissolving PVA in nitric acid. A suspension of PVA in nitric/sulphuric acid mixture is formed. The yield of PVN is best when the concentration of H_2SO_4 in the mixed acid is 10–30% (Fig. 64). In such a mixed acid the solubility of PVN is negligible and the only substances dissolved in the acid are some degradation viscous products in quantity of 2–3%. They can be precipitated with water.

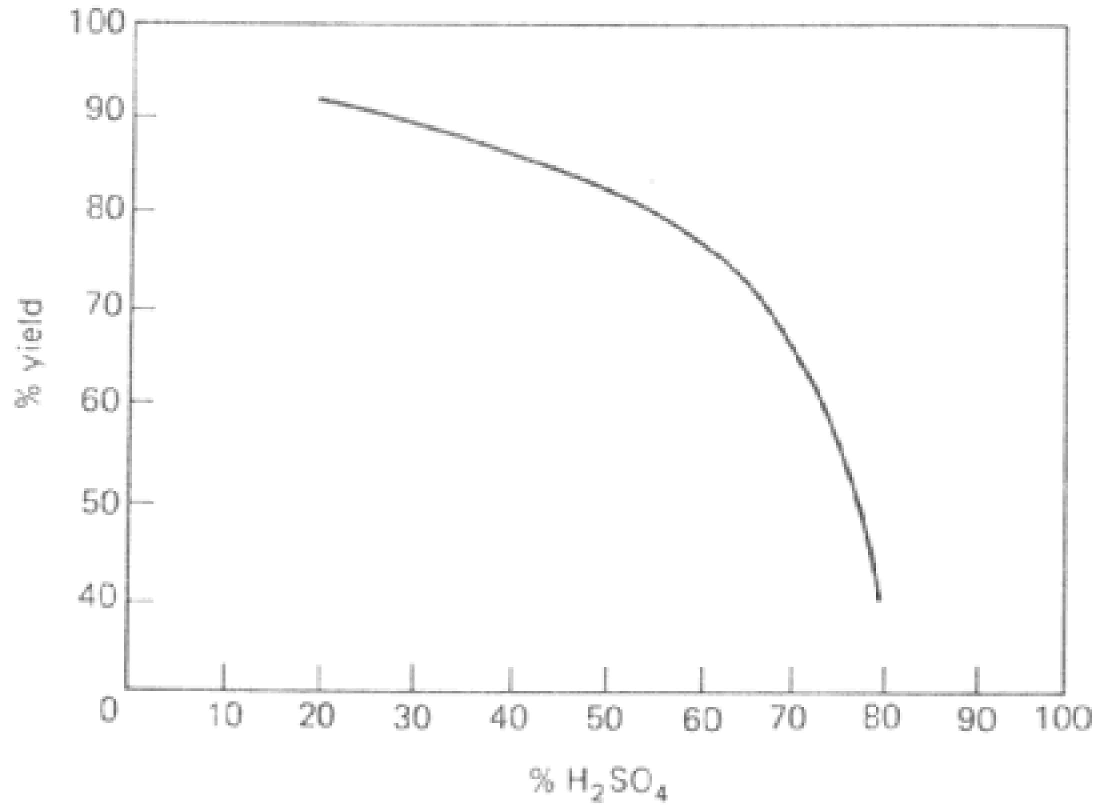


FIG. 64. Yield of PVN against the concentration of sulphuric acid in the mixed acid: $HNO_3 + H_2SO_4$.

A continuous method of nitrating PVA was described [30]. Owing to high viscosity of the solution the danger of overheating in some parts of the nitrator exists and: (1) a specially good mixing should be introduced, (2) the nitrating acid should be pre-cooled to −10°C. After the nitration is completed it is necessary to decant the acid which contains the above mentioned degradation products and to treat the product (free of the greater part of the acid) by adding water. The PVN formed fine hard grains which can be readily filtered.

The purification and stabilization of the PVN was carried out by washing the acid product with water of 60°C. At this temperature the product can soften and the grains can stick together. By adding some substances (the nature of which have not been disclosed) the sticking can be prevented and washing can be carried out even with boiling water. After the greater part of the acid has been removed the PVN should pass through a mesh filter to reduce the size of the grains and to make the removal of the last traces of the acid absorbed by PVN possible. The final product after the removal of water contained 60–70% water.

Diepold [25] gives the data as follows:

M_n	60,000–100,000
Nitrating mixture HNO_3 (1.51) H_2SO_4 (1.84)	90:10 to 70:30
Nitration temperature	0–10°C
Time of nitration	5–15 min
Stabilization	25–40 hours at 60°C.

The yield under these conditions should be 90% and the product should contain 14.8–15.1% N (i.e. degree of the nitration 88.7–92.2%).

A patent exists [31] for stabilizing PVN by dissolving the raw, decomposable PVN in an organic solvent which will be neutralized and then PVN, free of acid, will be precipitated by adding water. Calculations should be made to see whether the method is economically feasible.

Practical Use of Polyvinyl Nitrate

Experiments were carried out on PVN as a component of double base propellants PVN being used instead of nitrocellulose. *Encyclopedia of Explosives* [27] gives two compositions:

(1) with 82.0% PVN, 10.2% Nitroglycerine, 0.7% Dinitrotoluene, 6.1% Dibuthylphthalate 1.0% Diphenylamine,
(2) with 57.75% PVN, 40% Nitroglycerine, 1.5% KNO_3, 0.75% Ethyl Centralite.

Heat of explosion of these propellants was much the same as with nitrocellulose instead of PVN. However, the mechanical properties are different: decrease of tensile strength, increase of elongation at break and of flexibility. PVN did not change the burning rate, but increased the pressure exponent n ($V = k\, p^n$). Another disadvantage was that:

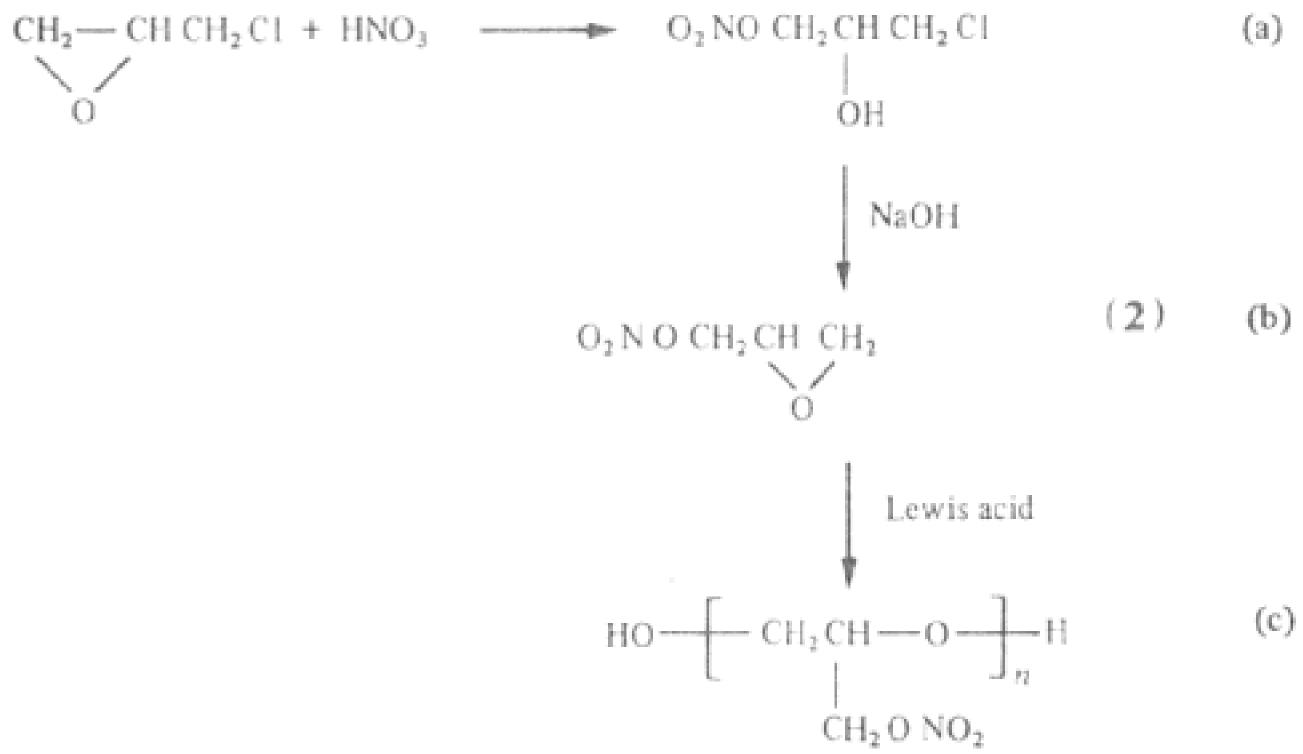
(1) atactic PVN which has a low melting point has a tendency to flow when mixed with other substances, (2) atactic PVN possesses a sticky nature which has created problems in extruding and shaping propellant grains.

The problem arises of how to obtain the isotactic polymer of PVN with high regularity and higher crystallinity. However, this does seem to be possible [32].

Modifications of Polyvinyl Nitrate

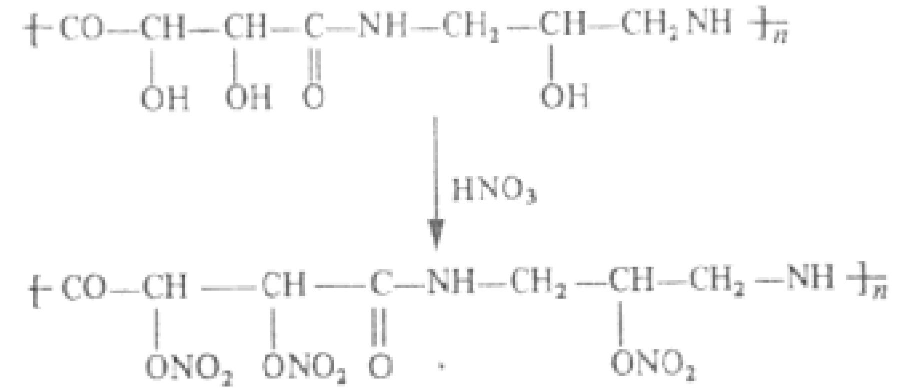
A Naval Powder Factory in the U.S.A. investigated the preparation of polyvinyl nitrate by nitration of polyvinyl acetate using epichlorohydrin as a cross-linking agent – according to Cohen [33].

The same source [33] informs us that the U.S. Naval Ordnance Test Station and Jet Propulsion studied the preparation and polymerization of glycidyl nitrate:



n – was 20–50 and hydroxyl terminated polymers could be cured with mixtures of diol, triol and diisocyanates.

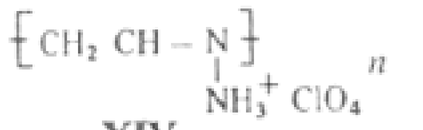
The Naval Powder Factory, according to [33] obtained *O*-nitro polymers of a relatively low molecular weight:



$$\left[-CO-\underset{OH}{CH}-\underset{OH}{CH}-\underset{\overset{\|}{O}}{C}-NH-CH_2-\underset{OH}{CH}-CH_2NH-\right]_n \xrightarrow{HNO_3} \left[-CO-\underset{ONO_2}{CH}-\underset{ONO_2}{CH}-\underset{\overset{\|}{O}}{C}-NH-CH_2-\underset{ONO_2}{CH}-CH_2-NH-\right]_n \qquad (3)$$

HYDRAZINE AND DIFLUOROAMINE POLYMERS

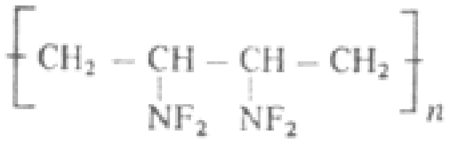
According to Cohen [33] (Bell Aerosystem Corp. and Food Machinery Corp.) obtained polyethylene hydrazine perchlorate (XIV)



$$\left[CH_2\,CH-\underset{NH_3^+\,ClO_4}{N}\right]_n$$

XIV

Information is given by the same source on a polymer with difluoroamino groups (XV) obtained by Rohm and Haas Corp.



$$\left[CH_2 - \underset{NF_2}{CH} - \underset{NF_2}{CH} - CH_2 \right]_n$$

XV

Pentaerythritol trinitrate (PETriN) is a convenient source of polymers through the esterification with unsaturated vinyl group containing acids, such as acrylic and methacrylic acid.

The monomers were described in Vol. II, p. 191 and Chapter X.

N-NITRO POLYMERS

A few polymers with *N*-nitro compounds were described in Chapter XIII of this book: formulae (17) and (19).

PLASTIC BONDED EXPLOSIVES (Vol. III, p. 203)

A considerable number of explosives are composed of Cyclonite and HMX and non-explosive plastic (usually thermoplastic) polymers. Some recent compositions are given below on the basis of the literature [34]:

	Density	Rate of detonation m/s
1. Cyclonite/Polyamide resin 90/10	1,79	8390
2. HMX/DNPAF/Polyurethane (DNPAF is acetyl-formyl-2,2-dinitropropanol)	1,84	8830
3. HMX/Teflon 90/10	1,86	8640
4. HMX/Polyethylene 92/8	1,72	8630

5. American plastic explosive:
   Cyclonite/Polyisobutylene/2-ethylhexyl sebacate/mineral oil in proportions 91/9.1/5.3/1.6 does not lose its plasticity at −54°C and retains its shape at +75°C.
6. British 'flexible' explosive SX-2 [35]:
   Cyclonite/polyisobutylene/Teflon in proportions 88/10.5/1.5 retains its plasticity at −58°C.

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CHAPTER 15

RECOVERY OF SPENT ACIDS

(Vol. II, P. 83)

The problem of recovery of spent acids has existed since the advent of nitration of glycerine and the problems of safety related to keeping the spent acid which contained a certain amount of nitroglycerine (Vol. II, p. 84, Fig. 26). The separation of nitroglycerine which can float on the surface of the spent acid created a safety problem. The method of Nathan, Thomson and Rintoul (Vol. II, p. 85) increased safety by preventing the formation of nitroglycerine on the surface. Although a small proportion of nitroglycerine is lost by solution and decomposition, the economy is satisfactory, as no costly investment is needed for the recovery of nitroglycerine from the spent acid.

However the methods being used at present for the manufacture of nitroglycerine, such as batch combined process (Vol. II, p. 95) and all continuous processes (Vol. II, p. 97) require that spent acid be dealt with correctly. Originally primitive arrangements were in use consisting in distillation of nitric acid and careful decomposition of organic products dissolved in the spent acids.

The progress was considerably speeded up with the advent of cast silicon iron as the main acid-resistant metal [1]. Some other modern materials were also introduced into the construction of the equipment, such as enamel, tantalum, teflon [1] and glass [2]. Generally speaking the spent acid from nitration of glycerine, glycols and pentaerythritol have a lot in common although they differ in some particular points. The common problems of by-products of the nitration of alcohols will be discussed below.

GENERAL PROBLEMS OF SPENT ACID FROM THE NITRATION OF ALCOHOLS

This particular problem was studied by Camera, Zotti and Modena [3, 4]. They identified some of the products of the action of nitrating acid on ethyl nitrate as a model for the behaviour of nitrate esters in acid solution. They came to the conclusion that the initial process consisted in hydrolysis of the ester. The hydrolytic equilibrium was disturbed by oxidation of the alcohol by liberated nitric acid. In the instance of ethyl nitrate the freed ethanol was oxidized to acetaldehyde. Some other products were also formed. Nitric acid was reduced to nitrous acid which can serve as a catalyst of a number of reactions. Among the other products formed were: acetic and oxalic acids, carbon dioxide and nitrogen oxides from nitrous acid: NO_2, NO, N_2O and nitrogen.

Spent Acid from Nitration of Glycerine

According to Plinke [1] the average composition of spent acid of nitroglycerine is

HNO_3	10%
H_2SO_4	70%
H_2O	17%
Nitroglycerine	3%

Compared with the composition given in Vol. II, p. 84 it differs only by the presence of 3% of nitroglycerine. This should be regarded as all organic matters deriving from the nitration of glycerine, the hydrolysis of nitroglycerine, oxidation of the resulting mixtures etc., much in terms of the work of Camera *et al.* [3, 4].

There are three known methods of dealing with nitroglycerine spent acid:

(1) Stabilization or
(2) denitration of the acid [1],
(3) re-use of nitrating acid after adding nitric acid [5].

1. Stabilization of Spent Acid according to Plinke [1]

This method is applied when the spent acid has to be re-used without the danger of keeping it for any length of time. To destroy nitroglycerine and organic impurities the acid is conveyed at a high temperature through a number of columns where nitroglycerine and other organic substances are oxidized by nitric acid. Nitric acid is reduced to nitric oxides which are directed to the absorption column washed with water yielding dilute nitric acid.

The diagrammatic presentation of the apparatus is given in Fig. 65. Nitrator (1) is fed with nitrating mixture and glycerine, nitroglycerine is separated (7) from the spent acid which enters columns (2–4). The columns are heated with steam through a heat exchanger (9). The acid freed of oxidized organic substances is cooled in (10) and flows out. Gaseous products – mainly nitrogen oxides and carbon dioxide – pass through a cooler (11) and enter column (5). Air is blown (8) into the column where cold water (12) circulates through a pump (6) and is injected additionally to the top of the column (5). Dilute nitric acid flows from the column.

2. Denitration of Spent Acid

(A) According to Plinke [1]. The spent acid can be denitrated without adding

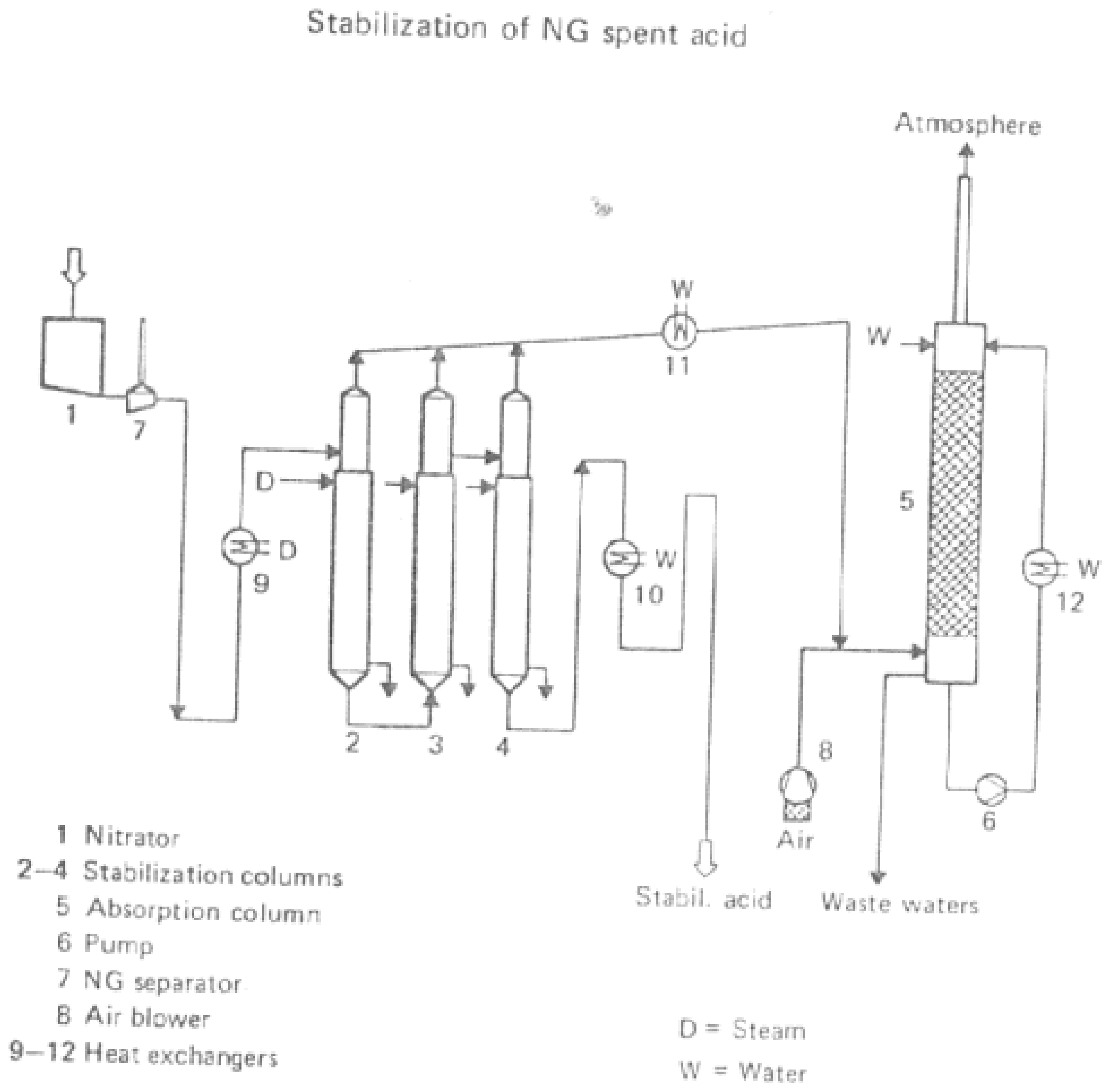


FIG. 65. Stabilization of spent acid of glycerine nitration. (Courtesy H. Plinke [1].)

other acids and nitric acid of 10% can be obtained. By adding sulphuric acid of 85–96% and (in some cases) 60% nitric acid a highly concentrated nitric acid of 98% HNO_3 can be obtained and sulphuric acid of 70% H_2SO_4. All organic compounds are destroyed and gases from decomposition (nitric oxides, nitrogen, carbon dioxide) are liberated from pre-bleaching and bleaching column. The scheme for the treatment of spent acid is given in Fig. 66.

Spent acid from (1) after separation of nitroglycerine (9) enters denitration column (5). If necessary, some nitric acid (60% HNO_3) is added from container (2). Sulphuric acid (85–96% H_2SO_4) is fed from container (3) to the top of the denitration column (5). The temperature of the denitration column is controlled by injecting steam and air. Sulphuric acid (68–72% H_2SO_4) freed of nitric acid and gaseous products is collected in tank (4) and pumped out (8). Distilled nitric acid enters pre-bleaching column (6) where it is freed of nitrogen oxides through dephlegmator (10). Pre-bleached nitric acid enters bleaching column (7) where air is blown through (11) to free the acid from the traces of nitric oxides entering through (10). Here nitric acid flows back to column (6) and gases are blown into the air. A system of heat exchangers (12–20) serves for heating or cooling and keeps the proper temperature – high or low. Nitric acid of 98 HNO_3 flows through valve N 98 to a tank. After bleaching nitric acid contains less than 0.1% nitrous acid.

General views of the denitration plant are given in Figs 67–69.

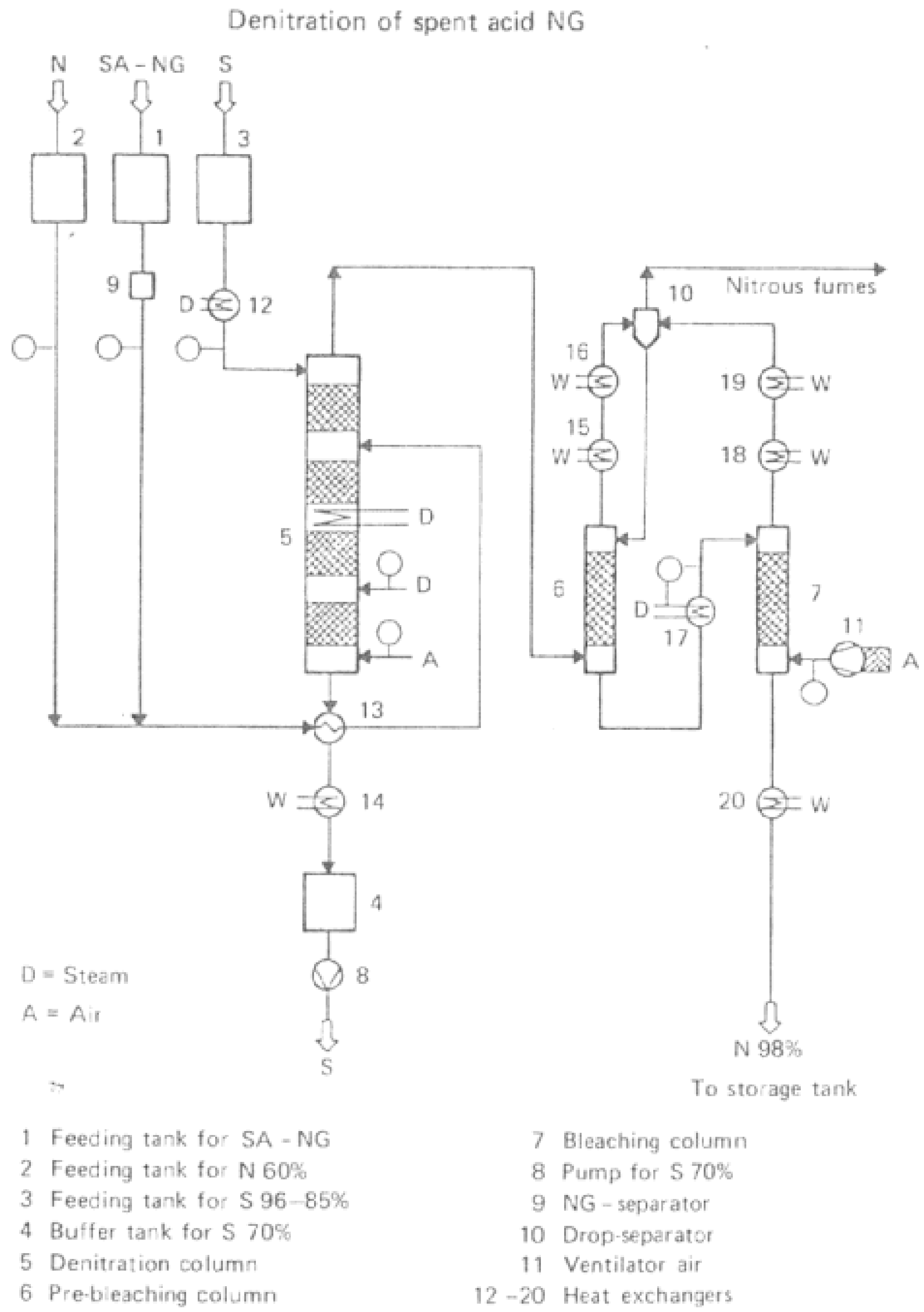


FIG. 66. Denitration of spent acid of glycerine nitration. (Courtesy H. Plinke [1].)

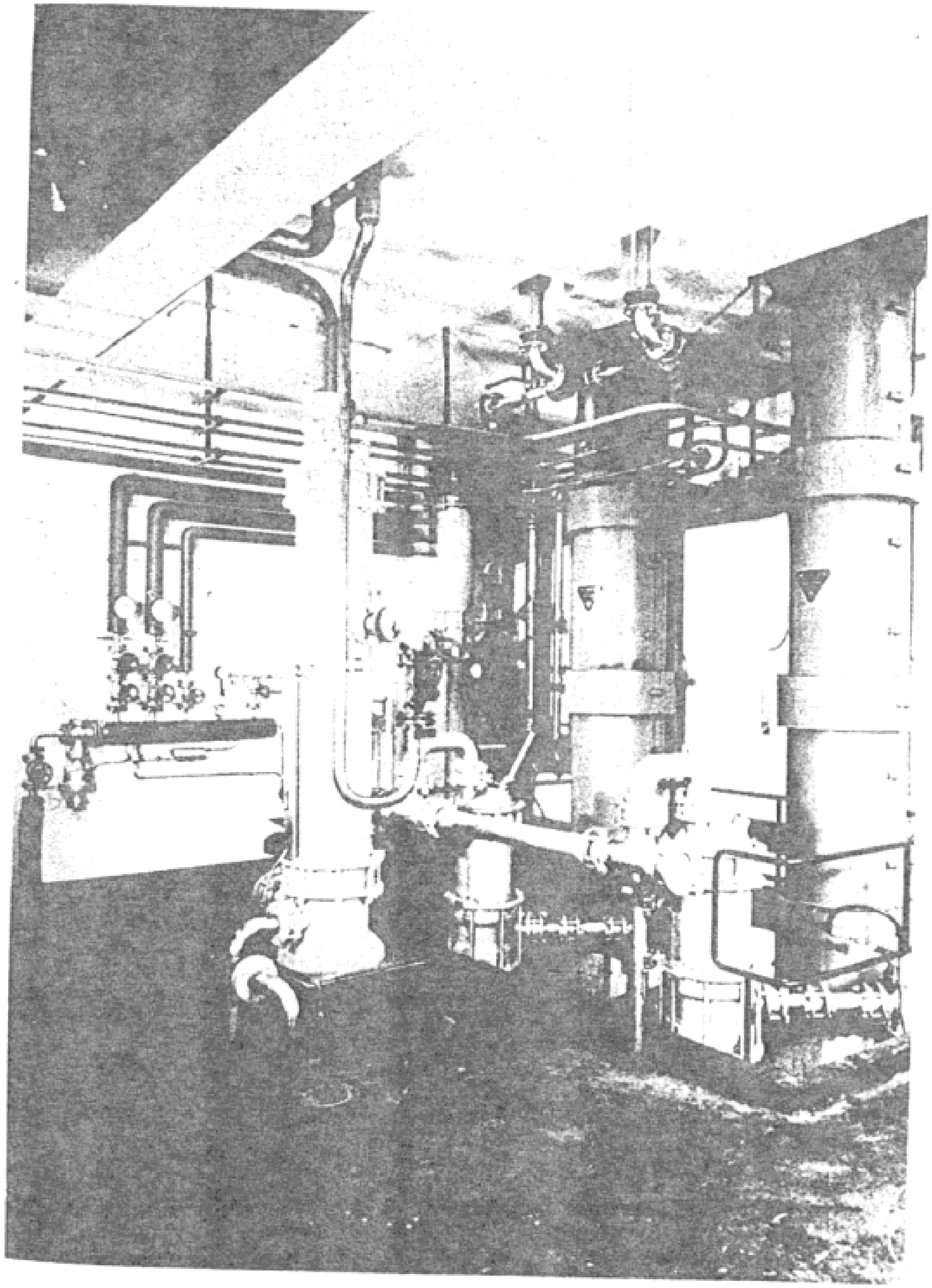


FIG. 67. Denitration of spent acid of glycerine nitration and nitric acid bleaching. (Courtesy 'Adolf Plinke Söhne', D-6380 Bad Homburg.)

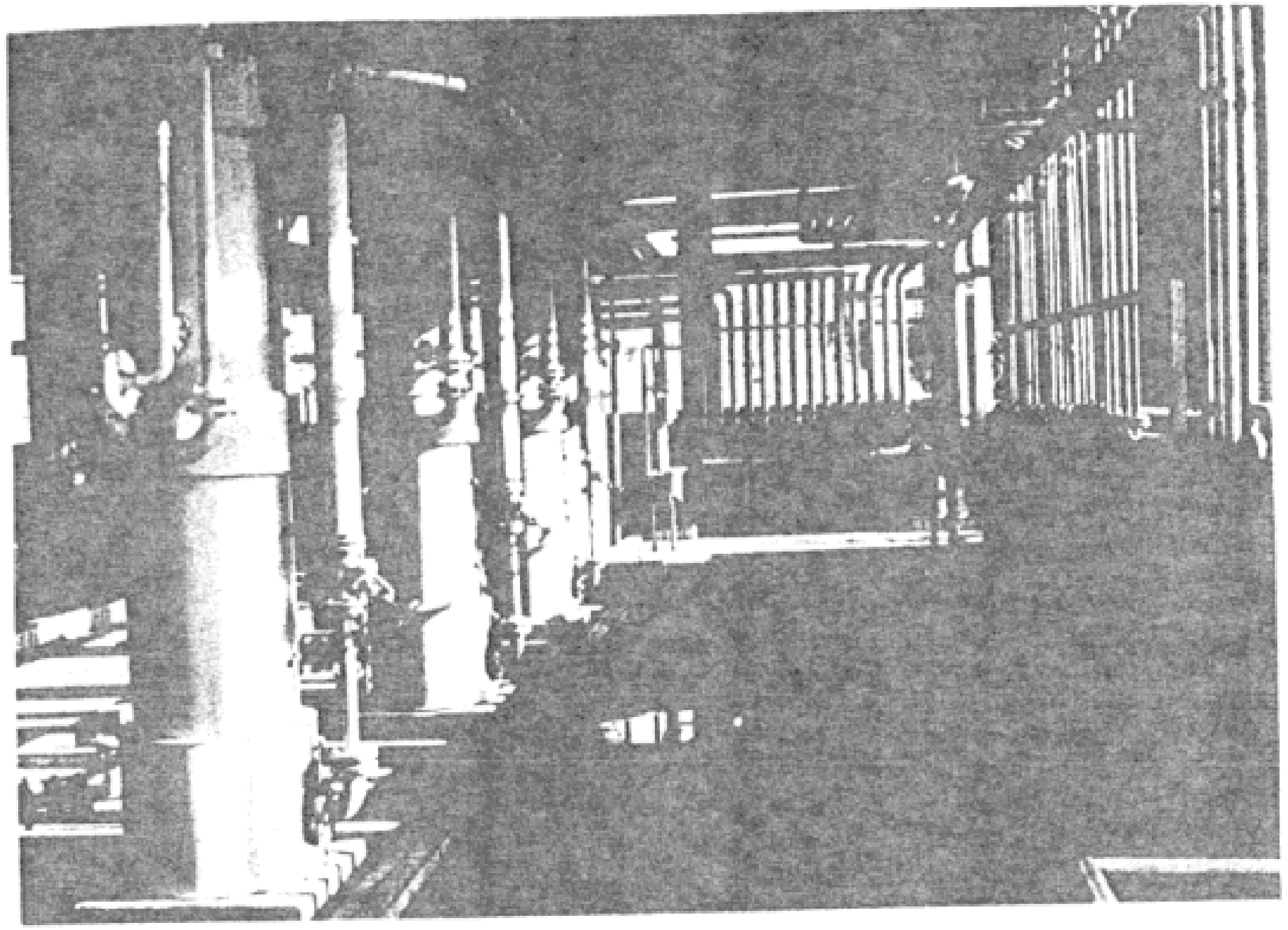


FIG. 68. Denitration of spent acid of NG, NC, NT. (Courtesy 'Adolf Plinke Söhne', D-6380 Bad Homburg.)

(B) According to Schott, Mainz [2, 6–8]. The progress of the method of concentrating nitric acid with sulphuric acid was connected with the use of borosilicate glass as a material for the construction plants in combination with tantalum as a heater material to carry out indirect heating of the concentration column [6]. This method of operation was realized by Messrs Schott & Gen., Mainz, who used tantalum heat exchangers on which the acid mixture was sprayed. The exchanger was mounted on the top of the concentration column where the greatest part of the nitric acid is. The heat exchangers are heated by saturated steam and evaporate the major part (*ca.* 90%) of the nitric acid contained in the mixture. Figures 70–72 give general views of some parts of the equipment. An important feature was the introduction of standardized dimensions which make possible the exchange of some parts of the equipment.

3. Re-use of Spent Acid from the Nitration of Glycine

Biazzi S.A. [5] is using an ingenious method of utilizing spent acid from the nitration of glycerine to nitrate toluene to dinitrotoluene. Toluene is added to the spent acid at a temperature gradually increasing up to 90°C. Nitroglycerine

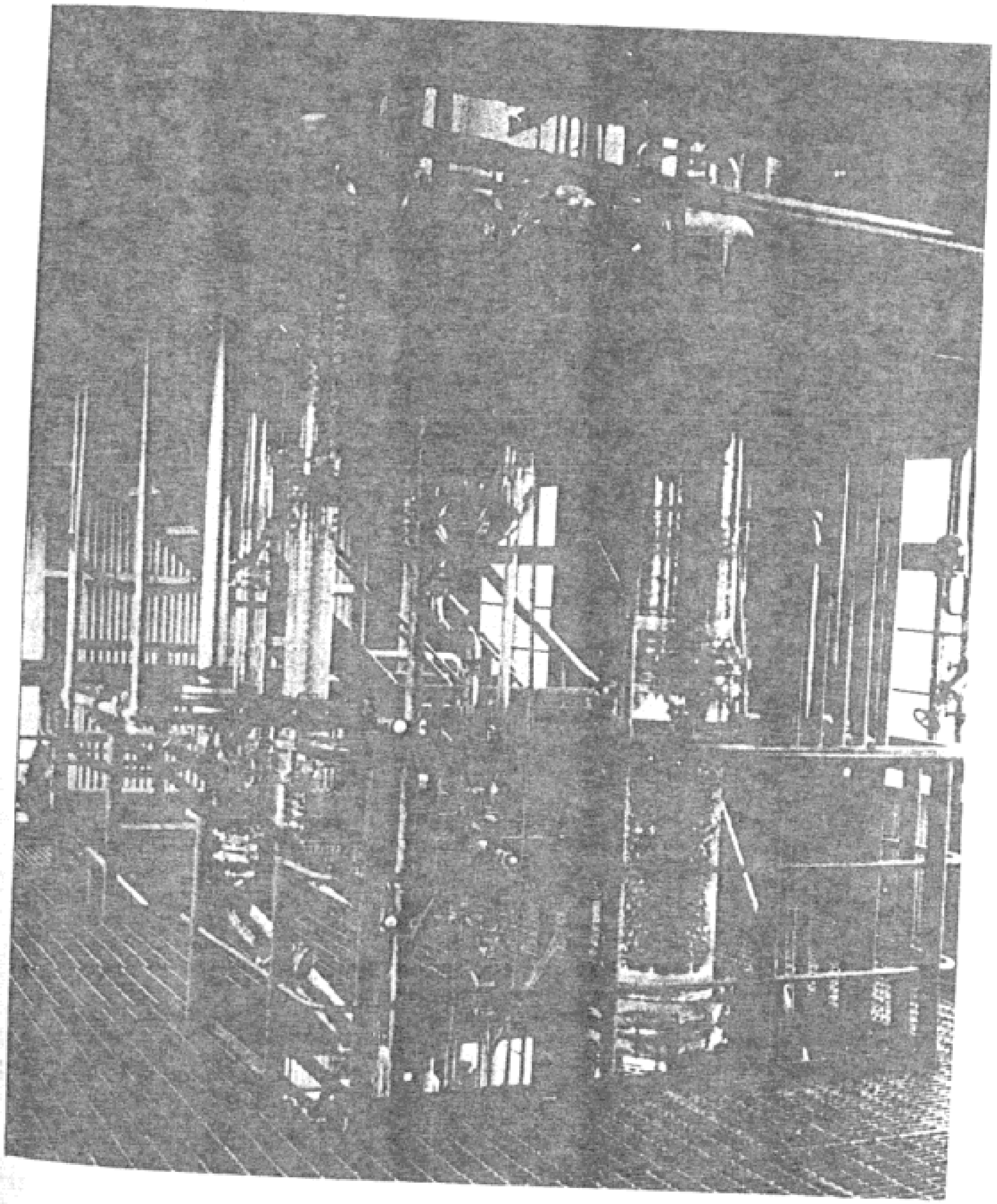


FIG. 69. Denitration and concentration of HNO_3. (Courtesy 'Adolf Plinke Söhne', D-6380 Bad Homburg.)

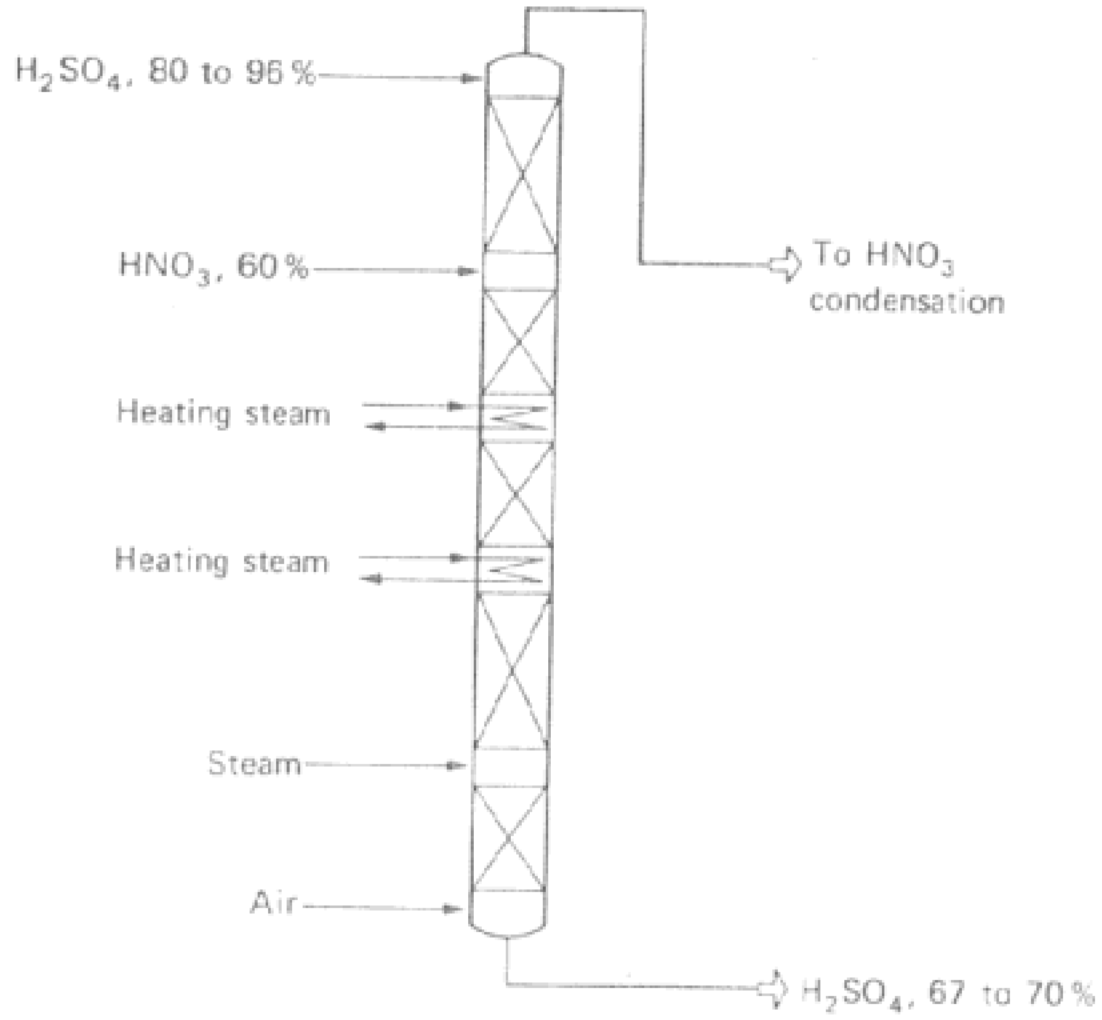


FIG. 70a. Concentration column. (Courtesy Schott & Gen., D-6500 Mainz.)

dissolved in the acid is decomposed and increases the concentration of nitric acid and thus participates in the nitration.

The economy of this method is based on the fact that no denitration plant is needed.

Spent Acid of PETN

The main problem of spent acid after the nitration of pentaerythritol is the instability of the spent acid. Several 'fume off' accidents of spent acid have occurred on its storage after the separation of PETN. Systematic study of the stability of spent acid was carried out by Ramaswamy and Subba Rao [9]. They found that the concentration of 75–80% HNO_3 made the nitric acid unstable due to the presence of organic compounds which can readily be subjected to oxidation. According to the above authors the oxidizing properties of nitric acid predominate at the critical concentration of 75–80%.

Ramaswamy and Subba Rao suggested two methods of stabilizing the spent acid of PETN manufacture.

(1) In the first method live steam of low pressure was injected gradually to keep the temperature at 70 ± 2°C. The injection was stopped when no further

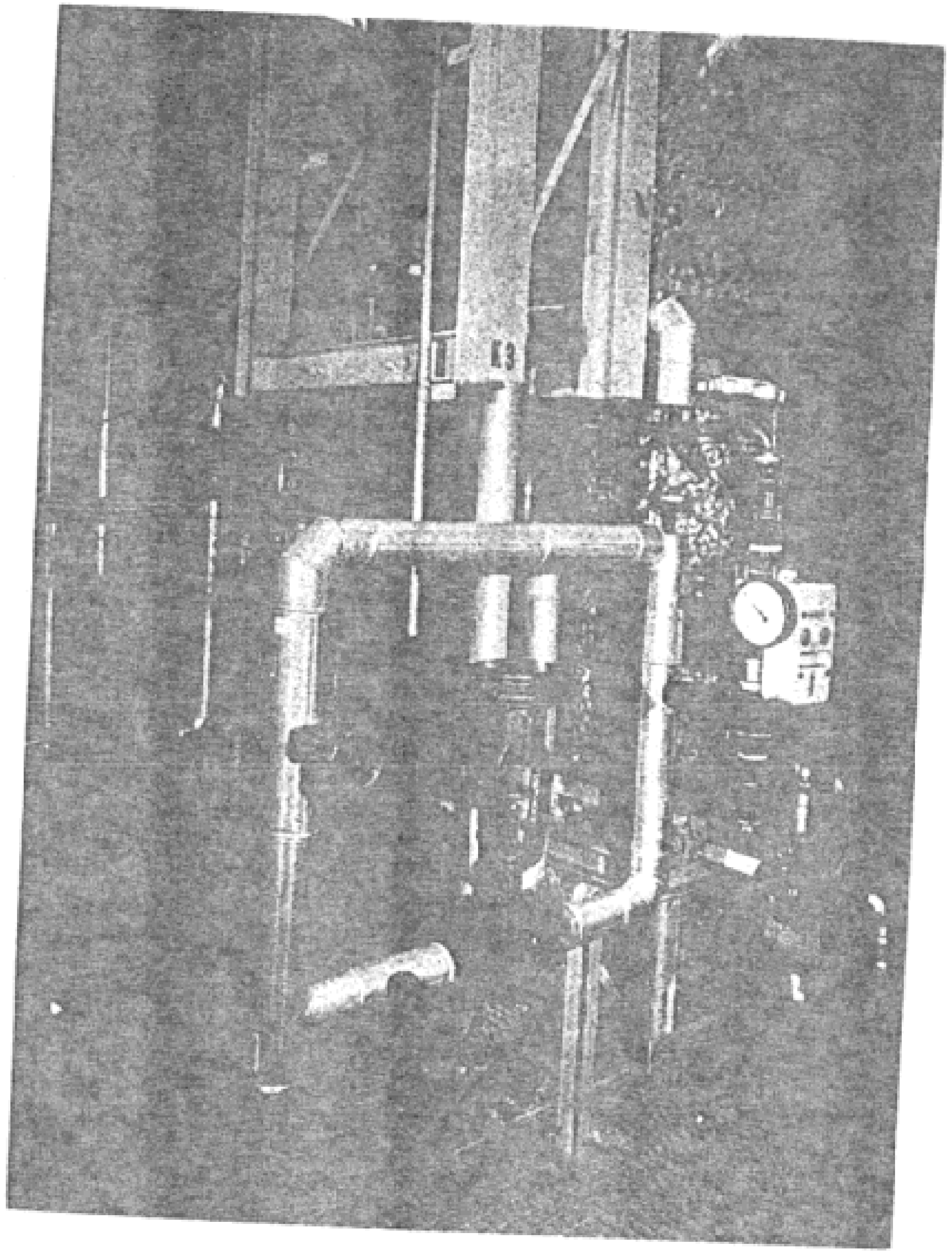


FIG. 70b. Concentration column. (Courtesy Schott & Gen., D-6500 Mainz.)

exothermic reaction was noticed. The concentration of the spent acid falls from 82 ± 2% to 72 ± 2% HNO_3, thus below the dangerous concentration.

(2) In the second method the spent acid was treated with steam so that its temperature was raised to 95–100°C. A highly exothermic and vigorous reaction was accompanied by an evolution of brown fumes and stirring was necessary by blowing in nitrogen or air. The reaction was facilitated by the presence of nitrous acid. The higher the concentration of HNO_2 the lower the temperature of the reaction.

In the normal process of PETN production the content of nitrous acid and organic by-products is below 0.2% and 0.3–0.4% respectively. Ramaswamy and Subba Rao pointed out the ease of hydrolytic reactions in the spent acid, followed by oxidation. They found formic, oxalic and mesoxalic acid among the decomposition products.

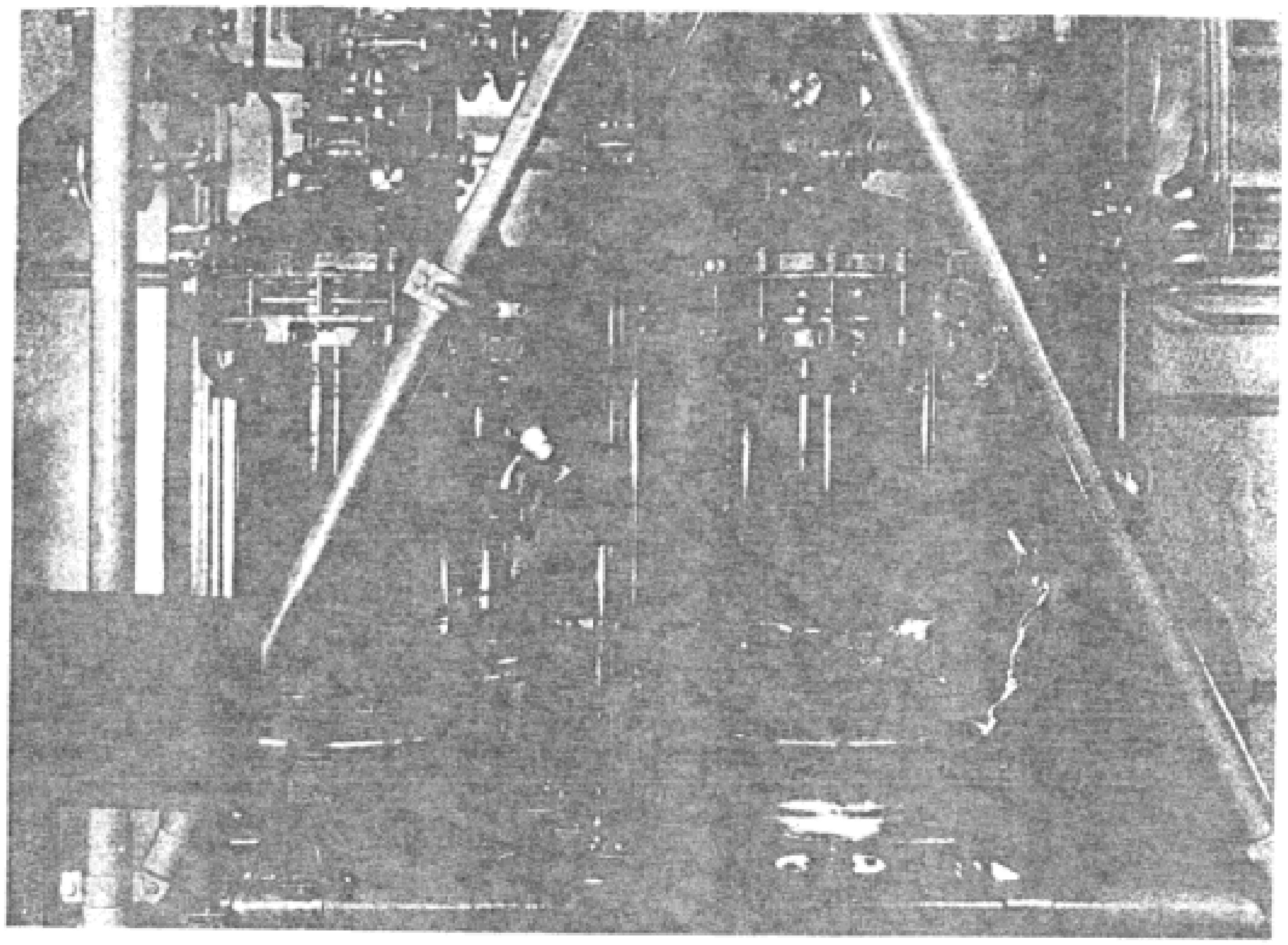


FIG. 71. Heat Exchanger made of standardized parts.
(Courtesy: Schott & Gen., D-6500 Mainz.)

Attention should be drawn to the statement by Camera [10] that PETN can be hydrolysed to tri and di-nitrate by nitric acid of 70–90% HNO_3 at 20 and 40°C (see also Chapter X, ref. 149). The unsymmetrically substituted pentaerythritols are particularly apt to vigorous reactions [11].

Plinke [1] described the process of stabilizing spent acid of PETN which, according to the same author contains 80% HNO_3 and 0.1–0.3% organic substances. The spent acid is distilled in a circulation evaporator to completely destroy organic substances and to obtain pure nitric acid. To reach the full decomposition of organic impurities, sulphuric acid of 70% H_2SO_4 is present in the evaporator and remains there to the end of the operation.

Figure 73 is a diagram of the stabilization of residuary nitric acid of PETN according to Plinke. Spent acid from (1) is pumped (4) to evaporator column (3) after being heated at (6). Hot sulphuric acid (70%) flowing from column (3) is cooled at (7) and recirculates to (3). Nitric acid distils from column (3), is cooled through a condenser (8), collected in tank (2) and pumped out through (5). This is nitric acid of 75–80% HNO_3. Nitrous gases escape between (8) and (2).

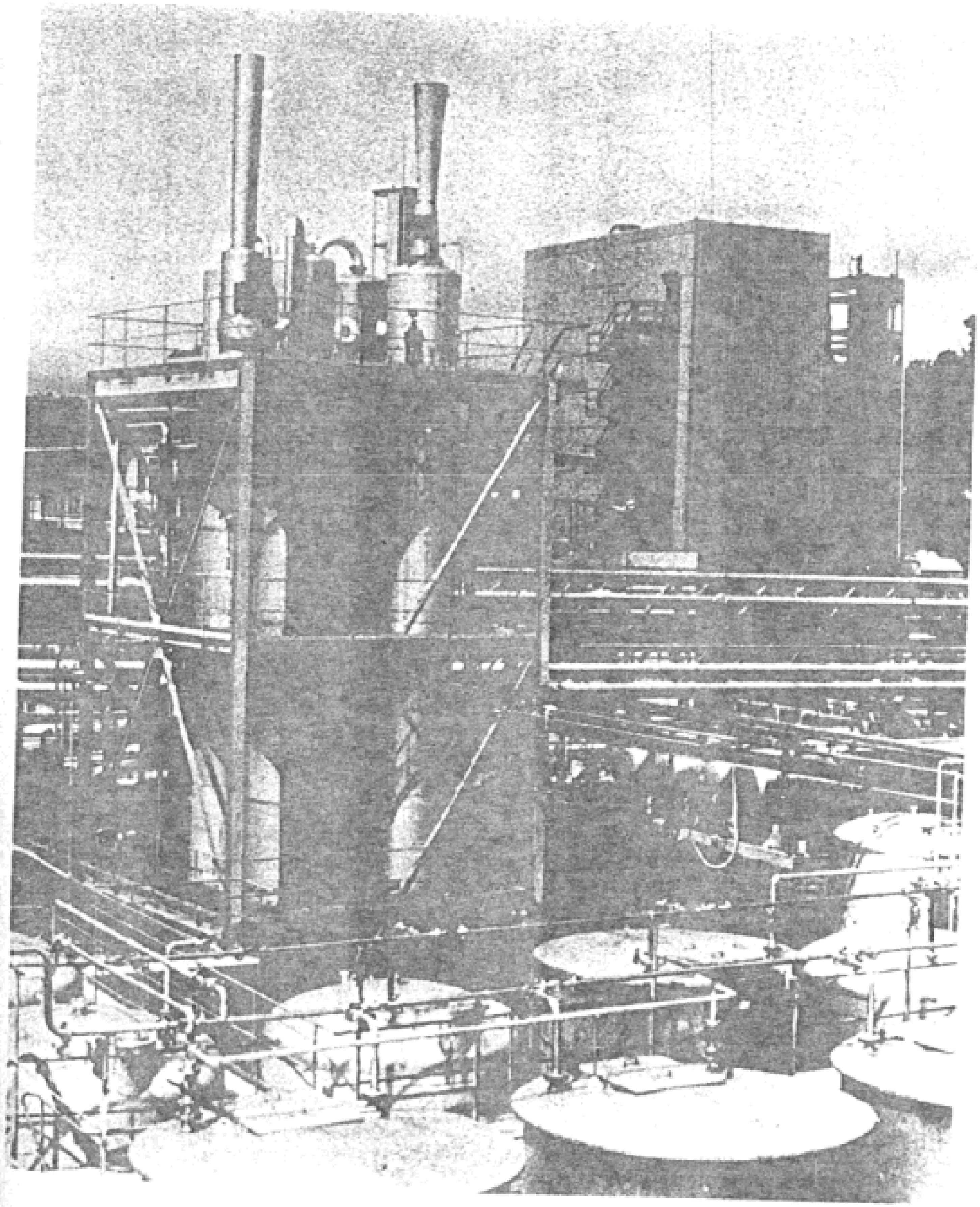
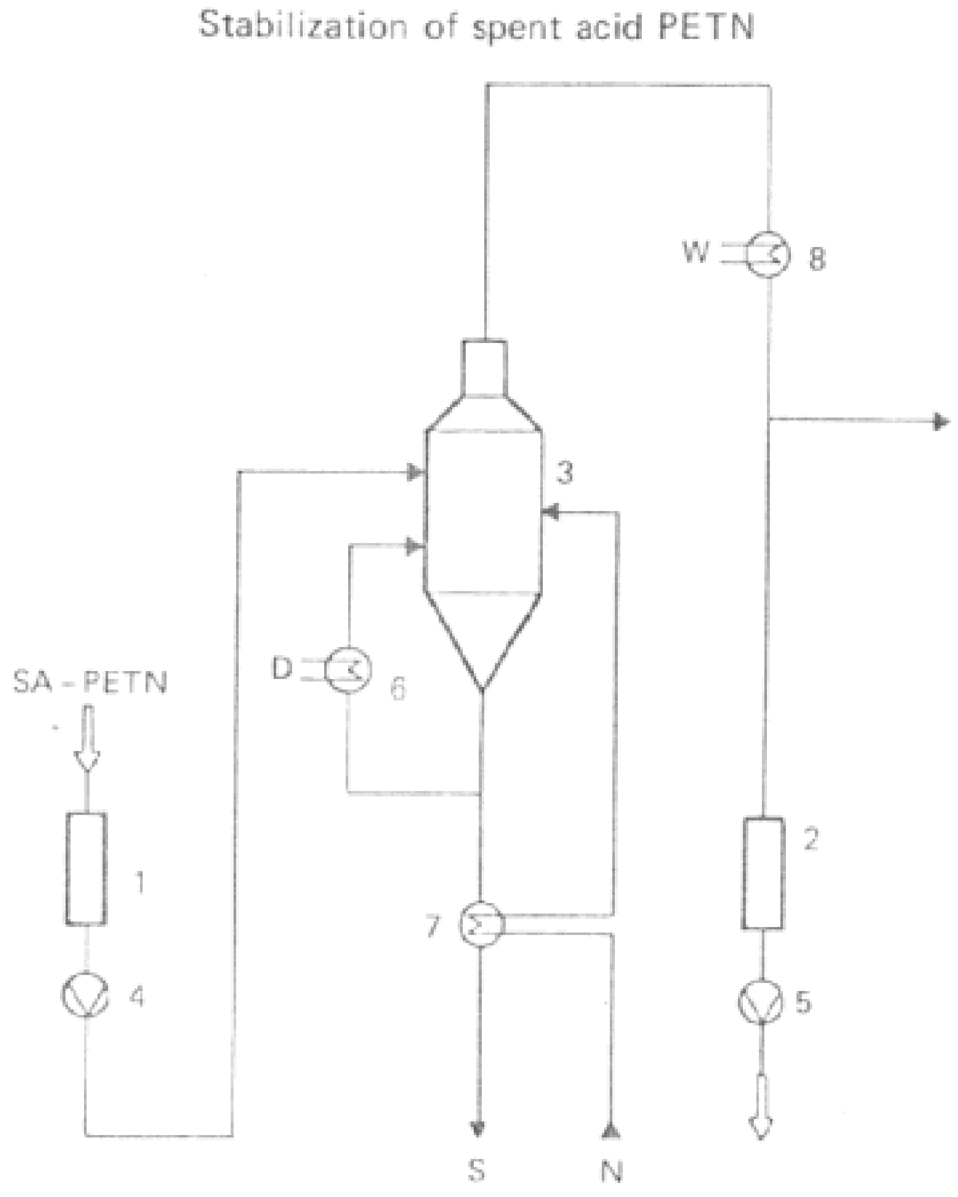


FIG. 72. General View, nitrous fumes absorption.
(Courtesy 'Adolf Plinke Söhne', D-6380 Bad Homburg.)



1 Tank for SA - PETN
2 Tank for N 75 - 80%
3 Evaporator column
4 Pump for SA - PETN
5 Pump for N 75 - 80%
6 Heater for evaporation
7 Heat exchanger for cooling S
8 Heat exchanger for cooling N 75–80%

D = Steam
W = Water

FIG. 73. Stabilization of spent acid of PETN.
(Courtesy, H. Plinke [1].)

Spent Acid from Cyclonite (RDX) Manufacture
(Vol. III, pp. 93, 98–102)

As described in Vol. III Cyclonite can be made by nitrating hexamine (hexamethylenetetramine) with nitric acid. The product is precipitated by pouring the solution into hot water in such a way that the concentration of the acid became 50–55% HNO_3 and the temperature 70–90°C was maintained. All unstable products were decomposed and NO_2 was evolved. This was a 'degassing process'.

A diagram of the concentration of spent acid obtained in that way was given by Plinke [1] Fig. 74. Spent acid from tank (1) enters through heat exchanger

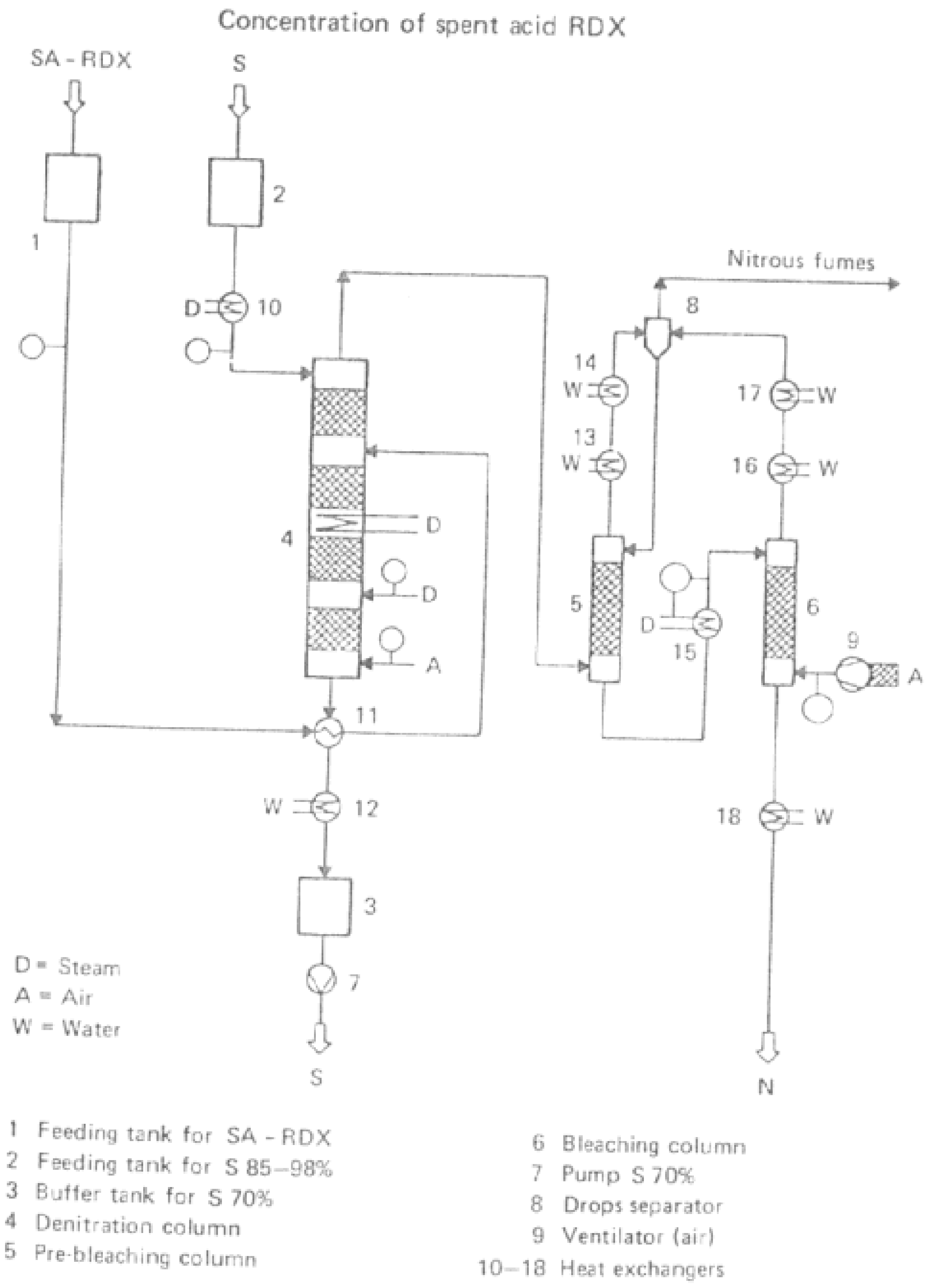


FIG. 74. Concentration of spent acid of Cyclonite (EDX).
(Courtesy H. Plinke [1].)

(11) to the denitration column (4). The column is fed from tank (2) with sulphuric acid (85–95%) pre-heated in (10). The column is supplied with steam and in the lower part – with air. Sulphuric acid (70%) flows down to a buffer tank (3) and through pump (7) to a storage tank. Distilled nitric acid enters the pre-bleaching column (5) and through a dephlegmator (8) to bleaching column (6). Air is blown to the bottom of the bleaching column (6) to help in evacuating nitrous fumes through (8). A series of heat exchangers (12–17) maintain the correct temperature for the whole system. Nitric acid (98%) leaves column (6) through cooler (18) to a storage tank.

Spent Acid from Nitrocellulose (Vol. II, p. 374)

Plinke [1] gives the average composition of spent acid from the nitration of cellulose: 22% HNO_3, 62% H_2SO_4, 15.8% H_2O, 0.2% nitrocellulose. Highly concentrated nitric acid can be distilled from such an acid without adding sulphuric acid. If sulphuric acid (85–86%) is added, the process is similar to that described in Fig. 74.

This operation is seldom performed and the usual procedure consists in adding concentrated nitric and sulphuric acid to the spent acid.

Spend Acid from TNT

It is very seldom that spent acid from TNT is subjected to distillation. If so, only dilute nitric acid can be obtained according to Plinke [1]. A higher concentration of nitric acid (over 50% HNO_3) can result only after adding concentrated sulphuric and nitric acid. The apparatus is much the same as with the following.

Spent Acid from Mononitration of Toluene

It has been pointed out by Dębowski and Ziółko [12] that the spent acid from mononitration of toluene should not be reused for dinitration by adding nitric and sulphuric acids. It contains 0.3–0.5% mononitrotoluenes and while adding concentrated nitric and sulphuric acids, further nitration of mononitrotoluene present can be produced but requires special precautions.

The authors suggested a simple method of dealing with the spent acid. They extracted the nitro compounds with toluene at 30°C and thus were formed:

(1) toluene with a small proportion of nitro compounds,
(2) spent acid free of nitro compounds.

Toluene (1) can be used for nitration, and (2) spent acid can be safely mixed with concentrated nitric acid and 20% oleum and re-used for mononitration of toluene.

ENVIRONMENTAL PROBLEMS OF DENITRATION

The denitration of spent acids offers some environmental problems. The major one being the escape of nitrous fumes from the denitration columns. According to Berkman [13] they can be introduced to a solution of sodium hydroxide to obtain sodium nitrate and nitrate aqueous solution. The same monograph describes the method of absorption with water [14]. It also gives a description of the industrial method by Andrew and Hanson [15].

An original method was proposed by Kulin and Tikhonenko [16]. They suggested the reduction of nitrogen oxides escaping from the denitration column with methane, for example:

$$CH_4 + 2\,NO_2 \longrightarrow N_2 + CO_2 + 2H_2O$$

$$CH_4 + 4\,NO \longrightarrow 2N_2 + CO_2 + 2H_2O.$$

The reaction can be catalysed by Ni and Cr at 500–600°C and helped by adding some air-oxygen.

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CHAPTER 16

SALTS OF NITRIC ACID

(Vol. II, p. 450)

AND OF OXY-ACIDS OF CHLORINE

(Vol. II, p. 476)

AMMONIUM NITRATE

As is well known ammonium nitrate is the most popular oxygen carrier in explosive mixtures which is also widely used as a fertilizer. Subsequently there is voluminous literature on the properties of ammonium nitrate. Among the greatest problems is its caking. It continues to raise interest and an excellent review has appeared recently [1].

Hygroscopicity of ammonium nitrate was considered to be the major cause of caking [2–5] but later the polymorphism of crystals of ammonium nitrate (IV ⇌ III, Vol. II, pp. 450–452) was recognized as an important factor [6–8]. Particular attention should be paid to the work of Sjölin [8] who studied the phenomenon of caking using X-ray and scanning electron microscopy. His conclusions are summarized as follows: caking is mainly caused by the phase transitions IV ⇌ III at 32°C and depends on dissolution and recrystallization of the solid at the phase transition. If no pressure is applied to the sample a porous powder is formed due to volume increase [14], if pressure is applied, it will result in large crystal surfaces and the dissolution–recrystallization process gives a hard product.

Shneerson *et al.* [7] drew attention to the fact that transition IV → III does not cause caking while the phase transition III → IV is of great importance and should be regarded as essential in the process of hardening. Thus hardening occurs during the process of cooling ammonium nitrate heated above 32°C.

Some substances have a great influence on the change IV → III. Particularly important is the role of water promoting the change [9–13]. Thus it has been shown by Brown and McLaren [10], Wolf and Scharre [11] that ammonium nitrate chemically pure and free of water requires a higher temperature for the transformation of form IV and at *ca.* 50°C it is directly transformed into form

II, whereas a trace of water favours the normal transformation IV → III at 32°C.

The above mentioned volume increase was described in the important paper by Hendricks *et al.* [14] and in Vol. II (p. 452, Table 110).

As the result of repeated transitions IV ⇌ III breakdown may occur of crystals or prills yielding fine particles which are readily caking through the absorption loss of moisture.

The paper by Thompson [15] should be mentioned as pointing out the importance of the capillary adhesion which can be the major factor responsible for the caking phenomenon narrow layer of the saturated solution between the particles shows a lowered meniscus of the solution, i.e. reduced pressure. Consequently the action of atmospheric pressure becomes sufficiently strong to compress the neighbouring granules into a solid block.

It can be seen from the above discussion that the phenomenon of caking is very complicated with several factors involved in it and there is practically no sufficiently simple explanation of the phenomenon. Subsequently no simple practical solution exists for preventing the phenomenon of caking ammonium nitrate and only a partial solution is known.

Some existing practical methods were mentioned in Vol. II, pp. 453–454. A more systematic description is given below:

1. Covering particles of ammonium nitrate with non-hygroscopic layers of polymers, such as polyvinyl compounds. This however should be limited to substances which could not produce harmful influence on the explosive properties of ammonium nitrate and (for underground work) would not give harmful products after detonation, such as chlorine compounds from polyvinyl chloride.

These conditions are fulfilled with paraffin wax or fuel oil if such an ammonium nitrate is used in explosive mixtures where the above substances are included in the formulation of the explosives. As pointed out in Vol. II (pp. 461–2) small amounts of organic substances increase the ease of detonation of ammonium nitrate and danger of shipping.

2. Non-reactive mineral compounds, such as kaoline in powder form in proportion 2.5% [4]. Carbonates should not be advised as they can react with ammonium salts to form unstable ammonium carbonate. Also silicates are not advised as they can produce silicium oxide which is dangerous in underground work as a cause of silicosis.

3. Salts of stearic acid, such as calcium stearate.

4. Addition of anhydrous salts readily forming hydrates, such as anhydrous: $Mg(NO_3)_2$ (1%) and $Al_2(SO_4)_3$ (2%) [8]. In some patents anhydrous sulphates have been claimed.

Among the agents preventing the transformation of crystalline forms three methods are of great importance (in addition to keeping the ammonium nitrate dry):

1. Introduction of some cations which could enter the crystalline lattice, such as K^+ which has an ionic radius (1.33Å) of the same order as NH_4^+ (1.43Å). The presence of 3–4% KNO_3 suffices to stabilize form III (Vol. II, pp. 454–5).

2. Introduction of some mineral substances. Among the minerals kaoline or kieselguhr in quantity 2.5% were suggested [4]. Brown, Green and Blanton [16] recommended adding a mixture of boric acid, diammonium phosphate and ammonium sulphate in quantity of less than 0.5%. They suggested a composition containing 0.2% H_3BO_3, 0.2% $(NH_4)_2HPO_4$ and 0.01% $(NH_4)_2SO_4$. Prills of unprecedented hardness resulted, completely stable over 32°C transitions. The authors found this mixture much superior to previously used kaoline or kieselguhr. Engel [17] found that the volume increase due to the phase transitions IV ⇌ III at 32°C was reduced by incorporating diammine complexes of Ni and Cu into the lattice. The transition temperature raised above 50°C. The effect of complexes of Zn was less marked.

Glazkova in her monograph [18] described water resistant ammonium nitrate 'Zh V' containing 0.07–0.10% 'iron sulphate' and 0.3–0.4% of an undisclosed hydrophobic component.

3. Addition of surface active agents, such as triphenylmethane dyestuffs, can prevent caking of ammonium nitrate in quantity as low as 0.05% (see Vol. II, p. 454) and [19].

It is now accepted that surface active substances are very helpful as anticaking agents. A review was published on the subject by Kołaczkowski and Biskupski [108]. Sodium alkylarylsulphonates and various substances with trade names were examined in quantity 0.05–0.50%. The authors draw attention to the fact that before the use of such substances experiments should be carried out on the influence of the additives on thermal stability of ammonium nitrate. Some of them appreciably lower the temperature of the decomposition of ammonium nitrate which should not be less than 220–240°C. It should also be borne in mind that the addition of an organic substance or (generally speaking) of a substance which can burn increases the sensitivity of ammonium nitrate to detonation. Small amounts, of the order of 1–4% of organic substances considerably increase the sensitiveness (Vol. II, pp. 461–462 and the description of accidents on p. 441, this volume). Thus the sensitivity to detonation of ammonium nitrate with surface active agents should be examined and mixtures with additives should be handled with precaution as with explosives.

Hygroscopicity of Ammonium Nitrate

The hygroscopicity of ammonium nitrate is its great drawback. The problem occurred particularly with the use of ammonium nitrate mining explosives their storage and use in damp places. The usual method of reducing hygroscopicity consists in incorporating small proportions of calcium, zinc and iron salts of fatty acids, usually stearic acid.

Silicon resins can also be used (Vol. III, p. 421). The problem of the hygroscopicity of ammonium nitrate is discussed in Chapter XIX on Mining Explosives.

Chemical and Explosive Properties

Andreev and Glazkova [20] carried out pioneering work on the action of various substances on the rate of burning ammonium nitrate. In their later paper [21] they examined the influence of the addition of various salts to ammonium nitrate on its rate of burning – Table 71.

TABLE 71. Rate of burning of ammonium nitrate in a closed vessel. Density of the samples 1.6–1.7 g/cm³ [21]

Addition of 10%	Mean pressure atm	Mean rate of burning g/cm³, sec.	Relative rate of burning
Pure NH_4NO_3	190	0.53	100
NaCl	357	1.43	270
KCl	335	1.27	240
K_2Cr_2	363	1.47	270
$K_2Cr_2O_7$	292	1.17	220
$BaCl_2$	322	1.57	290

Obviously the rates of burning are also influenced by different pressures in the closed vessel and therefore the figures cannot be taken as strictly comparable. Nevertheless higher rates of burning of mixtures containing barium chloride, potassium bichromate and sodium chloride are evident.

According to Rosser, Inami and Wise [74] ammonium bichromate, soluble in molten ammonium nitrate, was found to be a catalyst of the decomposition of ammonium nitrate at temperatures 460–520 K. For low concentration of the catalyst the principal products of decomposition were N_2, N_2O, H_2O, HNO_3. The catalysed decomposition was inhibited by ammonia and water, promoted by nitric acid.

The finding of Andreev and Glazkova [21] is interesting in that ammonium nitrate containing potassium bichromate can burn faster by adding potassium and ammonium oxalate, under low pressure (3 atm), but under higher pressure of the order of 300–400 atm. the presence of oxalates reduces the rate of burning.

The problem of burning ammonium nitrate and its mixtures is widely described in the excellent monograph by Glazkova [18]. The problem is not only of great theoretical but also of practical importance. It is connected with the use of ammonium nitrate explosives in coal-mines and their ability to burn which creates an additional danger of their use. In the present book it is discussed in Chapter XIX on Mining Explosives.

Some organic substances (e.g. cellulose) lower the thermal stability of ammonium nitrate. According to Findlay and Rosebourne [22] an ammonium nitrate–paper combination was shown to self heat at the temperature range used in bagging and shipping the fertilizer grade of NH_4NO_3, so that it often arrived at a sea-port appreciably hotter than when it was bagged (90 ± 20°C). Bag imprittlement and even charring by self-heating caused excessive spillage, contamination and required rebagging. Several spontaneous fires in rail trucks were recorded, preceding the Texas City catastrophe [23]. Immediately after the Texas City catastrophe the paraffin-wax coating of ammonium nitrate was replaced by kieselguhr – an inferior but much safer anticaking agent. Kieselguhr coated ammonium nitrate (fertilizer grade) was widely in use for AN/FO explosive mixtures [23].

A detonation of 80 tons of ammonium nitrate in plastic bags occurred in 1978 at Manouba in Tunisia [39]. The floor of the store house was covered with saw dust for the purpose of absorbing any liquid from broken bags. It was stated that saw dust mixed with oxidizing substances in the presence of moisture can undergo fermentation causing a temperature rise and ignition of ammonium nitrate. Prior to the detonation red fumes came from the store house, which indicated the beginning of the decomposition which ended in detonation.

HYDRAZINE NITRATES (Vol. II, p. 464)

Two hydrazine (or hydrazinium) nitrates are known: mono- and dinitrate.

Hydrazine Mononitrate

Mononitrate $NH_2\overset{+}{N}H_3\overset{-}{N}O_3$ exists in two forms: α and β. α-Form is stable and has m.p. 70.7°C, β-form is unstable, has m.p. 62.1°C [24]. β-Form is obtained by keeping the substance at 110°C for 30 min and cooling slowly to 61°C. The crystal structure was examined, and so were refractive indexes of α and β-forms: 1.065 and 1.458 respectively [25]. If a concentrated solution of β-form is cooled from 100°C down to room temperature α-form was separated [26]. The transformation enthalpy ΔH of form β to α is 2.0 kcal/mol [27]. Thermal decomposition was studied by a number of authors. At 100°C the evolution of ammonia is less prominent than that of ammonium nitrate: 0.005% as compared with 0.016% [28]. Shidlovskii and co-workers [29] found that the decomposition started at 180°C, increased above 240°C and became explosive at 270°C. The 'Bruceton up- and down-down' method (Vol. III, p. 445) gave 50% probability of ignition at 307°C [27]. Decomposition to 200–300°C under 1 atm. resulted in decomposition according to equation [30]:

$$4\,N_2H_4\cdot HNO_3 \longrightarrow 2\,NO + 5\,N_2 + 10\,H_2O. \qquad (1)$$

Decomposition *in vacuo* was investigated by Breisacher and co-workers [31].

When ignited, hydrazine nitrate burns very readily, the flame is extinguished upon removal of the ignition source. Shidlovskii *et al.* [29] found that the addition of 10% $K_2Cr_2O_7$ assures steady burning.

Thermochemical and some explosive data were collected by R. Meyer [32]:

enthalpy of formation	−620.7 kcal/kg
heat of explosion	924 kcal/kg
volume of gases	1001 l/kg
oxygen balance	+8.6%
density	1.64 g/cm^3
decomposition temperature	229°C.

High lead block test (408 cm^3) and velocity of detonation (8690 m/s) were given.

The high figures of the velocity of detonation and of lead block aroused much interest in the compound and have been reported by several authors.

Thus explosive properties were reported by H. K. James *et al.* [27]: the rate of detonation of molten hydrazine nitrate 75°C was found to be 8500 m/s, and ballistic mortar 120.4 ± 0.5 (picric acid = 100) or 142 (TNT = 100).

Some other authors also reported [32] high velocity of detonation: 8500–8510 m/s with cartridges of 6.4 cm diameter, pressed to density 1.59–1.6. Price [33] found that the infinite charge diameter detonation velocity can be expressed by the equation $D = 5390$ ($\rho\ HN\cdot 100$) where $\rho\ HN$ is the density in g/cm^3. Kurbangalina and Tinokhin [34] found that the critical diameter increases with an increase of water content and the rate of detonation can vary from 2000 to 8000 m/s.

Meyer [32] reported that mixtures of hydrazine nitrate with HMX (Octogen) pressed to high density can be over 9000 m/s.

Attention should be drawn to two monographs on hydrazine: [26] and [30].

Hydrazine Dinitrate

(Vol. II, p. 465)

Hydrazine dinitrate $NH_2NH_2(HNO_3)_2$ was described by Sabanejeff [35]. It is a substance which decomposed at *ca.* 80°C. When heated rapidly it melts at 103–104°C. It can be obtained by neutralizing hydrazine hydrate with two moles of nitric acid or by acting barium nitrate on hydrazine sulphate [26], [30]. It decomposed on steam bath or on standing at room temperature over sulphuric acid with the evolution of hydrazoic acid [35].

It is an explosive which is stronger, but less sensitive to impact, than Tetryl but weaker than PETN [33]. However owing to its low stability it is of little practical value.

Hydrazine Nitrate Complexes ('Hydrazinates')

Salts of bivalent metals (Ni, Co, Zn, Cd and Mn) form complexes with hydrazine nitrate of a general formula

$$\underset{\text{I}}{[M(N_2H_4)_2](NO_3)_2} \quad \text{and} \quad \underset{\text{II}}{[M(N_2H_4)_3](NO_3)_2}.$$

For the first time Ni salts (II) were obtained by Franzen and Meyer [36] and a number of them were prepared by Médard and Barlot [37]. According to the latter authors some of hydrazinatés possess initiating properties and are described in Chapter XVII on initiating explosives.

METHYLAMINE NITRATE (Vol. II, p. 465)

Methylamine nitrate (m.p. 111°C) recently gained much significance as an important ingredient of 'slurry' explosives because of its greater aptitude to detonation than that of ammonium nitrate. More data on explosive properties were recently given by R. Meyer [32]:

enthalpy of formation	−896 kcal/kg
heat of explosion	887 kcal/kg (the given figure formerly – 1200 kcal/kg – Vol. II, p. 466 – should be corrected as being too high).
Volume of gases	1027 l/kg,
density	1.422 g/cm^3.

According to Cottrell and Gill [38] unconfined methylamine nitrate melts and boils (230°C) without decomposition.

With regard to preparation of the compound, apart from the straight forward formation from methylamine and nitric acid (66%) (as described in Vol. II) another method based on the Plöchl reaction, by reacting ammonium nitrate with formaldehyde at 80–100°C, as was suggested by the author of this book [39] and brought to industrial application:

$$NH_4NO_3 + 2\,CH_2O \longrightarrow CH_3NH_3NO_3 + HCOOH. \qquad (2)$$

Although laboratory experiments have shown that methylamine nitrate is not very sensitive to impact, it gave a disastrous explosion at Potomac River, W. Virginia in 1976 [40] in two tank cars containing 86% solution of methylamine nitrate. The explosion probably took place due to friction in a pump or to a collision.

TETRAMETHYLAMMONIUM NITRATE $(CH_3)_4\overset{+}{N}\overset{-}{N}O_3$ (Vol. II, p. 466)

This substance was found to be difficult to bring to explosive decomposition.

However the mixtures of tetramethylammonium nitrate with polymers can burn in the presence of ferric oxide which proved to be an efficient catalyst for burning such mixtures [41].

Fe_2O_3 has a similar catalytic effect on the combustion of guanidine nitrate.

GUANIDINE NITRATE (Vol. II, p. 466)

Enthalpy of formation of guanidine nitrate was determined by Krivtsov, Titova and Rosolovskii [105]. It was found to be $-\Delta H_f = 93.0$ kcal/mol.

NITRATES OF AROMATIC AMINES

A number of nitrates of aromatic amines were recently described [42]. No information on their explosive or burning properties is available.

AMMONIUM CHLORATE (Vol. II, p. 476)

This substance has no practical application owing to its low stability, but it was important to study conditions influencing the decomposition and possibly the mechanism of decomposition. The early papers [43, 44] gave only a general description of the decomposition of the substance. A much more detailed account was given by Solymosi and Bánsági [45]. They studied the decomposition by measuring the pressure of non-condensable gases and the loss of weight at different temperatures. A measurable decomposition started at 50°C, but some days after the preparation of the substance according to (3),

$$NH_4Cl + NaClO_3 \longrightarrow NH_4ClO_3 + NaCl \qquad (3)$$

a slight decomposition was observed even at -5°C. The explosion of freshly prepared substance occurred at 90°C. The activation energy was calculated as being 22–25 kcal/mol. The addition of ammonia stabilized the substance, but the addition of chloric acid considerably increased the rate of decomposition.

Attention should be paid to the fact, that the substance is dangerous and all possible reactions leading to the formation of ammonium chlorate should be carefully avoided.

AMMONIUM PERCHLORATE (Vol. II, p. 477)

An enormous amount of work has been done in the last 30 years on ammonium perchlorate (AP). Originally it was reflected in the monograph by Schumacher [46] (Vol. II, p. 477) and more recently – the excellent review by Jacobs and Whitehead has appeared [47]. It contains all the important information available up to 1968. The pertinent data will be repeated in the present book to obtain a full picture of this compound and some more recent descriptions will be given here. Also the monograph of Glazkova [18] on catalytic decomposition should be mentioned.

Crystal Structure and Physical Properties

Two crystal structures of ammonium perchlorate are known: the lower-temperature orthorhombic form existing below 240°C and cubic form above that temperature [48]. The density of orthorhombic and cubic forms is 1.95 and 1.76 g/cm^3 respectively [47]. Ammonium ion undergoes an almost free rotation with the potential barrier of 0.55 ± 0.05 kcal/mol [49]. The heat of transition from orthorhombic to cubic system is accompanied by a heat effect of 2.3 ± 0.2 kcal/mol [50, 110]. AP is nonhygroscopic [81].

The specific heat of ammonium perchlorate [51] is 0.309 cal g^{-1} deg^{-1} between 15 and 240°C and 0.365 cal g^{-1} deg^{-1} above 240°C. The electrical conductivity was also examined [52–54]. The activation energy of electrical conductivity changed from 45 kcal/mol at high temperature (over 255°C) to 4 kcal/mol below 92°C.

Thermal Decomposition and Burning of AP

General information. Ammonium perchlorate (AP) is stable at room temperature. It begins to decompose above 130°C [56] or 150°C [55]. According to Andreev and Sun Tsuan-tsai [55] at 160°C half-life of AP is 25,000 min and at 270°C is 225 min (for comparison they gave the half-life figures for nitrocellulose at 160°C and for TNT at 270°C: 170 min and 20 min respectively). Thus the decomposition of AP is much slower than both above mentioned explosives. The decomposition of ammonium nitrate above 170°C (i.e. above its m.p. which is 169°C) is much faster than that of AP due to the fact that AP does not melt. Thus the half-life of ammonium nitrate at 286°C and of ammonium perchlorate at 280°C is 5 min and 170 min respectively.

The decomposition of AP with temperature follows an S-curve, which is typical for autocatalytic reactions. Thus, there is an initial increase in the rate of decomposition through the formation of the products of decomposition and the fall of the rate after these products were subjected to decomposition. The formation of an unusual product at lower temperatures (220–300°C) has already been described in Vol. II, p. 479. Above 350°C the reaction is no more autocatalytic.

Numerous products are formed during the decomposition of AP. They were examined in Dodé's pioneering work [56] and confirmed by Bircumshaw and Newman (Vol. II, p. 478). Further experiments were carried out by Rosser, Inami and Wise [57]. Dodé identified the products such as chlorine dioxide (at temperatures below 300°C), nitrogen, water, oxygen, nitrous oxide, hydrogen chloride, nitrosyl chloride, nitrogen trioxide and nitrogen dioxide, the latter three compounds being the result of the secondary reaction of nitric oxide with chlorine and oxygen.

Wise *et al.* [57] gave a quantitative summary of the products of decomposition between 250° and 325°C, for example at 275°C they found:

0.50	O_2	Moles per mole of decomposed AP
0.047	N_2	
0.35	N_2O	
0.39	Cl_2	
0.19	HNO_3	
0.16	HCl	
0.019	NO	

The authors tried to rationalize the reaction in terms of a decomposition equation beginning by electron transfer followed by proton transfer (4):

$$NH_4ClO_4 \longrightarrow NH_4^+ + ClO_4^- \longrightarrow NH_3 + HClO_4. \tag{4}$$

The proton transfer was earlier suggested by Davies, Jacobs and Russell-Jones [82]. A number of Soviet authors – Boldyrev *et al.* [118] confirmed the mechanism of proton transfer. According to Pearson and Sutton [75] perchloric acid decomposed to yield ClO_3 and ClO which were detected in fragmentation in a mass spectrometer.

It appears that the reaction of decomposition of AP is too complicated to be presented in one equation. Nevertheless the deflagration of AP starting at *ca.* 450°C can be depicted by equation (5) according to Kaye [81]:

$$4\,NH_4ClO_4 \longrightarrow 2\,Cl_2 + 8\,H_2O + 2\,N_2O + 3\,O_2. \tag{5}$$

Another equation for the decomposition of AP is (6) [47]:

$$2\,NH_4ClO_4 \longrightarrow Cl_2 + 4H_2O + 2NO + O_2. \tag{6}$$

Probably both reactions can run simultaneously.

A phenomenon of sublimation of ammonium perchlorate occurred simultaneously with decomposition as mentioned previously (Bircumshaw and Newman, Vol. II, p. 478), and suggested by Dodé [58], Jacobs and Powling [59] and made the process still more complicated.

The activation energy of thermal decomposition of AP varies from 17 to 40 kcal/mol according to various authors [47]. The wide discrepancy between their results was due to various conditions of the reactions, various techniques used and is a sign of the complicated nature of the reactions of the decomposition of AP.

Mass spectrometry fragmentation was investigated by a number of authors [60] (also references in [47]). More recent work was done by Volk and Schubert [61]. At 240° and 280°C they found the fragments: NH^+, NH_2^+, NH_3^+, H_2O^+, NO^+, O_2^+, Cl^+, N_2O^+, NO_2^+, ClO^+, ClO_2^+, ClO_3^+, $HClO_4^+$ m/e.

Thermal Decomposition of Irradiated Ammonium Perchlorate

(Vol. II, p. 481)

The work of Freeman and Anderson [62] was continued and confirmed the previous observation. Irradiation increases the number of nuclei and this affects the decomposition of the substance: the decrease in the induction period and an increase in the rate constant [63a]. A detailed kinetic study of pre-irradiation was made by Harley and Levy [63b]. They also found that the activation energy of thermal decomposition of AP was unchanged by irradiation at 28.4 ± 2.5 kcal/mol.

Influence of Pressure on Burning of AP

Ammonium perchlorate can burn on condition that it is confined and that the pressure inside the vessel is a minimum of 45 atm. [64], or according to other authors above 20 atm. [65]. The size of crystals of AP have a decisive influence on this limit of pressure. Thus it was found that very fine substance (UFAP = ultra fine AP) can burn in the open under atmospheric pressure [81]. A number of authors examined the deflagration of ammonium perchlorate at different temperatures and pressures: Watt and Patterson [119], Boggs and coworkers [67], Glazkova [66, 18]. Glazkova examined the influence of pressures as high as 1000 atm.

All authors drew attention to a number of factors influencing the data referred to burning AP such as: size of crystals, density, confinement (e.g. diameter of tubes), material of the tubes (e.g. glass, Plexiglas). The typical shape of curves: rate of burning/pressure is presented in Fig. 75 according to Glazkova [18]. The region below 300 atm. is depicted in Fig. 76 [67], and merits special attention. Here the analysis will be given as presented by Glazkova [66].

Four regions of burning should be distinguished, viz:

(I) From 20 to *ca.* 55 atm. A steady increase is marked in the rate of burning. The exponent n in the formula of burning $u = b \cdot p^n$ is *ca.* 0.77 according to [68].

(u – is the rate of burning in g/cm² sec, b – a coefficient, p – pressure).

(II) From *ca.* 55 to 150 atm. the slope du/dp is smaller, and the exponent n has a lesser value than in (I), for example 0.55.

Both regions were described by Glazkova as those of steady burning.

(III) From 150 to 300 atm. The burning is characterized by a rapid fall in the rate of burning with an increase of pressure [67]. The exponent n can acquire a negative value, for example −3.8. In some experiments Glazkova observed a plateau in this region of pressures. A plateau was also found by Manelis and Strunin [69].

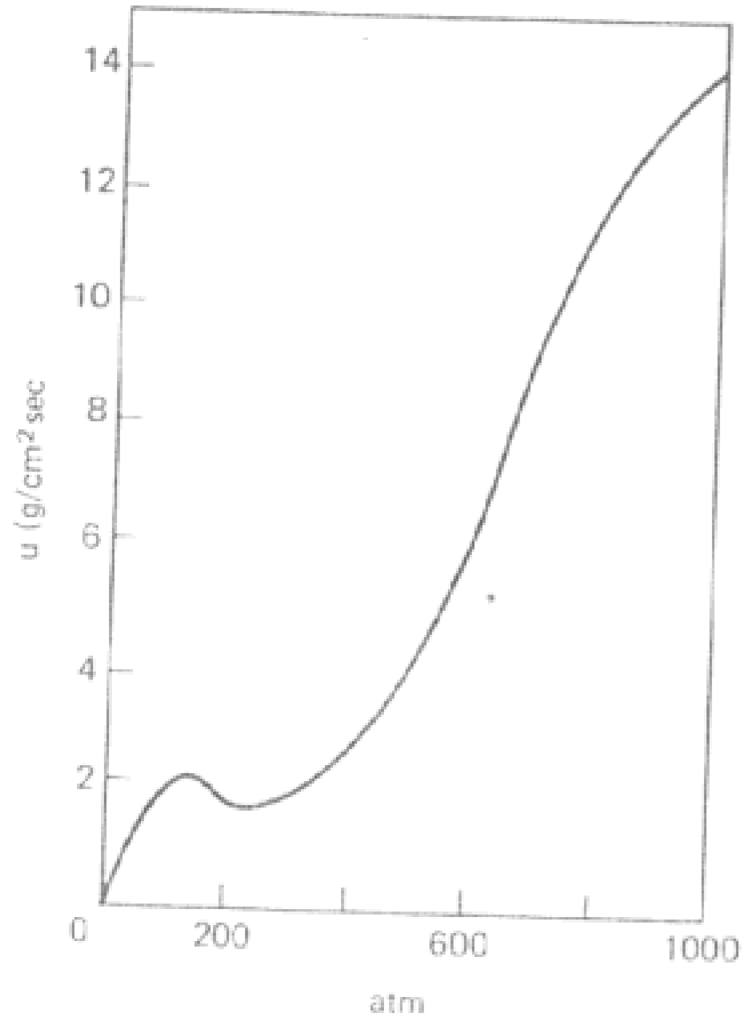

FIG. 75. Rate of burning against pressure of ammonium perchlorate, according to Glazkova [18].

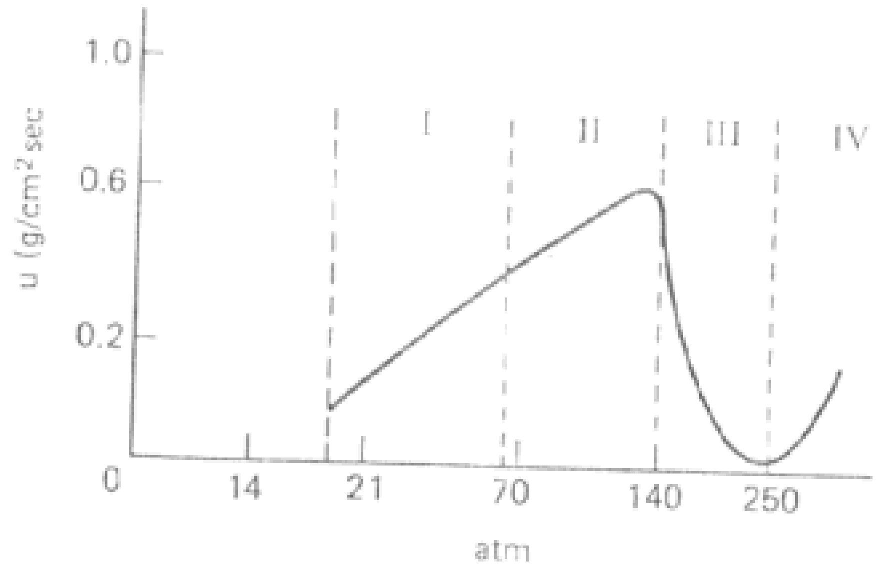

FIG. 76. Rate of burning of ammonium perchlorate below 300 atm. according to Boggs *et al.* [67].

(IV) From pressure over 300 atm. an increase is observed in the rate of burning which is particularly marked over 500 atm. The exponent n acquires a value $n > 1$.

Burning between 150 and 300 atm. (and according to Glazkova up to 500 atm.) is pulsing and unstable. Glazkova and Bobolev [70] rationalized it in terms of the formation of water as one of the products of the reaction of decomposition of AP. Water remains on the surface of crystals as a liquid. This follows from the temperature of boiling water under high pressure. This temperature can be higher than that of the surface of solid AP, for example: under 150 atm., the temperature of boiling water is 360°C whereas the surface has a temperature 320°C.

A factor of sublimation should also be considered. Guirao and Williams [71] described the deflagration of AP at pressure between 20 and 100 atm. and suggested that a dissociate sublimation process is likely to exist at the interface between the gaseous and condensed phases.

Density and Critical Diameter

Bakhman, Belyaev, Lukashenya and Polikarpov [72] studied the influence of the density of AP on the rate of burning under pressures 5–100 atm. The mass rate of burning increases with the increase of density. Thus confined samples with densities from 1.465 to 1.95 g/cm^3 increased by factor 2.66. Glazkova [66] carried out wide experiments on the influence of density and obtained a somewhat complicated picture: generally the rate of burning increases with density but follows the same rule as regards the influence of the pressure as depicted by Figs 75–76. A pulsing burning was observed under pressures 160–300 atm.

Samples of AP do not burn if they are confined in tubes of a diameter below a certain limit – the critical diameter. This was investigated by Glazkova [73] for the density 1.2–1.4. The smallest critical diameter corresponds to the substance burning under 100–150 atm., that is where the rate of burning is the highest. The maximum critical diameter is at 20 atm. and further increase of the pressure reduces the critical diameter.

It should be borne in mind that the results of different authors are not in complete agreement, due to the complicated nature of burning ammonium perchlorate, which depends on so many factors mentioned already and some other factors such as the size of particles of AP, a kind of confinement. The burning of AP under different pressures indicates that the rocket propellant with AP should not be used in systems where the pressure is over 150 atm. that is, where burning is unsteady (pulsating) and excludes the systems where the pressure is over 300 atm and the exponent $n > 1$.

Decomposition (at higher temperatures) and Burning of Ammonium Perchlorate with Various Additives

A considerable amount of work has been dedicated to the influence of additives on the decomposition of ammonium perchlorate. It started by the pioneering work of Friedman and co-workers [64] who studied the decomposition of ammonium perchlorate under pressure from atmospheric to 340 atm. They found that an addition of *ca.* 3% of some mineral compounds possess a catalytic action. The best catalyst was found to be cupric chromite containing 85% CuO and 15% Cr_2O_3. Ammonium perchlorate with 3% of cupric and chromic oxides begins to burn steadily under pressure over 135 atm. and 230 atm. respectively. With cupric chromite the steady burning was much faster and started under pressure of 100 atm.

The catalysts introduce some change in the composition of the products formed during the burning of AP. The main reactions of the decomposition of NH_4ClO_4, according to Rosser and co-workers [57] consists in the sequence of the reaction already described (4).

The experiments of Rosser, Inami and Wise [57] were the continuation of their work on catalytic decomposition of ammonium nitrate [74]. They examined the action of copper chromite. They found that it acted at the early stage of the reaction and its action disappeared after copper chromite was oxidized by the products of catalytic reaction. Cobalt oxide was found to be an exceptional catalyst: it produced NOCl and NO_2Cl as major products and only a trace quantity of N_2O_3. The authors came to the conclusion that copper chromite catalysed thermal decomposition of AP according to an electron transfer mechanism (4).

Pearson and Sutton [75] did not agree with this view. On the basis of their own experiments and those of other authors [77, 82] that both the catalysed and uncatalysed decomposition of ammonium perchlorate proceeds by proton transfer (4) and (7):

$$NH_4^+ ClO_4^- \longrightarrow NH_3 + HClO_4. \qquad (7)$$

An important work was done by Shimagin and Shidlovskii [76]. According to these authors the presence of HCl (equation 6) in the decomposition products is not affected by 5% of Cr_2O_3, MnO_2, Fe_2O_3, NiO, Cu_2O but these oxides suppressed the formation of N_2O and increased the concentration of NO. On the contrary zinc oxide strongly reduced the amount of HCl and did not suppress the formation of N_2O.

Pellett and Saunders [77] studied the action of ruby laser on the AP-catalyst system. The first products evolved were NH_3 and $HClO_4$ and after that the products of their reaction appeared: H_2O, ClO_2, NO, HClO, Cl_2 and NO_2. The decomposition of $HClO_4$ yielded HCl and ClO_2.

Strunin and Manelis [78] made the observation that the thermal decomposition of AP at 230–260°C was not influenced by pressure of 100 atm of an inert gas.

Kaye in *Encyclopedia of Explosives* [81] describes over 30 metal oxides and salts which provide a catalytic effect upon the thermal decomposition of AP. They are oxides of Al, Cd, Cr(II), Cu(I), Cu(II), Fe(III), Mg, Mn(III), Mn(IV), Mn_3O_4, Ni(II), Ni(III), V(V), Zn and chlorides: of the same metals. Also perchlorates of Cd, Cu(II), Hg(II), Mg, Zn possess a catalytic action.

Mechanism of Low-Temperature Decomposition of AP

The microscopic study of the formation and growth of nuclei in solid ammonium perchlorate was studied by a number of authors (Vol. II, p. 481). Raevskii and Manelis [79a] found that the decomposition centres of orthorhombic form consists of a large number of ellipsoid nuclei of 1–2 μm. They are not stationary but moving at the speed of the order 7–10 μm/min at 230°C. Their activation energy is 31 and 33 kcal/mol depending on the direction of the movement.

In the decomposition of the cubic form (above 240°C) they are spherical, randomly distributed throughout the crystals. The activation energy of their growth is 17 ± 1 kcal/mol above the transition point. The dislocation in crystals during their decomposition was revealed by etching the surface of crystals with ethanol [79b].

A number of other works on low-temperature decomposition were subjected to a detailed review [47]. Also the monograph of Glazkova [18] should be consulted.

Explosive Properties of NH_4ClO_4

The following are data according to Meyer [80]:

enthalpy of formation	–602 kcal/kg
heat of explosion	266 kcal/kg
deflagration point	350°C
lead block expansion	195 cm³

According to Kaye in *Encyclopedia of Explosives* [81]: dry, fine grade AP can detonate from No 8 blasting cap,

detonation rate of dry AP was 3400 m/s,
detonation rate wet with ethanol AP 4200 m/s,
detonation rate wet with acetone AP 4500 m/s,

(no information was given as to the density and the quantity of the liquid).

Lead block test gave 46% of picric acid, ballistic mortar – 100% of TNT.

An electrostatic discharge of over 5 joules was required to initiate a decomposition of AP.

Impact sensitivity was found to be 91 cm for 50% explosion (as compared with 61 cm with picric acid).

Heat Test at 100°C: after 48 hours 1% weight loss, between 48 and 96 hours 0.6% loss. No explosion occurred after 100 hours. The above data indicate a high stability of ammonium perchlorate.

The detonation equation (8) was given by Kaye [81]:

$$2\,NH_4ClO_4 + 4\,H_2O + O_2 + Cl_2 + 2\,NO. \qquad (8)$$

Price, Clairmont and Jaffe [83a] carried out an extensive investigation of detonation of ammonium perchlorate as a function of density and particle size.

They expressed their results in equation (9):

$$D_i = -0.45 + 4.19\,\rho_0 \tag{9}$$

where ρ_0 is the density in g/cm^3, D_i = detonation velocity in mm/μs corresponding to the infinite charge diameter.

Equation (9) is valid for $\rho_0 = 1.0$–1.26.

Price and co-workers [83b] extended their results to densities below 1.0 and their equation took the shape:

$$D_i = 1.146 + 2.576\,\rho_0$$

$$0.55 \leqslant \rho_0 \leqslant 1.0 \text{ g/cm}^3.$$

For $\rho_0 = 1.0$ the values of D were:

diameter d cm	
2.54	2.824 mm/μs
3.495	3.027
5.08	3.295
7.62	3.393

The extrapolated value D_i was 3.702.

At a still lower density, e.g. $\rho_0 = 0.55$ the D_i value was 2.530 mm/μs.

Decomposition occurred according to the equation

$$NH_4ClO_4 \longrightarrow 0.5\,N_2 + 0.5\,Cl_2 + 2\,H_2O + O_2$$

Manufacture of Ammonium Perchlorate

On a commercial scale AP is prepared by the interaction of ammonium chloride with sodium perchlorate. The less soluble AP precipitates and is filtered off leaving a solution of NaCl. A schematic diagram by Kaye [81] is given in Fig. 77.

According to Schumacher's patent [84] the reaction between anhydrous ammonia, concentrated hydrochloric acid and aqueous (56%) $NaClO_4$ and recycled mother liquor from the NaCl crystallizer are heated with steam to 90°C. By adding HCl the pH of the reaction is kept close to 7.0. The reaction liquor enters a crystallizer where the temperature is lowered to 35°C by vacuum evaporation and brought to a supersaturation. The crystals of AP are centrifuged, recrystallized, washed with a saturated solution of AP (to remove the traces of sodium chloride). The mother liquor enters the sodium chloride crystallizer where water is removed by vacuum evaporation and the mother liquor is recycled to the reactor.

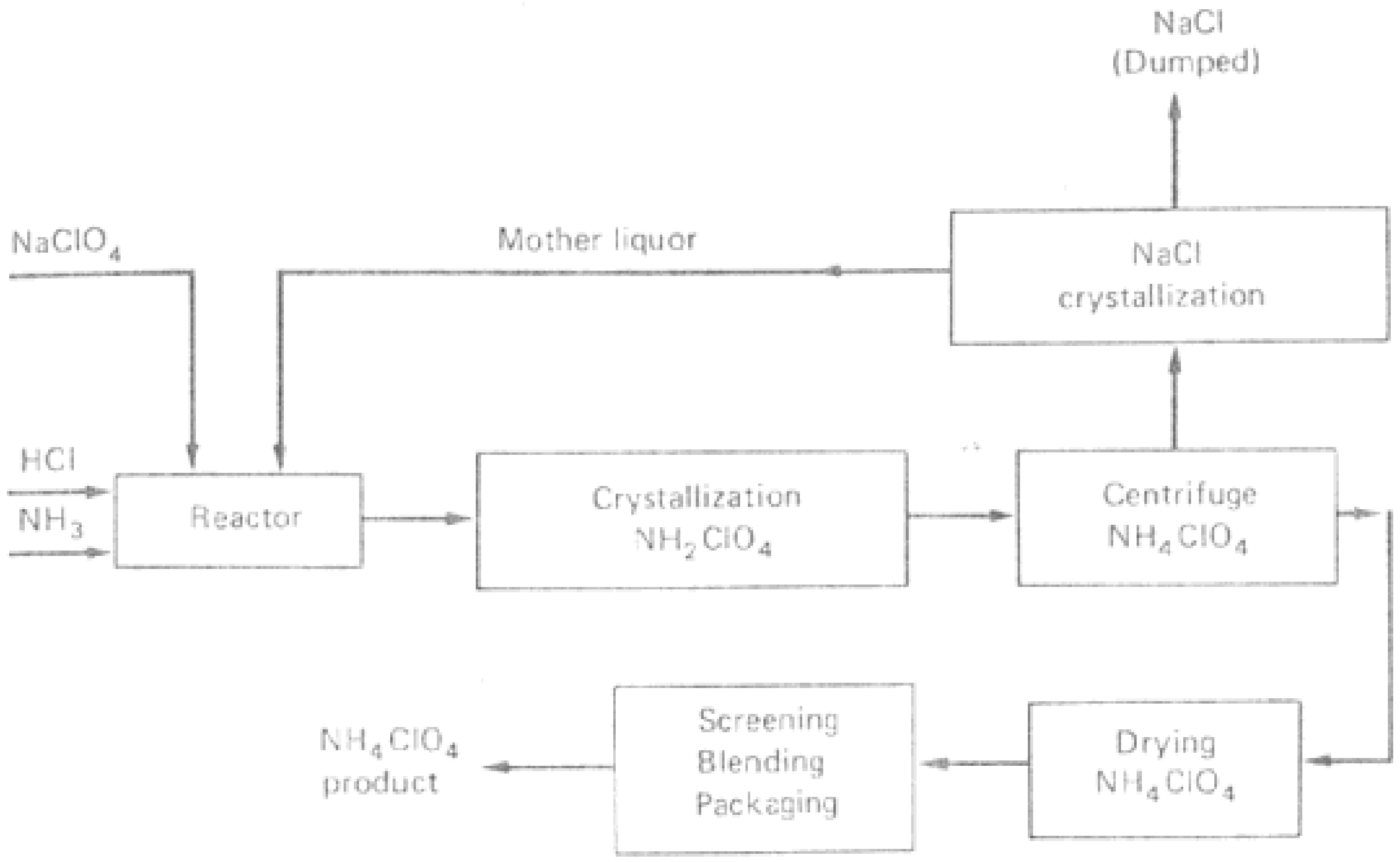

FIG. 77. Diagram of manufacture of ammonium perchlorate according to Kaye [81].

For high burning rate propellants a fine particle size ammonium perchlorate is required and can be produced by three processes according to Kaye [81]:

(a) In a jet mill in the atmosphere of nitrogen or helium at 82°C. The powder of AP of 5 μ is collected in trichloroethylene.

(b) By slurry grinding. A slurry of 85 parts of 1,1,2-trichloro-1,2,2-trifluoroethane (Freon 113) and 15% of AP and a small portion (0.15 parts) of a surfactant is ground for 160 hours to obtain a particle size of 1.72 μ.

(c) By freeze-drying. An emulsion made of AP in water and 1% Nopogen emulsifier and 0.1% Johnsons Wax. The emulsion is freeze-dried in a vacuum sublimator to give a product of particle size 0.37 μ. The Wax or some polymers such as 2-cyanoacrylate were added to prevent crystal regrowth.

Specification

The U.S. specifications [81] require 99.0–99.3% purity, total moisture 0.05–0.08%, surface moisture 0.02%, NH_4Cl 0.03–0.15%, $NaClO_3$ 0.02%, Bromates as $NaBrO_3$ 0.0–0.004%, K_2CrO_4 0.0–0.015%, iron (as Fe) 0.001% or (as Fe_2O_3) 0.0036%, ash (as sulphates) 0.25–0.30%, volatiles 0.04%.

Meyer [80] describes three grades of specification: A, B and C which are similar to the above, and in addition: water insolubles 0.01–0.03%, residue from sulphuric acid forming 0.3%, Na and K not more than 0.08%, $Ca_3(PO_4)_2$ 0–0.22%, pH 4.3–5.3 or 5.5–6.5.

Specifications also include particle size.
Meyer [80] mentioned seven classes:

(1) through 420–297 μ sieve, retained on 74μ sieve,
(2) and (3) through 297 and 149 μ sieve respectively,
(4) 50–70% through 210 μ sieve,
(5) through 297 μ sieve, retained on 105 μ sieve,
(6) 89–97% through 297 μ sieve,
(7) 45–65% through 420 μ sieve.

PERCHLORATES OF METALS (Vol. III, p. 230)

A considerable number of perchlorates of metals have been described in the monograph by Schumacher [46] and also in the Encyclopedia by Kaye [81]. A short review of the properties of metal perchlorates was given by Shidlovskii [85]. He compared the thermochemistry of their decomposition according to the general equation:

$$M(ClO_4)_n \longrightarrow MCl_n + 2n\,O_2 - \Delta H. \qquad (10)$$

He pointed out that three decomposition groups exist:

(1) Perchlorates of K, Rb, Cs decompose with a very small thermochemical effect, for example with $KClO_4$ it $-\Delta H = 0.6$ kcal/mol.

(2) Perchlorates of Li, Na, Mg, Ca, Ba which decompose with a small exothermic effect: Li and Na of $-\Delta H = ca.$ 6 kcal/mol. and Mg and Ba of the same value for equivalent. Thus for $Ba(ClO_4)_2$ $-\Delta H = 12.8$ kcal/mol.

(3) Perchlorates with a marked exothermic decomposition, for example silver perchlorate which gives $-\Delta H = 22.3$ kcal/mol. Silver perchlorate possesses explosive properties (Vol. III, p. 232).

It was found that when free of any organic substance, it is insensitive to mechanical action. However with a small amount of ethyl ether it shows a high sensitivity to shock and friction and has caused a few accidents.

Recently a less explicable accident has occurred [109] with cobalt (II) perchlorate. The salt had been prepared by allowing aqueous perchloric acid to react with an excess of $CoCO_3$, filtering off the excess carbonate, reducing the volume and crystallizing out the salt. The explosion occurred when the caked mass of crystals was placed in a mortar and tapped gently to break it up. No organic matter is thought to have been present. Extreme caution should be taken in handling $Co(ClO_4)_2$ and similar salts.

The mechanism of decomposition of barium perchlorate was examined by Jacobs, Solymosi and Rasko [113].

OTHER PERCHLORATES (Vol. II, p. 483)

Hydrazine perchlorate (hyzazinium perchlorate)

$$NH_2\,NH_3^+\,ClO_4^-$$

Conant and Rooj [93] studied the crystal structure: they found it to be orthorhombic with m.p. 131–132°C and density 1.939. Carleton and Lewis [94] studied the phase system with water and reported m.p. 142.4°C and a hydrate $N_2H_4 \cdot HClO_4 \cdot \frac{1}{2}H_2O$ losing water at 61–64°C. M.p. 137–138°C of the perchlorate was also reported [95].

Heat of neutralization of $HClO_4$ with N_2H_4 was – 44.4 kcal/mol and heat of formation $-\Delta H_f = 42.9$ kcal/mol [96] and $-\Delta H_f = 40.7$ kcal/mol [97].

It can be prepared by neutralizing aqueous solution of hydrazine with $HClO_4$ [95] or by double exchange of hydrazine salt with an inorganic perchlorate dissolved in lower alcohols [98].

The deflagration of Hydrazine Perchlorate was studied by Levy, von Elbe and co-workers [111]. They found that it could be catalysed by copper chromite, potassium dichromate and magnesium oxide. The entropy of vapourization and dissociation:

$$N_2H_5ClO_4 \longrightarrow N_2H_4 + HClO_4 \qquad (11)$$

is 73 cal/deg. mole. (A similar figure was found for the entropy of dissociation of ammonium perchlorate into NH_2 and $HClO_4$: 71 cal thermal dissociation of deg. mole.) Grelecki and Cruice [112] examined also hydrazinium diperchlorate (see below) and found its decomposition to be autocatalytic. On the contrary monoperchlorate is not autocatalytic.

Volk and Schubert [61] examined the fragmentation in a mass spectrometer. They found NH_3^+, NH_4^+, H_2O^+, H_3O^+, $N_2H_4^+$, $N_2H_5^+$, ClO_2^+, $HClO_4^+$.

On heating it decomposes at 230°C [95], but Shidlovskii *et al.* [96] gives the ignition temperature 277–280°C. On detonation the volume of gases is 864 l/kg [96].

Lead block expansion is the order of 113% of Picric acid or 122% of TNT [81].

Hydrazine Diperchlorate

$$[NH_3NH_3]^{2+}(ClO_4)_2^-$$

m.p. 191°C.

The compound has the density 2.21.

Salts of Hydrazine Perchlorate and Chlorate Complexes

(Vol. III, p. 230)

Complex salts of hydrazine and perchlorate were described also by Maissen and Schwarzenbach [99] and in the Encyclopedia [81].

Nitrosyl Perchlorate (Vol. II, p. 484)

Fragmentation in a mass spectrometer was described by Volk and Schubert [61].

Hydroxylamine Perchlorate

$$NH_2OH \cdot HClO_4$$

m.p. 87.5–90°C

It forms hygroscopic crystals, decomposing at 120°C. Heat of formation was $-\Delta H_f = 66.2$ kcal/mol. It was prepared by reacting hydroxylamine sulphate with $BaClO_4$. Impact sensitivity was of 15 cm by 2 kg falling weight [81].

Methylamine Perchlorate (Vol. III, p. 484)

$$CH_3\ NH_3\ ClO_4^-$$

m.p. 255°C (d)

The crystal structure was reported by Stammler [100] and Zanazzi [101]. The substance passes through a phase transition at 178°C. Densities of phase II at 77°C is 1.58 c/cm^3, phase I at 200°C is 1.58 g/cm^3.

The temperature of explosion by heating was found to be 338°C [102]. Mass spectrometry was examined by a number of authors, most complete being the study by Volk and Schubert [61]. They found fragments at 260°C: CH_3^+, CHN^+, CH_2N^+, CH_3NH^+, $CH_3NH_2^+$, Cl^+, ClO^+, ClO_2^+, ClO_3^+, $HClO_4^+$ m/e.

Guanidine Perchlorate (Vol. III, p. 485)

Markwald and Struwe [103] described the method of making this substance from cyanoguanidine and ammonium perchlorate. Some physico-chemical properties were reported [104]. Heat of formation according to Krivtsov and co-workers [105] was found to be $-\Delta H_f = 74$ kcal/mol.

Guanidine perchlorate is a powerful explosive: its rate of detonation can reach 7150 m/s at $\rho = 1.67$, and lead block expansion 400 cm^3 [106].

Nitroguanidine Perchlorate

This interesting substance, which is an exothermic compound, was obtained by Rosolovskii, Krivtsov and Titova [97]. Its enthalpy of formation is $-\Delta H_f = -51.5$ kcal/mol.

Fluoroammonium Perchlorate

$$NH_3F\ ClO_4^-$$

This substance was prepared by Grakauskas and Baum [107]: a solution of ethyl (or isopropyl)-*N*-fluorocarbamate in 70% $HClO_4$ was heated until CO_2 was evolved at 68°C. The excess of perchloric acid was removed under vacuum:

$$C_2H_5OCONHF + HClO_4 \longrightarrow NH_3FClO_4 + CO_2 + C_2H_5OClO_3. \qquad (12)$$

Fluoroammonium perchlorate has an appreciable vapour pressure, subliming at 46°C.

Nitronium Perchlorate (Vol. I, p. 19)

$$NO_2^+\ ClO_4^-$$

The substance forms hygroscopic crystals which melt on decomposition at 135°C without explosion.

The original product obtained by Hantzsch (Vol. I, p. 19) proved to be a mixture of nitronium perchlorate and perchloric acid monohydrate (Goddard and co-workers [116]). Nitronium perchlorate was obtained by distilling anhydrous perchloric acid onto an excess of dry dinitrogen pentoxide at −80°C and the mixture was kept *in vacuo* to remove volatiles. The product was composed of 89% nitronium perchlorate and 11% perchloric acid hydrate. Pure nitronium perchlorate was obtained by repeating the experiment in nitromethane with a large excess of N_2O_5 [117]. Cordes [114] examined the decomposition between 70 and 112°C and found gaseous products NO_2, Cl_2, ClO_2, NO_3Cl and O_2. M. D. Marshall and Lewis [115] established that at 65°C the major products were nitrosonium perchlorate and oxygen. Nitrosonium perchlorate further decomposes:

$$NO\ ClO_4 \longrightarrow NO_2 + Cl\ O_2 + \tfrac{1}{2}\ O_2$$

$$2\ Cl\ O_2 \longrightarrow Cl_2 + 2\ O_2.$$

PERCHLORIC ACID AND CHLORINE OXIDES

Thermal decomposition of ammonium perchlorate and perchlorates of other bases raised problems of the decomposition of perchloric acid and oxides of chlorine. This was extensively reviewed by Schumacher [46], Zinovyev [86], Jacobs and Whitehead [47], Pearson [87].

Perchloric Acid (Vol. III, p. 313)

Thermal decomposition of perchloric acid is a complicated process and the trend of decomposition depends on the temperature. The process is particularly complicated at temperatures below *ca*. 315°C. Above that temperature the reaction is homogeneous [8]. The following are products found in the region 200–440°C: Cl, Cl_2, O, O_2, H_2O and chlorine oxides [60, 88, 89].

Chlorine Oxides

Chlorine oxides are compounds of a relatively low stability, the most stable being Cl_2O and Cl_2O_7.

Chlorine monoxide (Cl_2O) is explosive if heated rapidly or overheated locally, but on careful heating the decomposition between 100° and 140°C is measurable [90].

Chlorine heptoxide (Cl_2O_7) was studied at temperatures of 100–120°C [91], it decomposed to chlorine and oxygen. The decomposition of liquid compound was examined [92] at 60–80°C.

The decomposition of other chlorine oxides are given in a review [47].

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CHAPTER 17

PRIMARY EXPLOSIVES: INITIATORS, INITIATING EXPLOSIVES, (IE)

(Vol. III, p. 129)

INTRODUCTION

With regard to the number of primary (i.e. initiating) explosives very little can be added to those already described in Vol. III. Thus the most used initiators are: Lead Azides, Lead Styphnate, Tetracene. Mercuric Fulminate which is the oldest and so far most popular initiator is gradually being withdrawn from use in some countries (e.g. in the U.S.A.) and replaced by lead azide. The other primary explosives, such as cyanuric triazide and diazodinitrophenol are good initiators but have not yet received wider application. A few more primary explosives have proved to be efficient initiating agents such as: silver, cadmium and cupric azides, triazidotrinitrobenzene, salts of acetylene, double salts of styphnic acid (lead salt) and tetracene, hexamethylenetriperoxide diamine.

A large group of explosives exists which have initiating properties: they are complex salts of metals with bases such as ammonia, amines, hydrazine etc. (Vol. III, p. 230). There is insufficient information on the properties of these compounds, their stability and their action on metals, therefore they cannot be recommended as yet for practical use.

A good initiating explosive (IE) should correspond to numerous requirement, such as:

1. Good initiating properties, that is, a small charge of IE should bring an explosive to detonation. This is usually connected with a short time of burning to detonation. A classic example is lead azide which has a remarkably short time of burning to detonation according to Patry and Laffitte [46, 47].

2. Safe handling and use in manufacture of elements of ammunition, such as pressing into the elements.

3. Ease of filling the initiating elements and ease of safe pressing.

4. Safe use of such elements, for example avoiding premature detonation when striking an object.

5. Stability on storage at room temperature and elevated temperatures (e.g. up to 150°C) and in some types of charges at low temperature. They should not react with carbon dioxide in atmosphere.

6. Absence of corrosive effect of the substance on metal used for initiating elements (cups and tubes).

7. Ease of safe manufacture of the substances.

Failure to answer one of the above conditions may cancel the practical application of the substance.

An important property of IE is their ability to burn to detonation under reduced pressure. This is of significance to space research, and will be discussed below.

BURNING OF IE UNDER REDUCED PRESSURE

There has been some controversy as to whether initiating explosives can burn and eventually detonate under reduced pressure. The earlier literature reported that they do not burn in a 'high vacuum' [39]. Muraour and Schumacher [40a] found that initiating explosives can burn to detonation under pressure of 10^{-3} to 10^{-4} torr. This was not in agreement with the earlier finding of Burlot [41a]. Burlot [41b] reported that different initiating explosives are characterized by a critical low pressure: the explosive cannot burn and detonate if the pressure falls below that limit. The critical pressure amounts to as much as 15 torr for mercuric fulminate and 2×10^{-2} torr for lead azide. Belaev [42, 44], Belaev and Belaeva [43] seem to confirm the view of Burlot, although they did not examine the pressure below 2–3 torr.

T. Urbański and Stanuch [45] undertook experiments to clarify the existing discrepancy particularly in view of the importance of the problem.

Their conclusion was that initiating explosives can be divided into five classes according to their behaviour when ignited with a resistance wire under reduced pressure. Here is their classification.

(I) IE which readily detonate when ignited either as loose powder or pressed pellets at pressure as low as 10^{-5} torr. Lead, silver and mercuric azides, silver and cadmium fulminates, lead styphnate and *m*-dinitrobenzdiazonium perchlorate belong to this group of compounds. All the above substances are characterized by a very short period of burning preceding detonation.

(II) IE which readily detonate when ignited as pellets at pressure as low as 10^{-4} torr. When in the form of loose powder they detonate under a pressure above 1 torr. Cyanuric triazide and hexamethylenetriperoxide diamine belong to this group of compounds.

(III) IE which burn without detonation when ignited as pellets under pressure of the order of 10^{-4} torr. Under atmospheric pressure they burn to detonation. When in the form of a loose powder they partially burn under pressure of 1 torr but under atmospheric pressure can burn to an explosion. Mercuric fulminate belongs to this group of compounds.

(IV) IE in the form of pellets which can detonate when ignited under atmospheric pressure, but do not detonate when the pressure is of the order 100–400 torr. At lower pressures of the order of 10^{-4} torr they do not burn. In the form of loose powder they burn under atmospheric pressure but do not detonate. Dinitrodiazaphenol and tetrazene belong to this group of compounds.

(V) Substances of this group do not burn to detonation even at atmospheric pressure when the pellets are not confined. A strong confinement is needed to bring their burning to detonation. Trinitrotriazidobenzene belongs to this group of compounds.

One more remark should be added to the behaviour of initiators as under (I) and (II) – still higher vacuum should be examined. Perhaps under pressure lower than 10^{-5} torr the primary explosives of groups (I) and (II) may behave differently from above and decompose without explosion. Thus the classification as above is valid only in limits for vacuum application.

Recently a monograph on initiating explosives written by Bagal [1] appeared. It contains chapters on:

1. Fulminates
2. Azides
3. Styphnates
4. Diazo compounds
5. Tetrazen and Tetrazoles
6. Peroxides
7. Acetylenides

Two other monographs have appeared which have been dedicated to azides: a collective volume edited by Patai [2] and two collective volumes on metal azides edited by Fair and Walker [3]. Also reviews have appeared on alkyl and aryl azides by Boyer and Canter (Vol. III, p. 196), and organic azides by L'abbé [4].

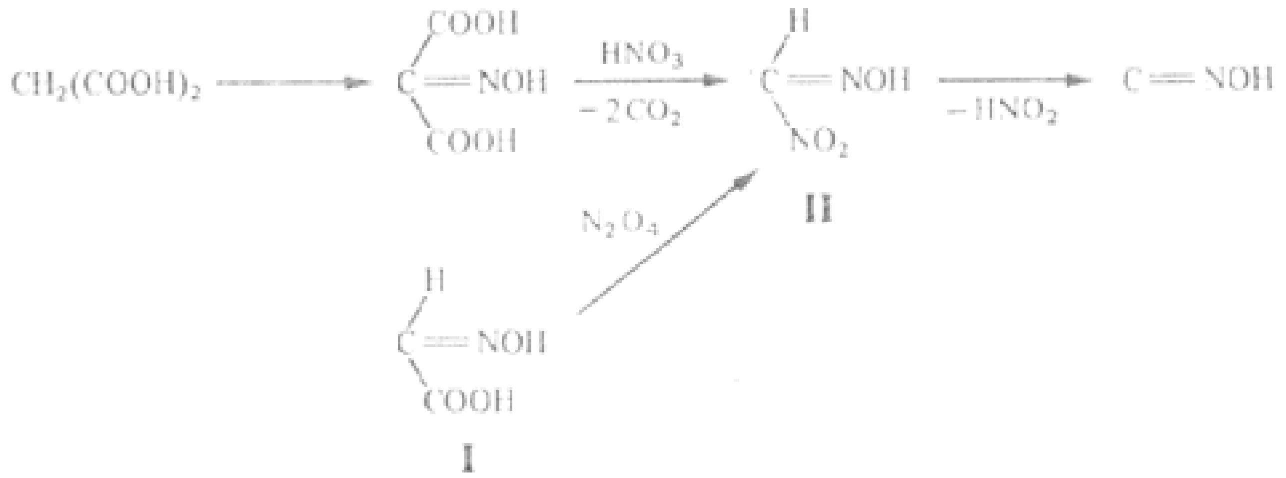
MERCURIC FULMINATE (Vol. III, pp. 129, 139)

The monograph by Bagal [1] contains a detailed description of the early history of the discovery of reactions leading to the formation of mercuric fulminate which began in 1800 thanks to the work of Howard (Vol. III, p. 129). Further work was done by Liebig [5], Liebig and Gay-Lussac [6], Gérard [7] and a number of other authors [8–18]. The correct structure of fulminic acid was given by Nef [19], supported by L. Wöhler and Teodorowits [20] and later by Wieland and Hess [21].

Polymerization of fulminic acid was studied by Wieland and Hess [21] and much later by Birkenbach and Sennewald [22]. These works led to rationalize the polymerization to a trimer given in Vol. III, p. 133 as formula VII.

Dansi [23] criticized the scheme of Wieland (Vol. III, p. 135). He could not obtain fulminates of mercury and silver by acting with their nitrates on isonitrosoacetic acid. The salts of isonitrosoacetic acid did not yield fulminates when acting with nitric acid (equations 5–8, Vol. III, p. 135). This casts some doubt on the accuracy of Wieland's scheme.

The structure of mercuric fulminate was also confirmed by Angelico through the ingenious formation of the compound from malonic acid (Vol. III, p. 136). Ponzio [24] found that nitrogen dioxide reacted with oxaminoacetic acid (I) yielding methylnitrolic acid (II) and therefore the reaction of Angelico-Ponzio should be presented by scheme (1) according to [1]:



(1)

Physical Properties

The problem of difference in colour of mercuric fulminate (grey and white crystals) does not seem to be fully solved. The view of Solonina (Vol. III, p. 138), Philip [25], Langhans [26], Marshall (Vol. III, p. 138) that the grey colour mercuric fulminate is due to some organic impurities seems to be correct. Crystallization of the substance from a solvent always yielded a white substance. The coloured products are probably resinous polymers of fulminic acid. The latter contains a double bond and is liable to polymerize. Whitening of mercuric fulminate by adding cupric salts appears to be an optical effect.

The density of mercuric fulminate on pressing into a No. 8 copper detonator case is according to Wöhler and Roth [27]:

Pressure kg/cm^2	100	250	500	1000	2000
Density g/cm^3	2.36	2.61	2.99	3.47	3.76

Technical mercuric fulminate contains (according to Bagal [1]) mercuric oxalate, mercurous oxides, inclusion of the reaction liquor, mercuric chloride. Bagal also mentioned the presence of metallic mercury which proved to be not always correct according to Solonina [28]. He examined samples of grey mercuric fulminate by keeping them and frictioning on gold plates and no formation of amalgamate was noticed.

Many authors stated that keeping most of the solutions of mercuric fulminate for a longer time leads to the decomposition of the substance. According to Solonina [28] a solution of mercuric fulminate in 22% aqueous ammonia produced a decomposition of the dissolved substance and mercuric oxide precipitated after 12 hours of keeping the solution at room temperature. Pyridine – a good solvent of mercuric fulminate – may also bring about decomposition with a precipitation of metallic mercury [26, 28]. Also a yellow coloured precipitate may be formed with a low content of Hg (*ca.* 58.5%) [1].

Chemical Properties

As pointed out in Vol. III (p. 140) mercuric fulminate is subjected to decomposition under the action of concentrated acids. Aqua regia produces chloropicrine. Thiocyanic acid gives an exothermic reaction with the formation of mercuric sulphide. If the temperature rises high – metallic mercury may be precipitated [1]. Nef [19] examined the action of hydrogen sulphide on silver fulminate and came to the conclusion that the salt of thioformhydroxamic acid (III) is formed. Cambi [29] tried to isolate the free acid. However it decomposed readily yielding thiohydrocyanide:


III

(2)

The reactions of metals with mercuric fulminate was described for the first time by Cheltsov in 1883 [30]. Dry mercuric fulminate did not react with metals – such as copper or brass, but in the presence of moisture a gradual formation of amalgamates occurs with time. Subsequently all elements containing mercuric fulminate and pressed into metal casing should be protected from moisture by varnish or air-tight casing.

Hygroscopicity of mercuric fulminate was examined by Kast [31]. He found that technical mercuric fulminate is non-hygroscopic: in 100% moisture atmosphere during 80 days at room temperature its weight increased by 0.16%. Mercuric fulminate reacted with potassium chlorate in a moist atmosphere and mercuric oxide resulted.

Sensitivity to impact. As a typical IE, mercuric fulminate is very sensitive to impact. Bubnov (according to [1]) reported that grey mercuric fulminate is slightly more sensitive to impact than the white species.

Chemical Stability and Behaviour at High Temperature (Vol. III, p. 141)

The earliest experiments on the stability of mercuric fulminate belong to Hoitsema [32] and Solonina [28]. Hoitsema examined the behaviour of mercuric fulminate under reduced pressure.

Solonina determined the ignition temperature and found it varied within the limits 157–172°C. When heating started at 100°C, the temperature was invariably 160°C.

Kast and Haid [33] found the following data: mercuric fulminate heated at the rate of 20°C/min exploded at 170–175°C, when kept at constant temperature explosion occurred:

at 190°C after 8–10 sec.
200°C after 7–8 sec.
205°C after 5 sec.

Behaviour at Low Temperature

Kling and Florentin [34] examined the behaviour of mercuric fulminate at low temperature: from −80° to −183°C and found that the velocity of detonation does not change with temperature at the density of 1.25 the figures were: 2365 m/s and 2350 m/s at room temperature and at −183°C respectively.

Clark [35] investigated the initiating properties of mercuric fulminate at different temperatures: +25°, −80° and −183°C to test the applicability of detonators in charges with liquid oxygen. He found a lowering of initiating power of detonators with a lowering of temperature, but the velocity of detonation did not change – in agreement with the observation of Kling and Florentin.

Action of Light

The following information on the work of Farmer [36] should be added to those given previously (Vol. III, p. 146). He examined the influence of sun-light on both grey and white samples and found white samples to be more sensitive to the action of light. Thus after 320 hours of irradiation white and grey samples evolved 0.37 and 0.14 ml of gas respectively. Patry and Laffitte [37] examined the influence on the induction period of irradiation of mercuric fulminate with ultraviolet light. The induction period was very much shortened by irradiation, for example, at 160°C freshly made sample and irradiated sample gave the induction periods of 252 and 9 sec. respectively.

According to Borocco [38] mercuric fulminate irradiated with ultraviolet light *in vacuo* was partly decomposed with the evolution of nitrogen and carbon monoxide according to the equation,

$$Hg(ONC)_2 \longrightarrow Hg + 2\,CO + N_2 . \qquad (3)$$

He also compared burning of samples: irradiated and previously heated to 100°C and found a similarity between the action of irradiation and pre-heating.

Burning under Reduced Pressure

As previously pointed out (p. 464) mercuric fulminate belongs to the group of IE which can burn to detonation under atmospheric pressure or pressure near to atmospheric. Under pressure of 10^{-4} torr it burned without detonation. Muraour and Wohlgemuth [48] examined the influence of the temperature of the charge of mercuric fulminate on burning under reduced pressure. At room temperature a pellet pressed under 3000 kg/cm^2 kept in vacuo, burned quietly. If preheated to 130°C it detonated within 10 min of keeping at this temperature without using an ignition wire.

'Dead pressing' of mercuric fulminate was described in Vol. III, p. 146. Muraour and Wohlgemuth [48] explain this phenomenon in terms of 'preheated' samples of the IE. If the sample is not 'dead pressed' it is sufficiently porous for the hot gases of decomposition to penetrate inside the charge and produce 'preheating' of the substance.

Initiating Properties of Mercuric Fulminate

Gedymin [49] used an original method for determining initiating properties of a mixture of 95% mercuric fulminate with 5% $KClO_3$. He determined the ratio (p) of the smallest ('critical') mass (m) of the initiating charge to the surface area (s) of the charge of the initiated explosive pressed into a cylindrical metal tube:

$$p = \frac{m}{s}.$$

For tetryl and TNT p is 1.12 and 1.52 respectively. The figures express the easier initiation of tetryl than of TNT.

Extensive experiments by Koester [50] on the initiating properties of mercuric fulminate are given in Table 72.

TABLE 72. Critical charges of mercuric fulminate

Initiated explosive	Critical charge g
PETN	0.35
Tetryl	0.36
TNT	0.38
Tetryl + 10% paraffin wax	0.36
Tetryl + 20% paraffin wax	0.44

Koester also examined the influence of the metal casing on the initiation properties of mercuric fulminate. The critical charge was found to be smaller in a hard metal (e.g. steel) than in a soft one (e.g. copper). The figures were: 0.24 g (steel) and 0.38 (copper).

Other Salts of Fulminic Acid (Vol. III, p. 157)

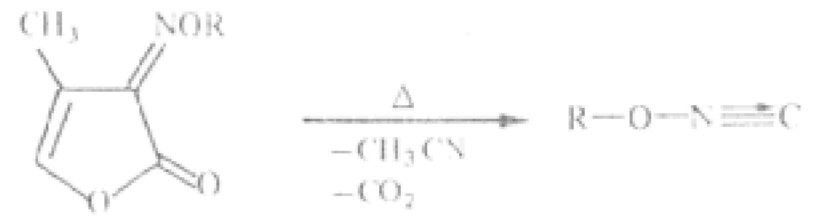
The only other salt of fulminic acid which was in some limited use was silver fulminate. However it no longer seems to be in use, and other salts were also of no use.

Manufacture of Mercuric Fulminate

No changes in the manufacture as described in Vol. III, p. 149 can be found. The only note of historical interest is that experiments were made by replacing ethanol with methanol in the manufacture of mercuric fulminate. Negative results were reported by Dumas and Peligot [51]. However Stahlschmidt claimed to have obtained mercuric fulminate from methanol as early as 1860 according to [1]. The discrepancy was explained later, e.g. [20], that methanol of Stahlschmidt contained dimethyl acetal – a derivative of acetaldehyde, and this discovery led to the finding [20] that mercuric fulminate can be obtained with a high yield and purity from acetaldehyde.

Esters of Fulminic Acid

Recently Wentrup, Winter and co-workers [182] described the reaction leading to the formation of esters of fulminic acid by vacuum flash pyrolysis (300–600°C) and matrix photolysis of 4-oximinoisoxazol-5(4H)-ones



The esters are unstable and decomposed above −100°C: when R = CH_3, it yielded formaldehyde and hydrocyanide.

HYDRAZOIC ACID, ITS DERIVATIVES AND SALTS (Vol. III, p. 161)

The chemistry of hydrazoic acid derivatives have recently created a wide literature [2, 3, 126, 184] owing to the fact that azides are convenient starting substances in preparative chemistry. This was reviewed by L'abbé [4] and partly by Boyer [52] in his recent paper on covalent oxygen bonding of nitrogen attached to carbon. Also a review on carbamoyl azides appeared [53].

Decomposition of Azides

Decomposition of azides very often begins with formation of nitrenes which contain uncharged nitrogen radical intermediate according to reaction (4)

$$R{-}N_3 \xrightarrow{\Delta \text{ or } h\nu} R{-}\dot{N}\cdot + N_2. \qquad (4)$$

Chemistry of nitrenes was also reviewed [54, 55].

The formation of free radical $H\dot{N}\cdot$ by decomposition of hydrazoic acid has been suggested by a number of authors since 1928 (see Vol. III, p. 167). This was substantiated by experiments on the decomposition of HN_3 by the flash photolysis of Thrush (Vol. III, p. 167). The formation of nitrene radicals from azides by flash photolysis was reported simultaneously and independently by Koto [56], Reiser *et al.* [57–59]. Reiser rationalized the reaction derived from flash photolysis of formation of azo compounds (5):

$$R\dot{N}\cdot + RN_3 \longrightarrow RN{=}NR + N_2. \qquad (5)$$

Nitrenes have triplet ground states. At room or higher temperature they can behave as triplet diradical and singlet electrophilic species. They have a very short time of several microseconds, but can undergo stabilization by a number of reactions, such as: isomerization to amines, dimerization to azo compounds, ring closure to heterocyclics, various addition reactions [4]. Curtius rearrangement [60] is one of the classical examples of passing through the nitrone formation.

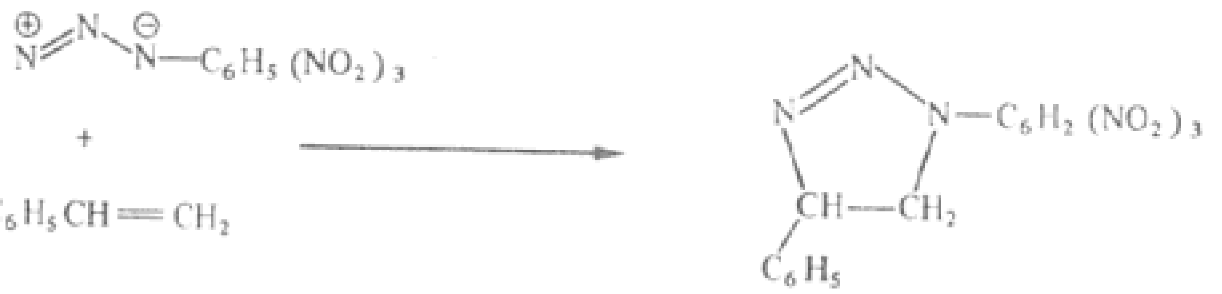
Infra-red study of thermal decomposition of N_3^- ion (e.g. KN_3 at 345–350°C) shows the formation of NCO^- as a by-product of CO_2 trapped during pressing and the possible reaction:

$$N_3^- + CO_2 \longrightarrow NCO^- + \tfrac{1}{2}O_2 + N_2. \qquad (6)$$

Azido compounds can be convenient intermediates in the synthesis of natural products containing amino group. Thus crystalline 4-amino hexoses can be formed by hydrogenation of 4-azido hexoses [70].

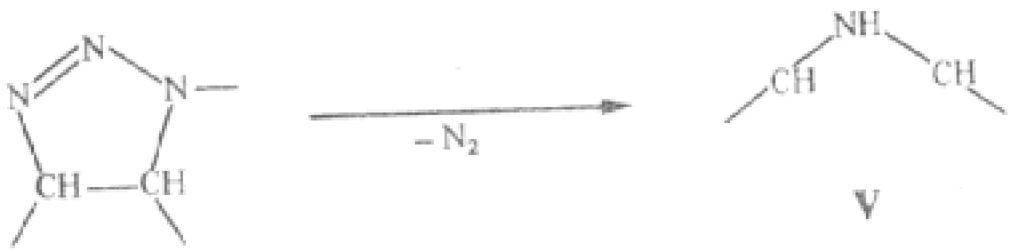
Heterocyclics from Azides

An important reaction is 1,3-dipolar cycloaddition reviewed by Huisgen [61]. An example can be seen from the reaction of styrene (dipolarophile) and picryl azide (1,3-dipole) yielding a triazoline (IV):



IV

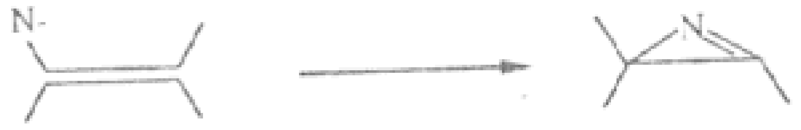
1,3-Dipolar addition should also occur between nitrenes and acetylenes [61]. The triazoles (IV) can lose N_2 yielding aziridines [72] (V)



IV

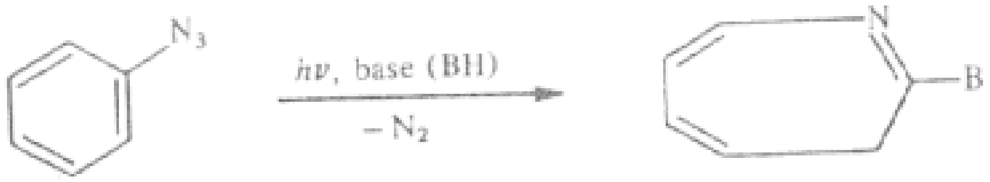
V

Pyrolysis of vinyl azides offers an interesting method of forming azirines [62] (VI)



VI

A similar result was obtained by photolysis of vinyl azides. The reaction can lead to azepines (VII) [63] possibly through the intermediate formation of aziridines [64] (as known, diazepines are an important group of tranquillizers [65]).

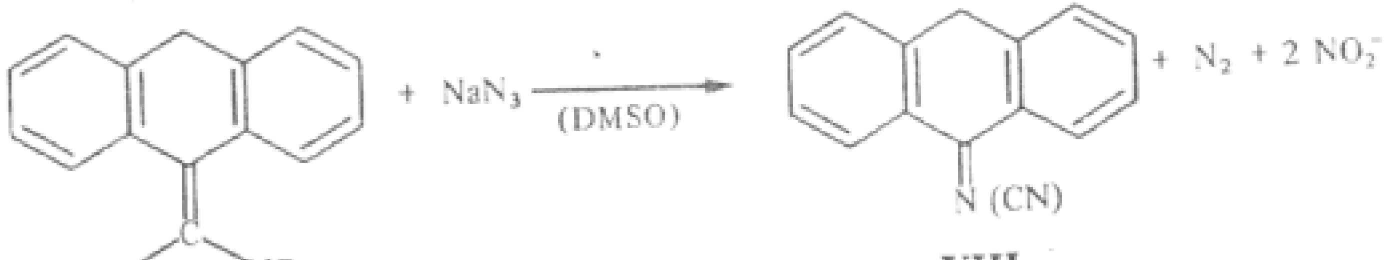


VII

The reduction of vinyl azides with sodium sulphite followed by hydrolysis can lead to ketones [71].

Other Reactions of Azide Anion and Radical

An unusual reaction was recently reported by Hoz and Speizman [65] on the reaction of azides with nitroalkenes, resulting in the formation of *N*-cyano compounds (VIII)



VIII.

The mechanism of the reaction is not quite clear.

Another interesting reaction comes from the fact observed by Forster and Fierz [67] that the azido-group can function under basic conditions as an *intra*-

molecular oxidizing agent. Thus α-azido ketones are transformed into α-diketones. The reaction was mentioned in the review by Boyer and Canter [68] and recently studied [69] as a two step reaction (7):

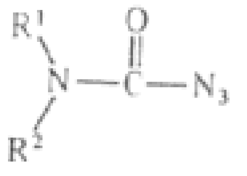
$$C_6H_5CH_2CN \xrightarrow[2.\ \text{excess } N_3^-/(CH_3)_2SO]{1.\ NBS/CCl_4} \underset{90\%}{C_6H_5CN} + N_2 + CN^- \qquad (7)$$

Minisci [186] described the addition of azide radical to double bonds. Particularly interesting is the addition of $N_3^{\cdot}$ in allilic position.

Some Organic Azides

Among different groups of organic azides a few are of some interest because of their properties.

Such are carbamoyl azides [53] of a general formula (IX)



IX

There are three methods of preparing IX:

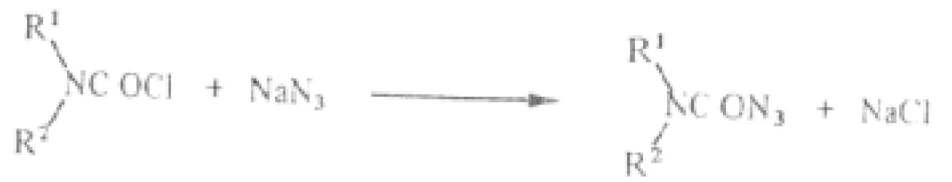
1. Diazotization of semicarbazide or other compounds containing the carbohydrazide grouping:

$$RNHCONHNH_2 \xrightarrow{HONO} RNHCON_3 + H_2O \qquad (8)$$

2. Reaction of isocyanate with hydrazoic acid:

$$RNCO + HN_3 \longrightarrow RNHCON_3 \qquad (9)$$

3. Reaction of carbamoyl chlorides with metal azides:



(10)

An imino-derivative of carbamoyl azides, guanyl azide can react forming 5-aminotetrazol (X) [73], a substance with explosive properties:

X

No similar cyclization can occur with carbamoyl azide.

An interesting azide which is in use as a source of triazolines and aziridines [72] is a cyanogen azide, $CN{\cdot}N_3$. It can be obtained according to Marsh and Hermes [74] as a colourless explosive oil by a simple reaction of sodium azide with cyanogen chloride. It is not stable at room temperature but in a 27% solution in acetonitrile at 0° to −20°C can be kept undecomposed (see also [75]). Later on Coppolino reported [76] that cyanogen azide can be decomposed when kept in solution even at −20°C. With alkenes it does not give very stable traizolines.

Carbon azide $C(N_3)_4$ is not known. However Müller and Dehnicke [105] succeeded in obtaining a complex salt with triazidocarbonium ion (XI) by refluxing antimony azidochloride in carbon tetrachloride:

$$Sb(N_3)Cl_4 \xrightarrow[\text{reflux (4 hr)}]{CCl_4} [C(N_3)]^+ (SbCl_4)^-$$

XI

It decomposed after melting at 145°C.

Danger of Handling Azides

The danger of handling apparently stable organic azides has recently been described [77]. Thus:

1. Ethyl azide exploded when kept at −55°C for a few minutes, the reason for the explosion could not be elucidated.

2. *p*-Toluenesulphoazide exploded during distillation under reduced pressure.

3. A derivative of siladiazide $(CH_3)_2Si(N_3)_2$ exploded after being kept for three years when the flask with the substance was opened. Also $Cl_2Si(N_3)_2$, $ClSi(N_3)_3$, $Si(N_3)_4$ – residues from the distillation of the products of the reaction between $SiCl_4$ and NaN_3 in tetrahydrofurane – exploded. This was probably caused by HN_3 evolved from the above products. This is not surprising in the light of the observation below.

Hydrazoic acid (Vol. III, p. 166) is relatively stable, but can explode spontaneously on handling. Curtius and Radenhausen [78] described two unexpected explosions: (1) when the substance was introduced into a barometer vacuum tube, (2) when the glass vessel containing the acid was removed from a cooling bath. A suspicion was advanced that hydrazoic acid stored for a long time in a glass container is more dangerous than the same acid freshly prepared, probably due to impurities taken from the glass [79–81].

4. Borazides: $(CH_3)_2BN_3$, $(Cl_2BN_3)_3$, $B(N_3)_3.Py$ exploded without any apparent reason when poured or taken with a nickel spatula.

5. Esters of azidoacetic acid, for example $N_3CH_2COOt\text{-}Bu$ can explode above 80°C [82].

6. Acyl azides can present danger in handling, for example during distillation *in vacuo*. An accident with toluene-sulphonyl (tosyl) azide has been described.

Cyanic Triazide (Vol. III, p. 194)

No practical application has been found for this interesting compound owing to its sensitivity to handling, impact, volability and hygroscopicity [142–144]. Nevertheless its structure aroused a certain amount of interest and the X-ray structure was examined [145]. It confirmed the structure given in Vol. III, p. 194, formula XI.

Explosive Properties of Hydrazoic Acid

Médard [88] reported thermochemical data for hydrazoic acid:

$$\text{heat of formation } -\Delta H_f = 71.66 \text{ kcal/mol (gas)}$$
$$= 64.37 \text{ kcal/mol.}$$

According to Bagal [1] aqueous solutions of hydrazoic acid can detonate: 70% aqueous HN_3 showed the rate of detonation 7300 m/s. Anhydrous hydrazoic (liquid) gave 8100 m/s.

As previously mentioned hydrazoic acid stored for a long time is more dangerous in handling than the product freshly prepared.

Gentle friction can produce an explosion of hydrazoic acid. An accident has been described of an explosion of the substance, caused by the friction of a piece of glass in a flask put there to produce more uniform boiling [94].

Ammonium Azide (Vol. III, p. 190)

This interesting salt attracted attention as it produces a considerable amount of gas: 1148 l/kg the highest figure for all explosives.

It is a crystalline substance, readily soluble in water and 80% ethanol, insoluble in ether and benzene. It melts at 160°C and begins to decompose. It is volatile and sublimes below 250°C under 150 mmHg. The vapour pressure at different temperatures was determined [1]:

at	48.0°C	85°C	125°C	134.2°C
was found	4.5	55.1	508.1	782.1 mm.

When heated under atmospheric pressure it decomposed while dissociating into NH_3 and HN_3 and finally the HN_3 exploded [103].

The easiest method of preparing ammonium azide [125] consists in the reaction of sodium azide with ammonium chloride in dimethylformamide at 100°C. After the reaction subsided, all was cooled to 60–70°C and dimethylformamide was distilled under reduced pressure. Ammonium azide crystallized out.

As previously mentioned (Vol. III) a practical application has not been found for the substance due to its volatility.

PHYSICO-CHEMICAL AND EXPLOSIVE PROPERTIES OF METAL AZIDES

The fundamental problem of why some azides (e.g. KN_3) are not explosive whereas others (e.g. $Pb(N_3)_2$) are, is still not fully understood. Nevertheless a great amount of information has been collected to date on various physico-chemical properties of azides which can partly throw some light on the problem (see Table 73, Fig. 79 and [189]).

They are assembled in Vol. 1 of [3] and include the chapters:

Introduction, R. F. Walker (p. 1),
(1) Synthesis and the Chemical Properties, T. A. Richter (p. 15),
(2) The Growth of Crystals, W. L. Garrett (p. 87),
(3) The Crystal Structures, C. S. Choi (p. 97),
(4) Molecular Vibrations and Lattice Dynamics, Z. Iqbal, H. J. Prask and S. F. Trevino (p. 131),
(5) Electronic Structure of the Azide Ion and Metal Azides, T. Gora, D. S. Downs, P. J. Kemmey and J. Sharme (p. 193),
(6) Slow Thermal Decomposition, P. G. Fox and R. W. Hutchinson (p. 251),
(7) Imperfections and Radiation Induced Decomposition, W. L. Garrett, P. L. Marinkas, F. J. Owens and D. A. Wiegand (p. 285),
(8) Fast Decomposition in the Inorganic Azides, M. M. Chaudhri and J. E. Field (p. 383),
(9) Stability and the Initiation and Propagation of Reactions in the Azides, J. Alster, D. S. Downs, T. Goza, Z. Iqbal, P. G. Fox and P. Mark (p. 449).

Vol. 2 of [3] contains a description of more practical problems:

Introduction, R. F. Walker (p. 1)
(1) Processes for the Manufacture of Lead and Silver Azide, T. Costain and F. B. Wells (p. 11),
(2) Analysis of Azides for Assay, and in Complex Media, H. Kramer (p. 55),
(3) Handling, Storability, and Destruction of Azides, B. D. Pollock, W. J. Fisco, H. Kramer and A. C. Forsyth (p. 73),
(4) The Sensitivity to Impact and Friction, L. Avrami and R. Hutchinson (p. 111),
(5) Electrostatic Sensitivity, M. S. Kirshenbaum (p. 163),
(6) Sensitivity to Heat and Nuclear Radiation, L. Avrami and J. Haberman (p. 199),
(7) The Role of Azides in Explosive Trains, M. Voreck, N. Slagg and L. Avrami (p. 249).

The reader, interested in the manufacture and use of azides should consult both volumes. Many problems described in the volumes are outside the scope of the present book.

Optical Properties

The optical and electronic properties of azides have been reviewed [3, (Vol. I, p. 224)]. So far it has been suggested that there are similarities between the alkali azides and halides but recently attention has been paid to the identification of defect centres formed by irradiation of azides. Deb [106] carried out experiments with thin films or single crystals of Na, K, Rb and Cs azides between 140 and 280 nm at low temperatures, such as 4–77 K. He noticed an induced luminescence in all alkali azides. Earlier work by Audubert [107] showed a faint emission of ultraviolet light from various azides during thermal decomposition. Singer and Mueller [108] observed chemiluminescence and electron emission from thermally decomposing alkali azides.

Photoconductivity of azides, including $Pb(N_3)_2$ was examined by a number of authors [109–111].

Slow Decomposition of Azides

Slow thermal decomposition was examined by Garner (Vol. III, p. 171). It was shown [112] that when silver azide is heated, silver is formed in an oriented way through the azide lattice. The rapid growth of nuclei by the surface migration of metal in lead azide seems to be demonstrated [113]. Choi and Boutin [114] showed the existence of azide radicals in the course of the decomposition.

Some substances, including impurities, enhance the decomposition of azides. The impurities can be present in the course of preparation of azides or formed during their storage. It is known that the presence of carbon dioxide in air may produce a decomposition of lead azide. Also water vapour in air even at room temperature may accelerate the decomposition. This problem was tackled by Reitzner [115]. He found that the induction period was the result of the reaction of water vapour with lead.

The problem of the action of radiation on azides, particularly lead and barium azide has been reviewed [116]. Irradiation prior to thermal decomposition often effects a reduction or elimination of the induction period, a decrease in activation energy and an increase in the rate of decomposition. Zakharov and co-workers [117] have found that the application of a moderate electric field can affect the rate of thermal decomposition of azides.

Through irradiation the optical density of azides increases as shown by Roth [118] and Wiegand [119]. The experimental facts supported the hypothesis that colloidal metal was produced by irradiation of lead azide and tallium azide. Colloidal disorder can be created by radiation. Lead produced by photodecomposition is reactive and can form some products on exposure to air. Thus basic lead carbonate was found lead azide irradiated with X-rays [120, 121]. Lead azide expands along one crystallographic direction under the action of X-rays [122] and nitrogen in the form of N_2 can be trapped by the irradiated lattice

[123]. The visual colouration of lead azide was strongly suppressed by hydrostatic pressure of the order of 10 kbar [124].

Among different regularities a remarkable relationship exists between the heat of formation (ΔH_f) of a number of azides and infra-red frequency ν_2 ranging between 620 and 650 cm^{-1}. This is shown in Fig. 78 (Explosive azides) form a group separated from non-explosive ones. N_3^- ion becomes more asymmetric in the more covalent salts making those lattices thermodynamically less stable [102].

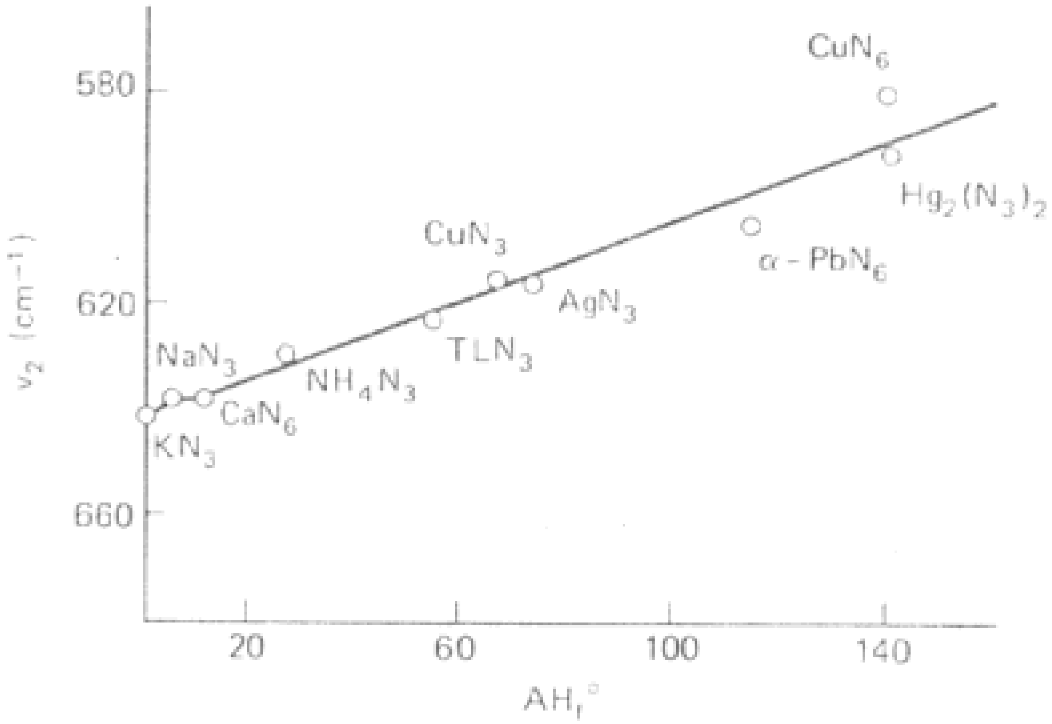


FIG. 78. Enthalpy of formation of azides ΔH_f^0 against infra-red frequency 580–600 cm^{-1}, according to [102].

Gray and Waddington [103, 104] determined experimentally and calculated enthalpies for the formation of azides. A great difference exists between non-explosive and explosive azides, as can be seen in Table 73.

TABLE 73. Azide enthalpies of formation ($-\Delta H_f$)

NaN_3	5.1 kcal/mol
KN_3	−0.3
$Ca(N_3)_2$	−2.4
$Ba(N_3)_2$	−5.3
α-$Pb(N_3)_2$	115.5
$Ag\ N_3$	74.2
$Cu(N_3)_2$	140.5

The above figures and Fig. 78 throw some light on the problem (p. 475) of why lead and silver azides possess marked initiating properties when the others do not.

Fast Decomposition and Explosion

A considerable amount of work has been carried out on the fast decomposition of azides. This was initiated by heat, friction, impact, shock, light, electric field and atomic particles.

Thermal initiation is given in Table 74.

TABLE 74. Thermal initiation of azides

Azides		Temperature of initiation, and melting, °C
Potassium azide	KN_3	350
Silver azide	AgN_3	251, explodes above the m.p.
Tallous azide	$Tl\ N_3$	334
Cuprous azide	$Cu\ N_3$ or $Cu_2(N_3)_2$	melts at *ca.* 205
Mercurous azide	$Hg\ N_3$	melts at *ca.* 210 and then explodes
Mercuric azide	$Hg(N_3)_2$	melts at *ca.* 195 and explodes at *ca.* 460
Cadmium azide	$Cd(N_3)_2$	explodes
Lead azide	$Pb(N_3)_2$	explodes

Impact sensitivity of lead and silver azides depends on the size of crystals or pellet thickness. The larger the crystals, the more sensitive they are. This and other problems related to the initiation of primary explosives are discussed by Bowden and Yoffe [125] and extensively reviewed by Chaudhri and Field [3 (Vol. 1, p. 383)].

LEAD AZIDE (Vol. III, p. 169)

Usually the advent of lead azide as a primary explosive is connected with the first patent by Hyronimus [83] in 1907. However, according to the literature [84] the first experiments with lead azide were carried out in Spandau (Germany) as early as 1893. They ended with a tragic accident and all experiments with lead azide were suspended. A number of doubts were expressed on the practical use of lead azide as an initiator [85, 86]. Also Kast [87] in his well known book raised the problem of whether lead azide and azides of other heavy metals could be used as primary explosives.

This view has prevailed in many countries. In the U.S.S.R. lead azide entered industrial production in 1929 (Bagal [1]). Between 1920 and 1930 a considerable amount of work was dedicated to the production of lead azide which would be less hazardous to manufacture and thus dextrinated product was manufactured.

Properties of Lead Azide

It was originally thought that lead azide existed in two allotropic forms: α and β (Vol. III, p. 169). Now it is accepted that the substance is polymorphic and exists in four forms: α, β, γ and δ. The α-orthorhombic is the only one acceptable for technical application. It is the main product of precipitation with traces of the other forms present [89]. The monoclinic β-form is stable when dry, but recrystallizes as the α-form. The presence of some organic dyes (e.g. eosin) enhances the formation of β-form and hydrophile colloids inhibit its formation. Breaking a needle of β-form may produce an explosion (contrary to the views of some authors; Vol. III, p. 173). The monoclinic γ-form is less stable than α and β [90]. It can be obtained from pure reagents at pH 3.5–7.0 or in the presence of vinyl alcohol. The triclinic δ-form precipitates from pure reagents at pH values of between 3.5 and 5.5 [90]. Both forms γ and δ are usually precipitated simultaneously and can be separated (with care!) by hand.

Apin (according to [1]) described a method of preparing needle like β-modification through a slow diffusion of aqueous solutions of sodium azide and lead nitrate.

Among different modifications of lead azide, basic salt $N_3Pb(OH)$ was prepared by Wöhler and Krupko [91] and showed less pronounced explosive properties: it deflagrated without detonating. Several basic lead azides have been prepared by Feitknecht and Sahli (Vol. III, p. 178).

An attempt was made to obtain $Pb(N_3)_4$ [92] from PbO_2 and hydrazoic acid. The product $Pb(N_3)_4$ was unstable and readily lost nitrogen to form $Pb(N_3)_2$.

Crystal Structure of α-$Pb(N_3)_2$

The crystal structure of α-$Pb(N_3)_2$ was examined with the help of three dimensional neutron-diffraction by Choi and Boutin [93]. These authors found four crystallographically distinct azide groups in a unit cell: azide (I), (II), (III) and (IV) – Fig. 79. Azide (I) is coordinated to four Pb atoms, two at each end. It is symmetric in both coordination and in N–N distances. Azide (II) is also surrounded by four Pb atoms but the coordination is asymmetric. The structure of azide (III) is very similar to azide (II) but the structure (III) is more symmetrical than (II). Azide (IV) is strongly asymmetric in both coordination and N–N distances.

Each Pb atom is surrounded by eight azide groups with bond lengths between 2.57 and 2.90 Å. It is further surrounded by four Pb atoms at distances 4.2–4.5 Å.

Spontaneous Explosions of Azides (Vol. III, p. 173)

Spontaneous explosions of saturated solutions of azides during crystallization

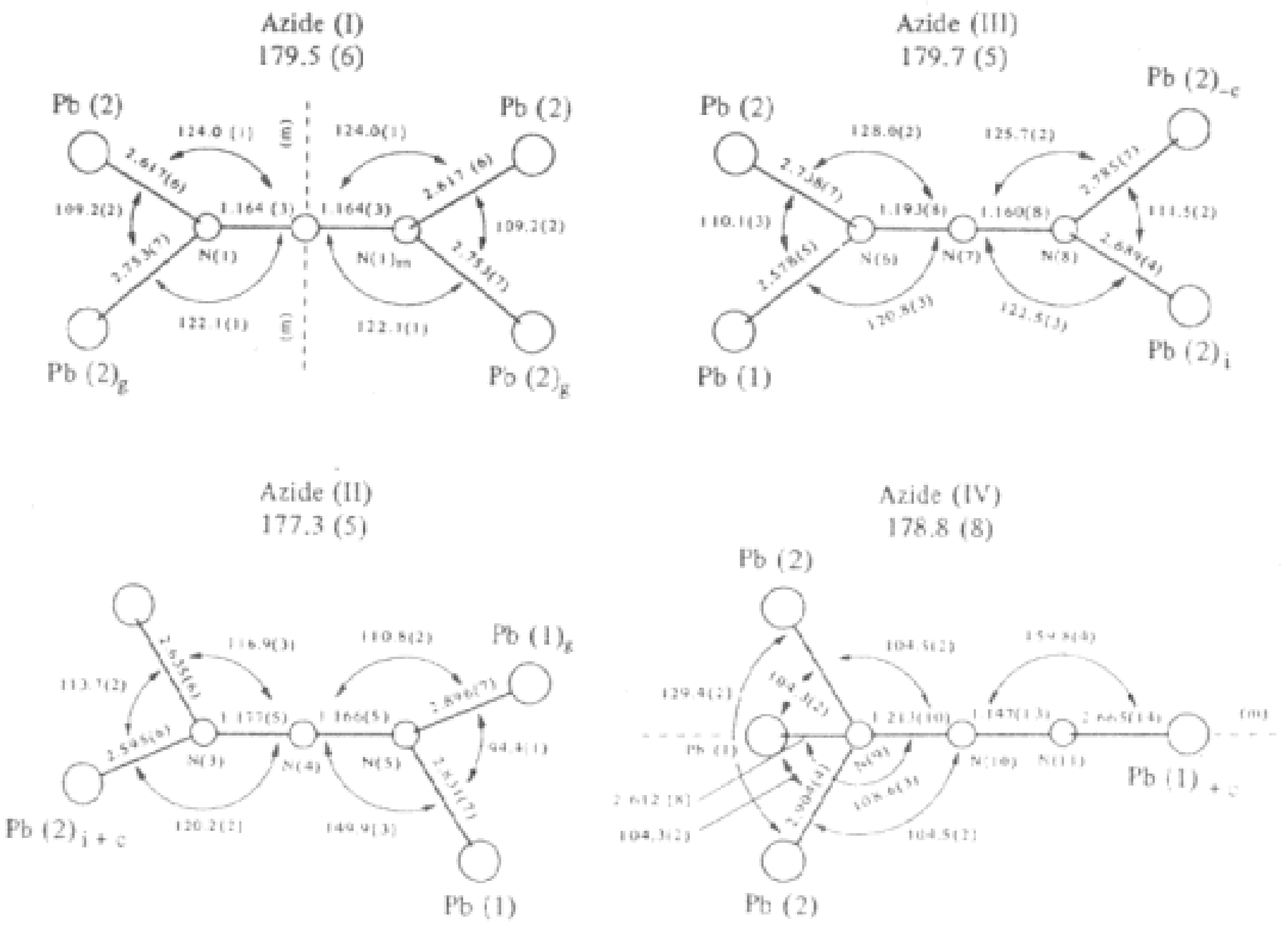


FIG. 79. Four crystalline forms of α-lead azide, according to Choi and Boutin [114].

have been described. Spontaneous explosions were described for cadmium [45], cupric and mercuric [96], lead [91, 96, 97, 98] azides. Rogers [99] gave a description of his experiments with lead azides and Taylor and Thomas [100] thoroughly examined the conditions of the experiments. They prepared a 0.7% lead azide solution in 50 cm³ of hot 5% aqueous ammonium acetate and allowed it to cool to room temperature. After 11,400 sec (i.e. 1800 sec before the expected time of explosion) the crystallized out large crystals were filtered out and the liquid was left to stand. At the expected time a major explosion of the liquid occurred, but the filtered crystals remained intact. The authors tried to rationalize the phenomenon in terms of formation of nuclei and electric discharge of different layers of nuclei.

Fox, Jenkins and Taylor [101] discussed the three hypotheses which materialized to explain the phenomenon of spontaneous explosions, these are:

(1) the release of stored energy which is high enough to cause an explosion [97],
(2) reactive intermediates were formed in the solution [98],
(3) discharge of sparks between growing crystals [100].

The third hypothesis seems at present to be the most probable. To verify it, Fox *et al.* [101] placed a metal electrode near the surface of the solution and measured the accumulation of electric charge. Indeed, in the solution in which explosions took place very strong charge fluctuations preceded explosions. Small lead detonators fired by Taylor and Thomas did not induce the explosion of the liquid which emanated from the crystals of lead azide. This indicated that the product – crystals of lead azide – have not yet existed in the solution. Stirring and introducing additives suppressed spontaneous explosions. Stirring dispersed the charges and did not allow their localized accumulation. The additives were absorbed by crystals at an early stage and created a lower spark sensitivity.

Sensitivity of Lead Azide

Sensitivity to high temperature was extensively studied [124]. Chaudhri and Field [127] recently described a dependence on temperature of initiation of α-lead azide on crystal thickness, while studying individual single crystals of known size. There was a drop in the explosion temperature from 415 to 385°C for an increase in crystal thickness from 4 to 30 μm. Crystals of less than 3 μm thickness did not explode even up to 450°C. They did not melt at this temperature.

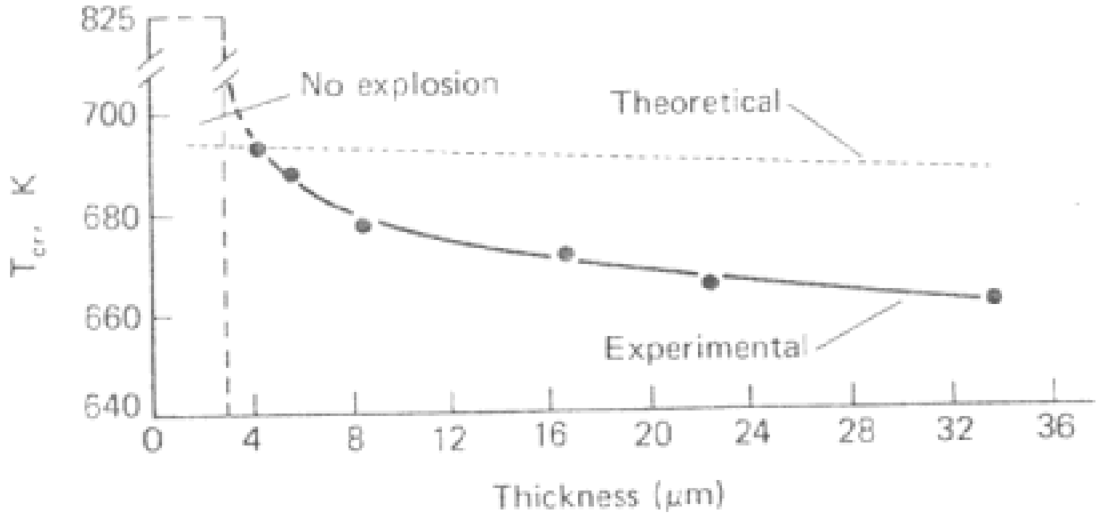


FIG. 80. Critical explosion temperature against crystal thickness, according to Chaudhri and Field in [3, Vol. I, p. 383].

In vacuo no critical size of crystals was observed [128]. The previously mentioned behaviour of primary explosives at high *vacuo* [39–45] may explain the failure to find the critical size of lead azide under very low pressure.

As has been mentioned large crystals of lead azide are more sensitive to impact than the small ones [124]. This was noticed by Solonina as early as 1910 [1].

Direct flame (e.g. from black powder), sparks of electric discharge and glowing electric wires do not readily ignite lead azide and Claessen [129] suggested adding lead styphnate to increase its ease of ignition.

Lead azide is less sensitive to impact than mercury fulminate, as reported by Kozlov (according to [1]).

To increase the sensitivity of lead azide to impact, tetrazene was added in German detonators 'Duplex', according to Bagal [1]. Mixtures of 90–93% lead azide and 10–7% tetrazene were used.

Chaudhri and co-workers [190] determined the rate of detonation of single crystals of α-lead azide. Crystals of cross section 2 mm × 2 mm and above detonated at 8000 m/s, and smaller size (*ca.* 1 mm) exploded at 3000 m/s.

Stability and Reactivity of Lead Azide

Roux [130] kept lead azide at 50°C for 25 months, and at 80°C for 15 months and has not noticed any change of properties. Extensive experiments on the stability of lead azide were carried out by Solonina (in 1910) and Bubnov (in 1940) – according to [1]. The following are conclusions based on their work:

(1) Dry lead azide does not react with metal casing made of aluminium and copper or their alloys (brass, duraluminium).
(2) In the presence of carbon dioxide, moist lead azide did not react with aluminium.
(3) In the presence of carbon dioxide or other acidic compounds, moist lead azide can react with copper casing. Hydrazoic acid was evolved which reacted with copper or copper oxides to yield copper azides.

As recently discovered moisture without carbon dioxide can also promote reactions of lead azide.

As known copper azides are sensitive IE and considerable work has been done to protect metals from reaction with lead azide.

The Manufacture of Lead Azide (Vol. III, p. 178)

The description below is based on information from [1] and [3 (Vol. 2)].

'Colloidal' lead azide. This is a pure form of lead azide (over 99% purity) in fine particles of 3–4 μm. It is non-hygroscopic but not readily pourable and hence less adaptable for mass production. It is particularly sensitive to electric discharge and hence used for electric detonators. For this purpose 'colloidal' lead azide is often mixed with a concentrated nitrocellulose solution in ethyl ether–ethanol or other solvents.

Colloidal lead azide is obtained by adding at 25°C 4% aqueous solution of sodium azide to a small excess of lead nitrate solution. The precipitate is filtrated and washed with water and dried. Its density under 3000 kg/cm^2 pressure is 2.77 g/cm^3 (as compared with 2.93 g/cm^3 of crystalline lead azide).

British 'Service' lead azide. This is a crystalline lead azide containing a small proportion of lead carbonate on the surface of crystals. It is obtained by adding

1 M lead acetate and 2 M sodium azide solutions to the reactor which contains a quantity of sodium carbonate solution. The lead acetate is started a little ahead of the sodium azide so that some lead carbonate is formed which serves as a seeding agent for lead azide crystals. It contains 98.1% $Pb(N_3)_2$, crystals are large (*ca.* 55 μm), density under 15,000 kg/cm^2 is 3.31. Its temperature of explosion is 350°C with an induction period of 5 sec. It is non-hydroscopic, contrary to the dextrinated lead azide which is slightly hygroscopic due to the presence of dextrin.

Dextrinated lead azide. Dextrinated lead azide is made by adding, over a period of 30 min at 60°C, a dilute (3%) sodium azide to an equal volume of a lead acetate solution (7%) which contains dextrin from potato starch in a quantity of 6% to the expected yield of 6% of lead azide. The dextrin solution is made slightly alkaline with sodium hydroxide. The product contains *ca.* 92% of lead azide.

According to [3 (Vol. 2)] in Sweden a temperature of 75°C is maintained during the reaction, and du Pont Co. introduced 0.25% calcium stearate as an agent for coating the dextrinated particles. According to [1] the hygroscopicity of dextrinated lead azide can be higher than 0.5%.

British RD 1333 lead azide. The significant feature of this type of lead azide is the presence of sodium carboxymethylcellulose (CMC) without using sodium carbonate.

Here are the salient features of the process: 1.21 sodium CMC solution (10 g NaCMC/litre) were mixed with 0.145 litre of Empilan AQ 100 solution (100 g contains 100% ethylene derivative of lauric acid/litre) made up to volume of 15 litres with water are kept at 25°C. During a period of 60–70 min, introduced simultaneously, the solutions of sodium azide (108 g NaN_3/litre) and lead acetate (315 g $(CH_3COO)_2Pb \cdot 3H_2O$/litre) – 14 litres of each while stirring. The product precipitated and is washed by decantation, filtered and dried. The yield was 3.3–3.3 kg lead azide. The content of $Pb(N_3)_2$ 96.3%.

According to the U.S. experiments the temperature of the reaction 30–35°C should be maintained. The quantity of CMC is a critical parameter. The product should have a right viscosity and the degree of etherification. The rate of stirring should not be below a certain norm (e.g. 200 rpm).

British RD 1343 lead azide. This is almost identical with RD 1333 except that the wetting agent is omitted and the sodium azide is made more alkaline. It did not cause a deposit to build up a water line in the reaction kettle, leading to reduced cleaning operation.

Special Purpose Lead Azide (SPLA) [(3 (Vol. 2, p. 44)]. The Special Purpose lead azide was introduced in the U.S.A. It is of a greater sensitivity and lower hygroscopicity than dextrinated lead azide. It does not differ much from RD 1333 preparation. The difference is in temperature 37 ± 2°C and faster introduction of reagents (30 min).

Polyvinyl Alcohol Lead Azide (PVA Lead Azide). Polyvinyl alcohol was used instead of dextrin in Germany [2]. In the U.S.A. it is in use in Olin Mathson Corporation [131]. The addition of 3% PVA makes lead azide of better initiating properties, higher density and an easier inflammability than dextrinated lead azide [1].

Gelatine Lead Azide (GAM). Animal gelatine was used for crystal modification of lead azide with the addition of a small amount of molybdenum sulphate [132]. It is claimed that the product is safer in handling than usual lead azide.

Spheroidal dextrinated lead azide. In the 1950s a spheroidal form of dextrinated lead azide was developed by Taylor and co-workers [185] and was named RD 1352. The method was tried in the U.S.A. and described in [3, (Vol. 2, p. 32)].

It consists essentially in reacting aqueous solutions of sodium azide and lead azide in the presence of solutions of dextrin and Tamol SN (surface active agent) at 60°C with an agitator revolving at 275 rpm. After cooling, the mother liquor was decanted, the precipitate washed with water, alcohol and dried.

The picture of the product by this interesting method is given in Fig. 81 (b, c). For comparison British Service lead azide (a) is also given.

SILVER AZIDE (Vol. III, p. 182)

A correction should be made to the description in Vol. III of some properties of silver azide: it is non-hygroscopic, according to C. A. Taylor and Rinkenbach [133] and Costain [3, (Vol. 2, p. 51)]. The hygroscopicity described previously was probably due to impurities.

The photosensitivity was discussed in Volume III.

Silver azide is soluble in ammonia to form a complex, upon evaporation of ammonia the azide is recovered unchanged. In nitric acid it dissolves with decomposition and the evolution of HN_3. On exposure to light silver azide turns first violet and finally black, as colloidal silver is formed and nitrogen evolved [3 (Vol. 1, p. 58)].

A suspension of silver azide in boiling water decomposes with colouration similar to that of the photodecomposition [91]. When heat-dried the azide turns violet at 150°C, and melts at 251°C to a dark liquid. At 253°C it starts evolving nitrogen and metallic silver. When heated rapidly it explodes at 300°C emitting a green light [91, 3 (Vol. 1, p. 58)].

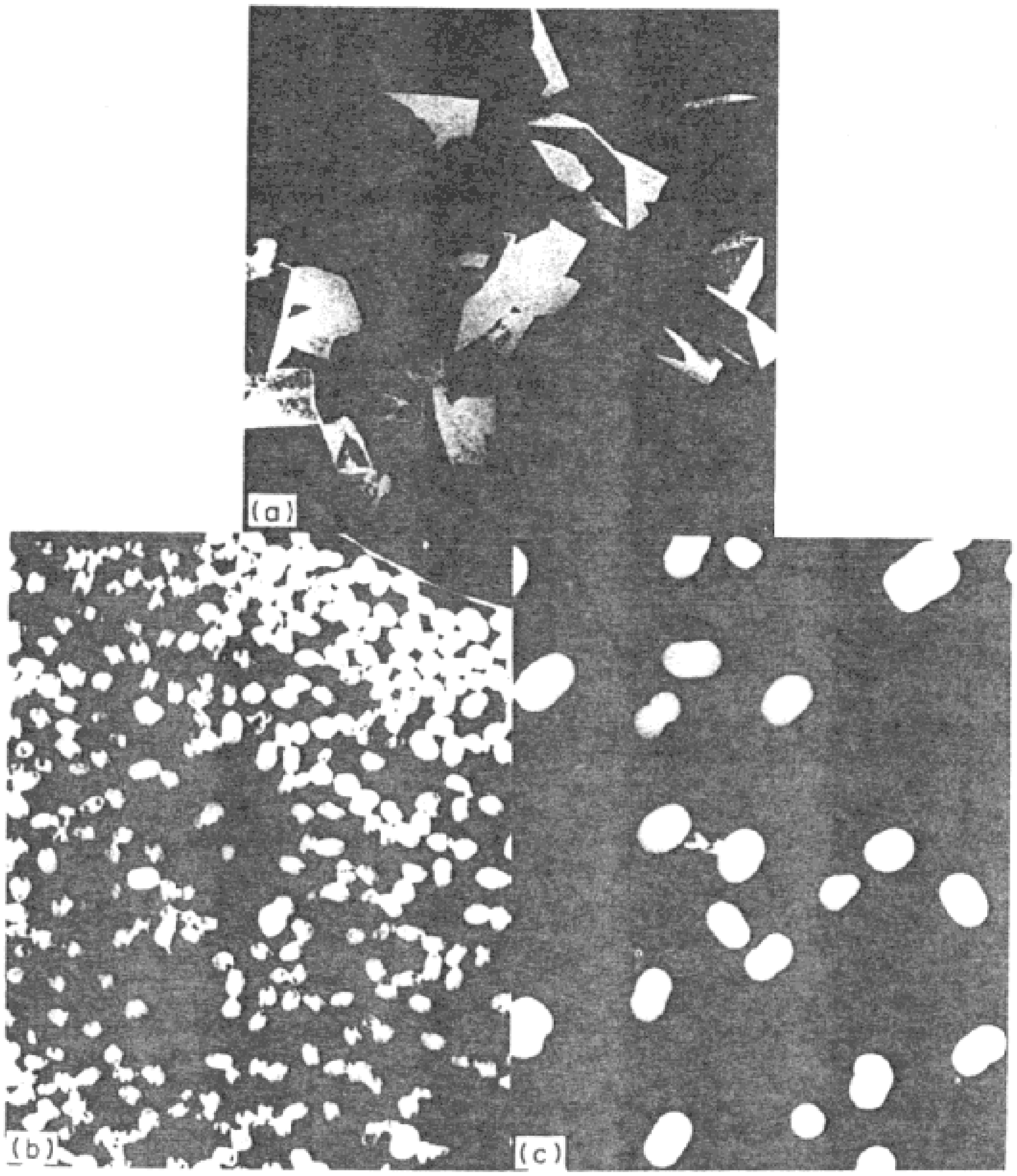


FIG. 81. British Service 170x (a)* and Spheroidal Dextrinated Lead Azide (Picatinny Arsenal) x 50: (b) 20 min and (c) 30 min respectively after start [3, Vol. II].
*British Crown copyright reserved.

Silver azide crystallizes in an orthorhombic form with four molecules per unit cell. This was established by a number of authors [134–137]. The unit cell has dimensions of: $a = 5.6170$, $b = 5.9146$, $c = 6.0057$.

It has better initiating property than lead azide (Vol. III, p. 177).

Silver azide is now in use in small and strong detonators in the U.K., U.S.A., Holland, Sweden and Germany. The main obstacle against the use was originally the fact that silver azide was not in a suitable form for pouring and pressing into detonators. During the early 1950s G. W. C. Taylor [138], Williams and Peyton [139] developed processes for making granular AgN_3.

The method used in Picatinny Arsenal [2] is as follows. The reaction was carried out in a 10-litre stainless steel kettle with a stirrer. The reagents were: 2.0 l of filtered 2N silver nitrate solution, 2.0 l of filtered 2N sodium azide solution, 1.07 l of filtered pure ammonia (28%) solution. Silver nitrate followed by ammonia was introduced into the reaction kettle. Under vigorous mixing sodium azide solution was introduced and the content was warmed to 75°C within 5 min. Silver azide started to precipitate *ca.* 5 min later.

At this point 50 ml of acetic acid 3N solution was added over 5 min to induce seed-crystal formation. Distilled water was added at a rate of 40–60 ml/min to maintain the original level and avoid evaporation losses.

When the total time at 75°C was 30 min, heating was increased to reach 97°C within 10 min and over the next 60 min the temperature was raised to boiling point which indicated that all the ammonia had boiled off. Cold water (3.5 l) was added and brought into the jacket to cool the content of the vessel. During the cooling, 50 ml of 3N acetic acid was introduced into the kettle. After 10 min the temperature reached 30°C, the stirring was stopped, silver azide was allowed to settle and the solution was decanted. The product was decanted with two portions of 3 l distilled water. The product was collected on a cloth-filter, washed with ethanol (95%) and dried for 40 hours at 50°C. The yield was 540 g (90%).

Vigorous stirring during the evaporation of the content of the vessel is very critical. Without stirring large flat crystals are produced. The quantity of acetic acid added for seeding was important for achieving uniform bulk density.

Cadmium Azide $C_d(N_3)_2$

Cadmium azide was obtained by Curtius and Rissom [200] and Bassière [95]. Some work has been dedicated to its properties (Vol. III, p. 186).

According to Bowden and Singh [201] it is not decomposed by α- and γ-radiation. It shows the rate of detonation 4200 m/s. According to Wöhler and Martin [202] it is less sensitive to impact than lead azide, but more sensitive than silver azide.

Storage of Azides

Experiments on the storage of lead azide have shown [3 (Vol. 2)] that different types of lead azide withstand long storage. Some samples taken after 25 years of storage under standard storage conditions did not show any deterioration.

Toxicity

All azides are toxic, but their toxicity is due to the evolution of hydrazoic acid. The solid, insoluble azides such as lead and silver azides are practically non-toxic. Considerable studies were dedicated to the toxicity of sodium azide. It was found that the minimum lethal dose of NaN_3 is 35–38 mg/kg body weight [140]. Chronic poisoning with NaN_3 was studied by Bassendowska and co-workers [141]. They showed that the maximum permitable concentration of NaN_3 in air is 2 mg/m³, provided the skin of the worker is well protected.

Destruction of Lead Azide

Lead azide can be destroyed by acting with sodium hydroxide 10% solution at 20°C which gives $Pb(OH)_2$ and aqueous solution of NaN_3: (method of Kramer) [3 (Vol. 2, pp. 85–86)]:

$$Pb(N_3)_2 + 2\,NaOH \longrightarrow Pb(OH)_2 + 2NaN_3. \qquad (11)$$

Sodium azide can be recovered by evaporation and crystallization.

Another method was suggested by Richter [3 (Vol. 2)]. It consists in using a more concentrated (20%) sodium hydroxide:

$$Pb(N_3)_2 + 4\,NaOH \longrightarrow Na_2PbO_2 + 2\,NaN_3. \qquad (12)$$

Here lead compound remains in solution in the form of sodium plumbate. Careful acidification of the solution with nitric acid leads to the formation of lead azide.

Data for lead azide [142] (Vol. III, p. 172)

Enthalpy of formation	+391.3 kcal/kg
Volume of detonation gases	231 l/kg
Density	4.8 g/cm³
Deflagration point	320–360°C
Lead block test	110 cm³
Impact sensitivity:	
pure product	0.25–0.40 kpm
dextrinated	0.3–0.65 kpm
Specification (U.S.A.).	
Net content (by determination as $PbCrO_4$)	min. 91.5%
Moisture	max 0.3%
Mechanical impurities	nil
Water solubles	max 1%
Lead content	min. 68%
Copper content	nil
Reaction	neutral

Bulk density	min. 1.1
Deflagration point not below	300°C

Lead azide detonators for coal mining have copper tubes. For all other blasting aluminium caps are used.

MANUFACTURE OF SODIUM AZIDE

It is appropriate to give a description of the basic compound used for producing azides. Below is a short description based on that of Bagal [1].

As known this is a two-step reaction (13):

$$Na + NH_3 \longrightarrow NaNH_2 + \tfrac{1}{2} H_2 - 21 \text{ kcal} \qquad (13a)$$

$$NaNH_2 + N_2O \longrightarrow NaN_3 + H_2O. \qquad (13b)$$

(a) Sodamide (Fig. 82)

Sodium should be of 99.5% purity. Gaseous ammonia – in a steel bottle (1) warmed to 30°C – should not contain more than 1% water. It is dried over NaOH and KOH in (2) before entering the 200 l reactor (3) made of stainless steel with an air-tight cover and a stirrer with 100 revolutions/min. It should be warmed to 150–200°C, washed inside for 5–10 min with gaseous ammonia and loaded with 28 kg of sodium. The reactor is heated to 360°C and ammonia introduced (4). At the beginning a temperature of 380°C is maintained. When the gases leaving the reactor contain 80% hydrogen, the temperature should be lowered to 340–350°C, as a higher temperature may produce a distillation of sodamide which would cause deposits to form in the gas conduction pipes. The end of the reaction is manifested by the fall of hydrogen content to 2–8%. One batch of sodamide consumes 35–40 kg of ammonia. The yield of sodamide was not given.

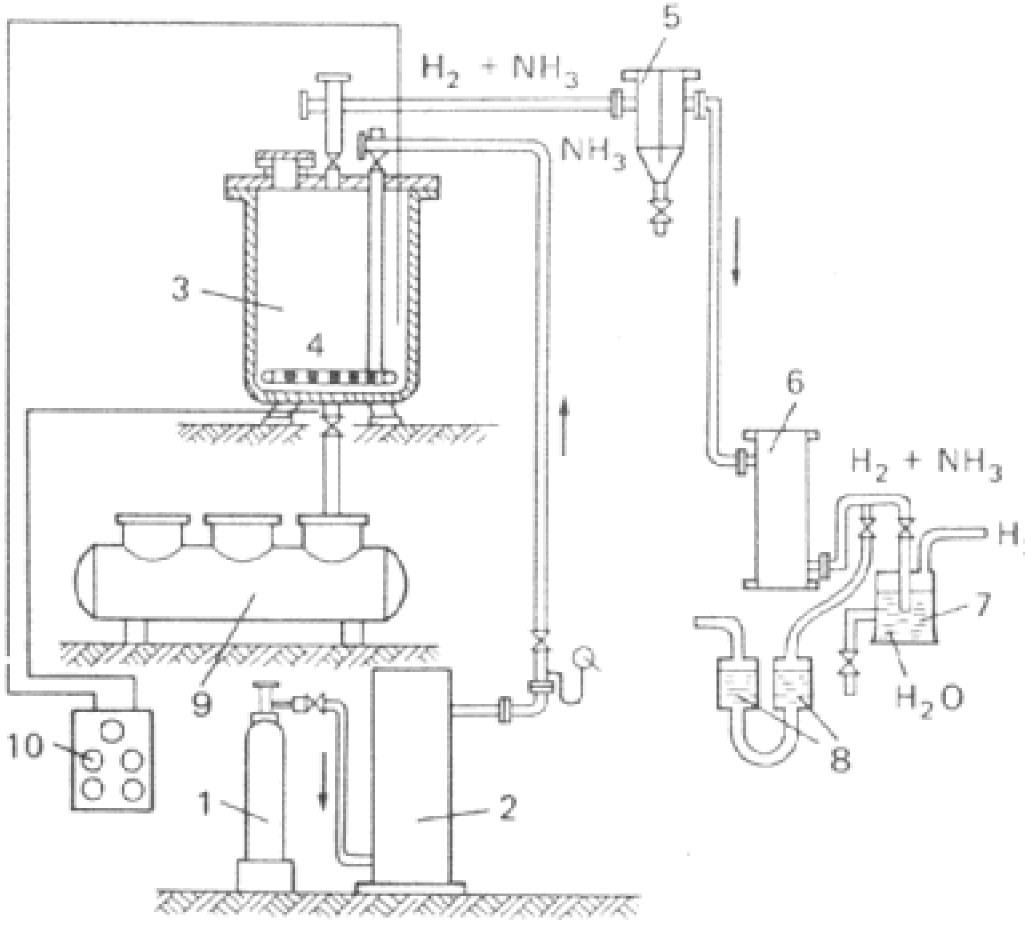


FIG. 82. Amidation of Sodium, according to Bagal [1] 1 – ammonia steel bottle, 2 – drying column, 3 – reactor, 4 – perforated ring, 5 – dephlegmator, 6 – safety column, 7 – water container, 8 – flowmeter, 9 – sodium azide reactor, 10 – controls.

The gases from the reactor are passed through the dephlegmator (5) and safety column (6) which prevents a return of gases to the reactor. Finally the gases enter water container (7) and retain out flowing ammonia.

It is important not to introduce ammonia after the process has ended, as it can form undesirable impurities (an 'over amidation').

(b) Sodium Azide (Fig. 83)

The reaction is carried out in a horizontal heated electrical apparatus made of steel. Before starting the reaction it should be thoroughly dried by warming to 170–200°C. To check the tightness of the apparatus ammonia is blown through for 5–10 min. Hot melted sodamide (350°C) is poured from the amide apparatus. The reaction of sodamide with nitrous oxide is exothermic and there is little need of heating the reactor. The best temperature of the reaction is 200–220°C. At 250°C the reaction is too fast and may lead to an explosion. To achieve the uniformity of the reaction nitrous oxide is introduced into both ends of the reactor.

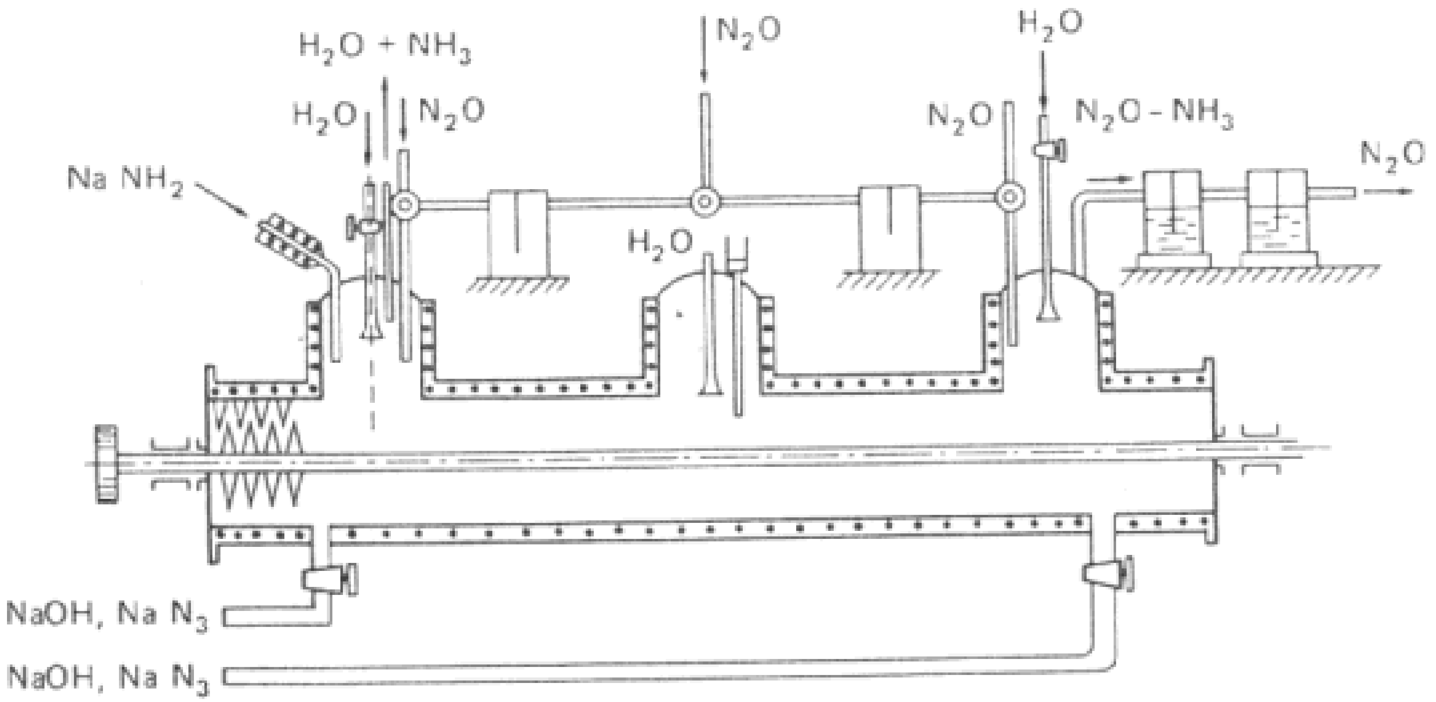


FIG. 83. Reactor for production of sodium azide, according to Bagal [1].

An analysis of out going gases should be carried out. They should contain 35–40% N_2O and 25–30% NH_3. The end of the reaction is manifested by the fall in the ammonia content to 3–5% NH_3 and the fall of temperature. The time to carry out the reaction of one batch is *ca*. 30 hours and the yield is 28–30 kg.

The content of the reactor is cooled to 100°C and washed with water. Care should be taken with this process, as water reacts vigorously (exothermic reaction) with unreacted sodamide. Sodium azide with sodium hydroxide is taken by water (200 l), filtered and evaporated to a density of 1.55–1.57 at 20°C. Sodium azide is collected, washed with a small quantity of water and finally with ethanol.

Sodium Azide Formation in Liquid Ammonia

This method was worked out in the U.S.S.R. [1] and based on a reaction at relatively low temperature in liquid ammonia. Both reactions: amidation and azidation can be carried out in the same reactor – autoclave of 200 l capacity and pressure up to 100 kg/cm^2.

Liquid ammonia dissolved sodium and the solution (under the action of catalysts) reacted to form sodamide. Sodamide is practically insoluble (*ca*. 0.1%) in liquid ammonia and precipitated as a fine powder. The catalyst is ferric oxide in quantity 3–5% (relative to sodium). The reaction takes 30 min to 1 hour at *ca*. 50°C. Hydrogen escapes from the autoclave at 40–60 kg/cm^2 through a safety valve working at this pressure.

The suspension of sodamide in liquid ammonia can readily react with nitrous oxide. Nitrous oxide kept in steel bottles under pressure is introduced into the autoclave under 25 kg/cm^2 maintaining the reaction temperature of 50°C.

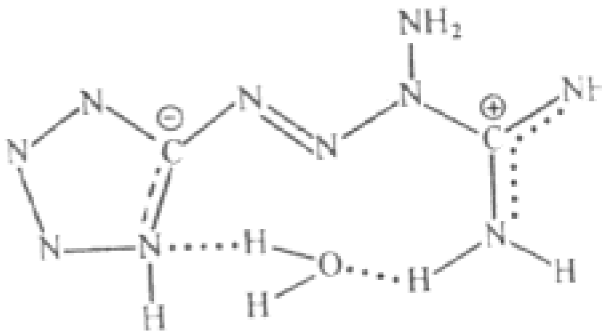
The reaction of N_2O with $NaNH_2$ in liquid ammonia is a somewhat complicated reaction. At first the reaction forms a complex 2 $NaNH_2$, N_2O. In the presence of an excess of ammonia over 0°C sodium azide is formed. However in the presence of sodium hydroxide the basic sodium azide ($NaN_3.2NaOH$) results. A higher temperature (e.g. 30–50°C) favours the formation of the basic compound, while a temperature of *ca*. 0°C prevents the formation of this substance.

Finally, a good solubility of sodium azide and practically no solubility of sodium hydroxide in liquid ammonia makes the separation of sodium azide from sodium hydroxide possible. Sodium azide retained on a filter should be washed with liquid ammonia. After ammonia has been evaporated, pure sodium azide remains with a yield of 99%.

TETRAZENE (TETRACENE) (Vol. III, p. 206)

Relatively recent X-ray analysis by Duke [147] confirmed the structure given by Patinkin, Horowitz and Lieber (formula I, Vol. III, p. 207). This is depicted

by formula (XII) where the substance is presented as a zwitterion of 1-amino-1-(1H-tetrazol-5-yl)azo guanidine hydrate.



XII

The heat of explosion is 558 kcal/kg and heat of formation – H_f = –70 kcal/mol.

The following properties are according to the U.S. Military Specification [148]:

Colour and appearance	white to light yellow coloured needle shaped crystals
m.p. and explosion	130 ± 2°C
Granulation	100% should pass through No 45 sieve
Specific gravity	1.65 ± 0.05
Heavy metals	absent

Meyer [142] gives some additional requirements:

moisture	max. 0.3%
aqueous extract	no acid present (on universal paper)
pouring density	0.3
deflagration point	min. 138°C
lead block test	155 cm^3

It is slightly more sensitive to impact than mercuric fulminate.

Bubnov (according to [1]) gave the figures of density depending on the pressure applied:

pressure	100	200	300	400	500	600	1000	1600
density	1.052	1.179	1.289	1.304	1.377	1.401	1.493	1.503

Pouring density was given as 0.45.

It is non-hygroscopic: at 30°C and relative humidity 90% it absorbed 0.77% water. It does not attack metals at room temperature [149], and does not react with concentrated ammonia at room temperature, sodium and potassium hydroxides decompose the substance and ammonia is evolved.

With concentrated acid it forms salts: hydroxide, perchlorate, sulphate nitrate. They are all explosive and their initiation temperature is *ca.* 140°C.

The practical use is limited to detonators which are initiated by another primary explosive and tetrazene is used as an intermediate booster or when mixed with another primary explosive to increase its sensitivity to flame or spark. The mixture tetrazene was used in explosive rivets (Vol. III, p. 240). Dynamit A.G. patented [150] mixtures of tetrazene with lead azide for this purpose.

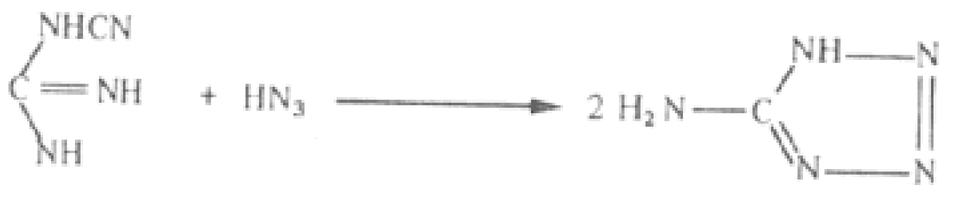
A few initiating compositions with tetrazene have been described in the Encyclopedia [148]. The most important seems to be 'Sinonydsatz' developed in Germany as a replacement for mercury fulminate mixtures. It proved to be non-corrosive and did not erode barrels of firearms. Their composition was: lead styphnate 25–55, tetrazene 1.2–5.0, barium nitrate 25–45, lead dioxide 5–10, anthymony sulphide 0–10, calcium silicide 3–15, powdered glass 0–5%.

Duplex-Cap (detonators) contained 0.3 g of a mixture of lead azide (92.5%) tetrazene (7.5%) pressed at 100 kg/cm^2 over 0.05 g of unwaxed PETN pressed at 300 kg/cm^2.

Tetrazole Derivatives and their Salts (Vol. III, p. 210)

Since the advent of Tetrazene attention has been paid to other compounds which contain tetrazole ring. An excellent review on Tetrazoles was given by Herman in the Encyclopedia [190]. Silver and mercury salts of 5-nitrotetrazol were suggested in Germany during World War II to replace the fulminates. According to the same source [190] mercuric salt of 5-nitrotetrazol proved to be a powerful initiating explosive. It is sensitive to friction, has an explosion temperature of 210°C. It seems that it is too sensitive for practical use.

The chemistry of tetrazol derivatives was reviewed by Bensen [192]. The simplest and most versatile derivative is 5-aminotetrazol (Vol. III, p. 210). It is usually obtained by the method of Stolle and Schick [151] from cyanoguanidine and sodium azide in an acid medium:

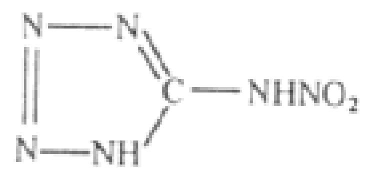


(14)

XIII

m.p. 203°C

Nitramino derivative of 5-aminotetrazol (XIV)

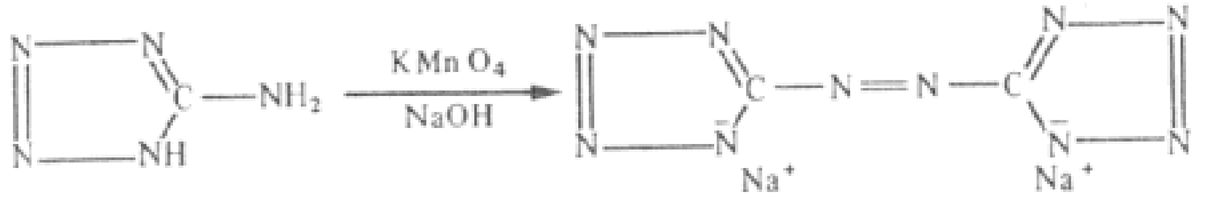


XIV

was claimed [152] to yield a lead salt with initiating properties. The *N*-nitro compound (XIV) was described by Lieber *et al.* [153].

Azotetrazol

According to Thiele [154] oxidation of 5-aminotetrazol with potassium permanganate in the presence of an excess of sodium hydroxide yielded sodium salt of azotetrazol:



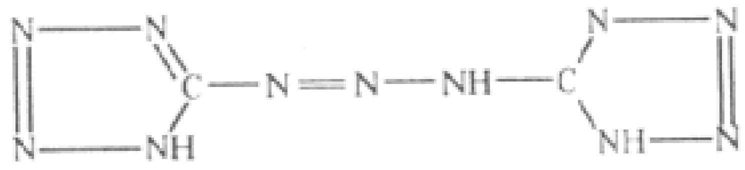
XV Sodium salt

Basic lead salt of azotetrazol (bulk formula $C_2H_{10}Pb \cdot 5H_2O$) was used in Germany during World War II. A description of the method of manufacture according to Bagal [1] is given here. The starting substance was sodium salt of 5-aminotetrazol (XIII). The sodium salt dissolved in a solution of sodium hydroxide at 70–80°C was charged with a 25% excess of potassium permanganate at the rate which would maintain the temperature 95–100°C. The solution should be brown. The filtered solution was cooled, the precipitated sodium salt was collected and dried at a temperature below 30°C.

To obtain the basic lead salt a solution of 3% sodium salt of XV containing 0.775% NaOH was prepared. The solution was poured into 7.5% solution of lead nitrate in a tilted reactor at 43–44°C. The precipitated basic lead salt was collected, washed with water of 30–30°C, ethanol and kept as ethanol moistened product. The yield was a 78% based sodium salt of XV.

The salt was used for electric igniters. The substance was mixed with nitrocellulose varnish and fixed on the resistance bridge.

Another important derivative of tetrazol is 1,3-ditetrazyltriazine (XVI)

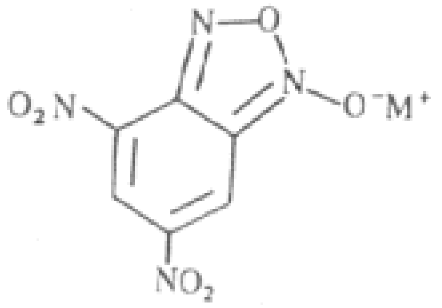


XVI

This was obtained by K. A. Hofmann and Hock [155] as described in Vol. III, p. 210. The compound forms colourless thin plates, crystallizing with 1 mole of water. It has masked acidic properties and can readily form salts with metals. On boiling with dilute hydrochloric acid it yielded 5-aminotetrazol (XIII) and nitrogen. The compound was described in review [156]. Sinha, K. R. K. Rao and Sankaran [157] made an extensive study of the properties of the substance and its salts. Lead salt has an explosion temperature of 185°C. Bahadur [158] described lead double salt of XVI and styphnic acid as an initiator. Practical experiments have shown that the salt is too dangerous to handle.

FUROXANE DERIVATIVES

Attention was recently drawn to the initiating properties of some salts of nitro derivatives of benzofuroxane. Potassium and barium salts of 4,6-dinitrobenzofuroxane as primary explosives were suggested by Piechowicz [193]:



No information is available as to the practical application of this salt.

The potassium salt was described as early as in 1899 by Drost [194], and a number of authors [195, 196] mentioned explosive properties of the salts of the above compound.

Benzofuroxane can be obtained according to Green and Rowe [195] by oxidation of *o*-nitroaniline with sodium hypochlorite. Nitration of benzofuroxane at 5–20°C yielded 4,6-dinitrofuroxane [194–196].

An excellent review on furoxanes was given by Kaufman and Picard [197].

Pepekin, Apin and co-workers [203] determined the energy of dissociation of the bond N → O in benzofuroxane. They found a value of 59.5 kcal/mol.

NITRO DERIVATIVES OF PHENOLS (Vol. III, p. 212)

An experimental work on thermal decomposition of the salts of picric and styphnic acids has been carried out by Andreev and Lu-Bao-Fen [159]. Ammonium, potassium and lead salts were examined, and the results summarized in Table 75.

The curve: rate of decomposition/temperature shows an autocatalytic trend of reactions.

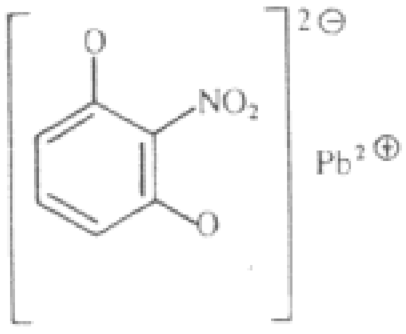
The decomposition of styphnates occurs at a lower temperature than that of picrates.

Lead Mononitroresorcinol (LMNR)

The lead salt of mononitroresorcinol was in use in electric detonators for making fuseheads. Some of them may be composed of this salt and dextrinated lead azide [159, 160].

TABLE 75. Thermal decomposition of picrates and styphnates

Salt	Interval of temperature res °C	E kcal/mol	Half-life time at 230°C, minutes
Potassium picrate	250–300	41.2	8600
Lead picrate	230–260	60.2	920 explosion at 260°C
Hydrogen Potassium Styphnate	170–200	47.6	262 explosion at 200°C
Di-potassium Styphnate	200–240	51.7	210 explosion at 250°C
Lead Styphnate	200–230	36.4	143 explosion at 240°C



XVII

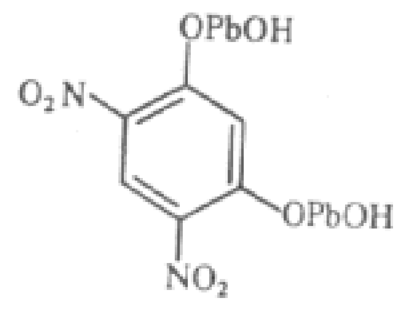
The main problem in making LMNR is the use of 2-mononitroresorcinol which should be obtained by very careful nitration of resorcinol. Resorcinol is heated with fuming sulphuric acid at 100°C for 30 min. The solution is cooled to 25°C. After adding mixed acids it is allowed to stand for 30 min. The addition of water follows and distillation of the product with steam. It forms orange coloured prisms, m.p. 84–88°C, boiling p. 232–234°C [161, 162a].

Lead 2,4-Dinitroresorcinate (Vol. III, p. 220)

The Encyclopedia of Fedoroff and Sheffield [162b] gives some figures on the properties of lead dinitroresorcinate. It explodes at 265°C (induction 5 sec), heat of explosion is 270 kcal/kg. It is slightly hygroscopic: at 30°C, 90% relative hygroscopicity is 0.73%. It has low initiating property: 0.4 g did not initiate tetryl pressed at 70 kg/cm^2.

Basic Lead 4,6-Dinitroresorcinol

The salt was developed in Great Britain during World War II [162c]. Finely ground (40 g) resorcinol was gradually introduced to 98% nitric acid (400 g) at −15° to −20°C. The low temperature was kept by adding solid carbon dioxide to the nitration vessel. After all the resorcinol was introduced, the nitra-



XVIII

tion mixture was cooled to −50°C and then drawn into 5 times its volume of water with ice.

The crude product was purified by dissolving in 5% NaOH solution and pouring the solution into hot boiling 12% sulphuric acid. The precipitated dinitroresorcinol was washed with water. The yield was 27.5 g, that is, *ca.* 40% of theoretical.

The product reacted with an excess of freshly precipitated lead hydroxide suspended in water at 90°C.

According to existing information [162c] large scale manufacture of the salt in Great Britain was carried out by reacting dinitroresorcinol freshly filtered from nitric without purification with lead hydroxide at 90°C.

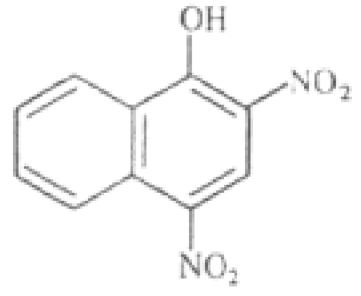
Lead Styphnate (Vol. III, p. 213)

No relevant facts can be added to those reported previously. The following are data taken from Meyer's textbook [142]:

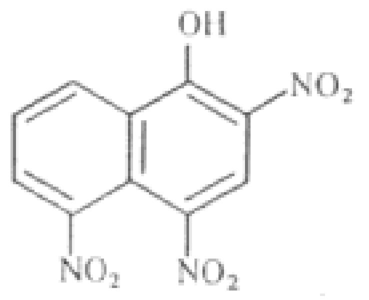
density	3.0
deflagration point	275–280°C
heat of explosion	370 kcal/kg
lead block test	130 cm^3 (according to [162d])
(it is 40% of TNT or 39% of picric acid).	
detonation velocity	4900–5200 m/s
Specification	
net content	min. 98%
moisture	max. 0.15%
lead content (determined as $PbCrO_4$)	43.2–44.3%
Heavy metals other than lead	max. 0.05%
Ca and Mg	max. 0.5%
Na	max. 0.07%
pH	5–7
nitrogen content	min. 8.8%
bulk density	1.3–1.5
deflagration point	min. 270°C

Lead Salts of Nitronaphthols

Recently Japanese authors [163] suggested the use of lead salts of di- and trinitro-α-naphthol, for example XIX and XX:



XIX



XX

According to the authors the salts are less sensitive to heat, impact, friction and electric discharge than the corresponding salts of phenol and resorcinol.

Complex Salts (Vol. III, p. 230)

In addition to complex perchlorates (Vol. III) Ni, Co and Cd form the following complex salts with hydrazine nitrate:

$Ni(N_2H_4)_3(NO_3)_2$ – deflagration at 215°C
$Co(N_2H_4)_3(NO_3)_2$ – deflagration at 210°C
$Cd(N_2H_4)_3(NO_3)_2$ – deflagration at 245°C

According to Médard and Barlot [164] they could be recommended as primary compounds. They possess the advantage that they are less sensitive to impact than mercury fulminate and lead azide. Their disadvantage is that they are difficult to ignite.

Nickel salt was examined in detail. It expands in lead block of *ca.* 85% of picric acid. The velocity of detonation in an 8 mm diameter plastic tube was found to be 2900–3100 m/s.

1,3,5-Triazido-2,4,6-Trinitrobenzene (Vol. III, p. 193, formula IX)

The substance is readily transformed into benzotrisfuroxane (Vol. I, pp. 603–604, formula II and Vol. III, p. 193, formula X). Kinetics of the transformation was studied by Korsunskii and Apina [181] – see Chapter IV.

Dinitrobenzenediazooxide (Dinitrodiazophenol DDNP, DINOL)
(Vol. III, p. 201)

Little can be added to the information given in Vol. III. According to Fordham [183] it has a velocity of detonation of 6900 m/s at a density of 1.58. As compared with other initiating explosives it is relatively insensitive to impact and friction. It has good storage properties and an application has been found in both commercial and military detonators, particularly in the U.S.A.

Salts of Acetylene (Vol. III, p. 227)

Silver acetylide. Although silver acetylide has not received practical application it has been the subject of a few published papers. Stettbacher [165] was first to draw attention to the very strong initiating properties of silver acetylide. He found that the initiating charge is 0.07 g (for AgN_3 and mercuric fulminate he found figures of 0.02 g and 0.29 g respectively).

Tamman and Kröger [166] compared the properties of the acetylide and the double salt $Ag_2C_2 \cdot AgNO_3$. The latter was obtained by acting with acetylene on a solution of $AgNO_3$ in dilute nitric acid. The initiation temperature was found to be 202–207°C (depending on the rate of heating). Silver acetylide gave figures of 143–148°C. A wide description of the properties of the double salt $Ag_2C_2 \cdot Ag\ NO_3$ was given by Stadler [167]. It was obtained by introducing acetylene into a solution of 50 g $AgNO_3$ in 200 cm^3 water and 30 cm^3 nitric acid (d 1.4) at 80–90°C. The velocity of detonation was 2250 m/s and 4450 m/s at densities of 2.51 and 5.36 respectively. The lead block expansion was 136 cm^3. The heat of explosion for the double salt was 183 kcal/mol (for silver acetylide 70.3 kcal/mol).

MANUFACTURE OF PRIMERS

One of the leading explosives factories in Europe, Vihtavuori Works in Finland, has developed a modern process for the manufacture of primers after the explosion in 1961 [180]. The main novelty being remote control.

The building for the manufacture of primers has a corridor running through the middle and on both sides of the corridor are steel–concrete chambers. The outer walls of the chambers are lightly built. In the corridor walls, part of the concrete is replaced by 30 mm steel plate, to simplify the fixing of the control apparatus. The explosives – lead styphnates, lead azide and tetrazene are kept and transported from one stage to another in 1 kg canisters. They are grasped with tongs and transported from one chamber to another by trolleys moved by a cable. Steel trapdoors in the dividing walls are opened and closed by remote control.

Lead styphnate and lead azide are precipitated in correct proportion and mixed by a continuous process.

The five production operations: precipitation, mixing, filtration, drying and sieving are carried out in one chamber. Drying is carried out in the filtration apparatus by washing with solvents and drying with warm air. The explosive is transferred from one apparatus to another by tongs and levers fitted through the armour plating.

The explosive taken into canisters is transferred to another chamber where it is pressed into the proper metal elements.

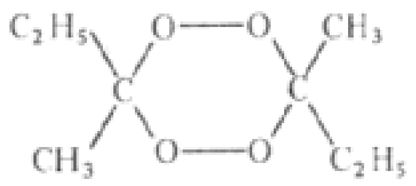
PEROXIDES (Vol. III, pp. 225, 299)

Peroxides as explosives have no practical application with the exception of concentrated hydrogen peroxide, containing over 80% and 90% H_2O_2 (Vol. III, p. 299) as an oxidant in rocket fuel. It also became an important oxidant with a wide application – among reactions with concentrated hydrogen peroxide the reaction $NH_2 \rightarrow NO_2$ was achieved to obtain hexanitrobenzene (Chapter VI). The reactions of radical polymerization under the catalytic action of acyl and ketone peroxides are well known. Among the latter use has been found for propione peroxide and peroxyacetic acid became a most important epoxidation agent.

A number of monographs and reviews have been published on peroxides in addition to those mentioned in Vol. III (p. 227) [168–176, 168–175]. The problems of peroxide reactions is outside the scope of the present book and only those related to explosives will be described here.

Some peroxides, such as BaO_2, SrO_2 are in use in pyrotechnical compositions [176]. This is outside the scope of the present book.

Propione Peroxide (XXI)

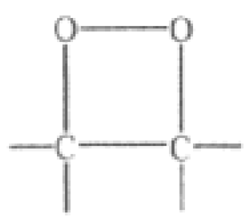


XXI

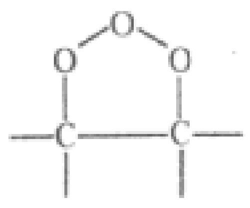
found a wide application as an initiator of radical polymerization. It is much less sensitive to impact and friction than acetone peroxide (Vol. III, p. 225).

Hexamethylenediamine peroxide which has two assigned formulae (Vol. III, p. 225, formulae I and II) was examined with NMR technique by T. Urbański [174], who found that formula I by Baeyer and Villiger [177] was the correct one.

Among peroxides with explosive properties are those from 1,2-diketones (XXII) [178]. They were prepared by ozonolysis or by the action of singlet oxygene on alkanes, or by sodium hydroxide action on bromoperoxide



XXII



XXIII

They possess marked explosive properties. The kinetics of decomposition of ozonides (XXIII) was followed by Mile and co-workers [179].

Superoxides

The name 'superoxide' was introduced in 1934 to signify an exceptional degree of reactivity of superoxide radical anion $O_2^{\overline{\cdot}}$ in KO_2 [187]. It was obtained by acting with dioxygen on metals such as potassium (and Rb, C_5). It is marked by nucleophilicity. In aprotic media it reacts rapidly with primary and secondary alkyl halides to yield dialkyl peroxide and with acyl chlorides to yield diacyl peroxides. Superoxides are reduced to peroxides under some experimental conditions. They were recently reviewed by Sawyer and Valentine [188]. No explosive properties of metal superoxides or their mixtures have been recorded.

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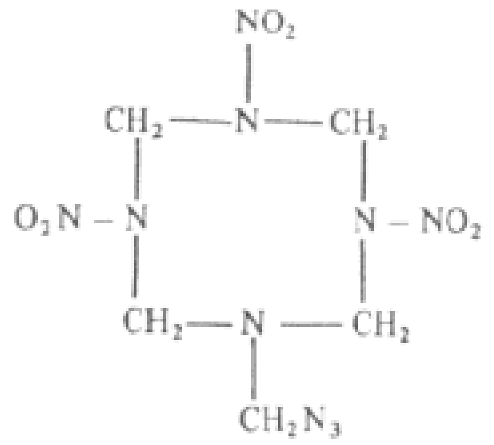
APPENDIX TO CHAPTERS XIII AND XVII

An interesting *organic azide* related to octogene (HMX) was recently described by Frankel and Woolery [204].



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CHAPTER 18

BLACK POWDER (GUN POWDER)

(Vol. III, p. 322)

Black powder is still little known as regards the mechanisms of reactions occurring during its burning, although it has been known for more than 2000 years.

Owing to new tools such as differential thermal analysis [1], and advances in solid-state chemistry [2–5], advances in free radical chemistry and ESR technique [6] and catalysis a theoretical and experimental approach to the problems of mechanism was made possible (Vol. III, p. 335).

Concling [7] recently gave an interesting review on burning black powder and pyrotechnic compositions. He presented diagrams of differential analysis of the behaviour of potassium nitrate, sulphur and their mixture when heated. Figure 84 shows a diagram of KNO_3+S mixture.

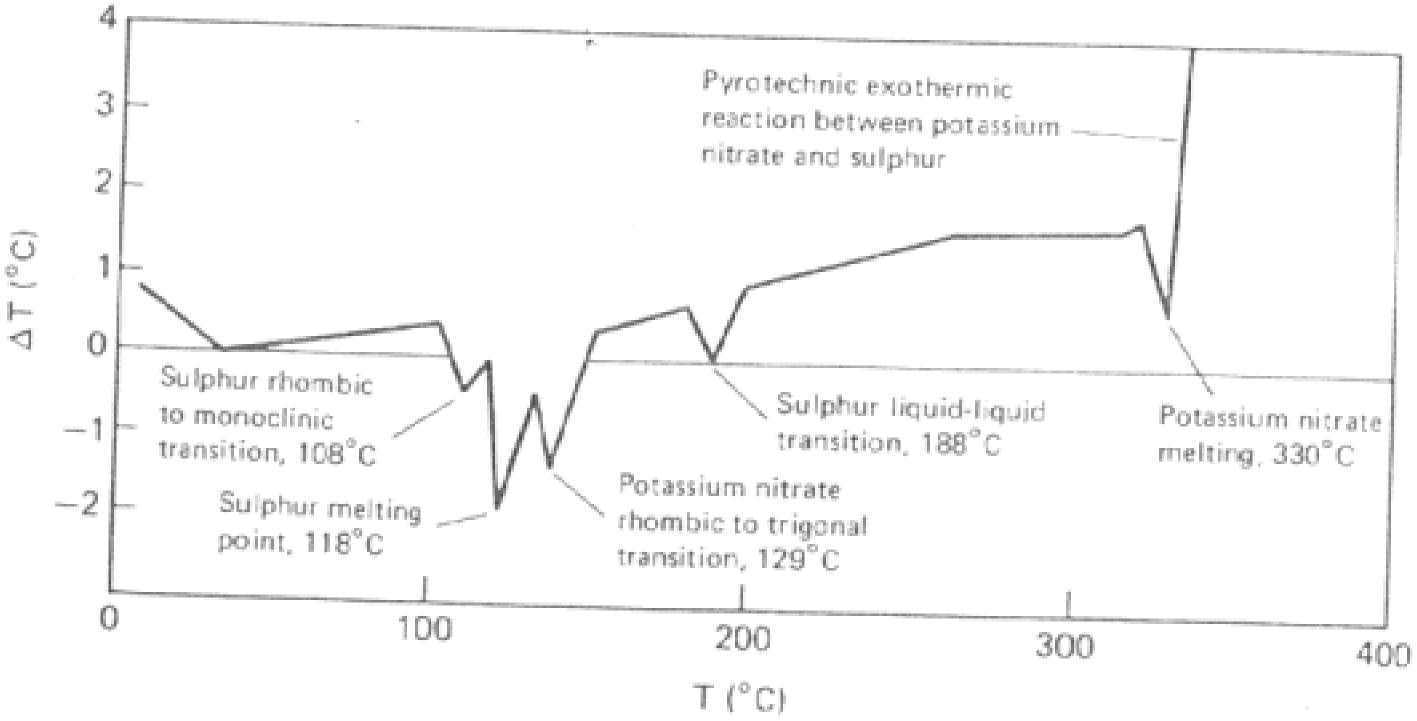

FIG. 84. Differential calorimeter diagram of KNO_3+S according to Concling [7].

One of the problems in burning black powder is: at which moment does the main reaction begin (e.g. Vol. III, p. 338) and whether the reaction occurs in the condensed phase or the gas phase.

Andreev [8] in his monograph pointed out that the burning of black powder

occurs mainly in the condensed phase. This explains the experimental facts that the rate of burning depends very little on the pressure and the heat transfer does not go through the gas phase but through the solid or liquid (molten) phase. Also the transformation of the solid phase to liquid occurs through endothermic processes which do not favour the reaction. Glazkova *et al.* [9, 10] systematically examined the deflagration and thermal decomposition of mixtures of potassium nitrate with carbon, sulphur and both these components. Here are her main conclusions:

(1) the rate-controlling reactions of potassium nitrate with charcoal occurred in the condensed phase,

(2) the stoichiometric mixture of sulphur with potassium nitrate indicated that the burning does not depend on density and the rate-controlling reaction occurred in a gas-phase.

The rates of burning of mixtures of potassium nitrate with sulphur are higher than those of potassium nitrate with carbon.

It follows from Fig. 85 on the mixture of three components: KNO_3, carbon and 5% sulphur, that the rate of burning was greater in the samples pressed to the theoretical than to the lower density.

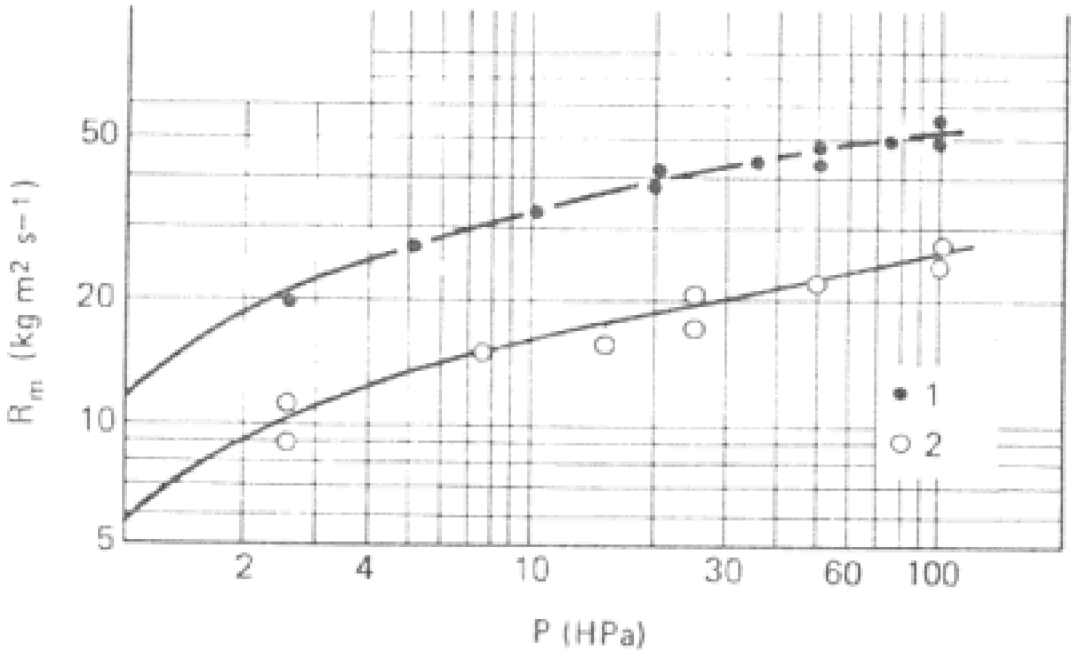

FIG. 85. The rate of burning of a mixture of KNO_3, carbon and 5% sulphur at a lower (1) and higher (2) density, according to Glazkova *et al.* [10].

This meant that the rate-controlling reaction occurs mainly in the condensed phase.

Glazkova also examined the action of catalysts such as lead chromate: it leads to an increase in the importance of reactions in the condensed phase.

Bowden and Blackwood [11] pointed out the important part played by charcoal in the process of burning black powder and the role of soluble constituents present in charcoal.

It is known that unpaired electrons and free radicals are present in charcoal [12]. Also another fact is that the grinding of polymers and charcoal produce the break of covalent bonds $\geqslant \mathrm{C-C} \leqslant$ to form free radicals $\geqslant \mathrm{C}\cdot$ [13].

T. Urbański advanced the view [14, 15] that free radicals in charcoal considerably influence the properties of black powder. The concentration of free radicals in charcoal depends very much on the temperature of carbonization in the range 245–650°C (Fig. 86). 'Ammonpulver' – a mixture of 85% NH_4NO_3 and 15% charcoal – was prepared from charcoal made at various temperatures of carbonization of cellulose.

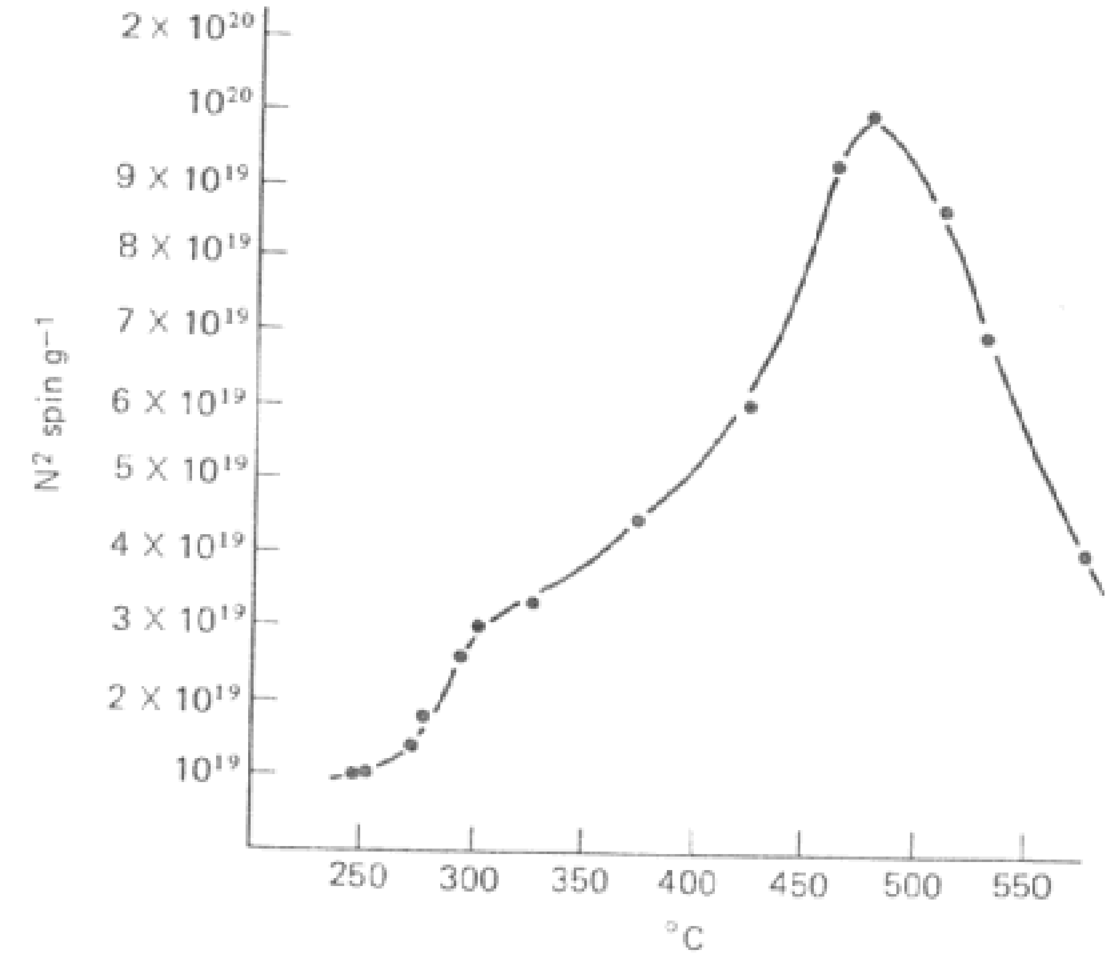

FIG. 86. Spin concentration in charcoal against the temperature of carbonization of cellulose, according to T. Urbański *et al.* [6].

The rate of burning of 'Ammonpulver' was expressed as a coefficient of vivacity determined in a Sarrau-Vieille-Burlot closed vessel [16]. The coefficient of vivacity against temperature of carbonization of cellulose is given in Fig. 88. It follows from the comparison of Figs 86 and 87 that the rate of burning of Ammonpulver has the same trend as the concentration of free radicals in the charcoal. Subsequently it follows that the concentration of unpaired electrons in charcoal is at least one of the factors influencing the rate of burning of black powder.

Modifications of Black Powder

One of the characteristics of black powder is that it is a fast burning mixture. Numerous modifications have been introduced, some with the aim of reducing the rate of burning.

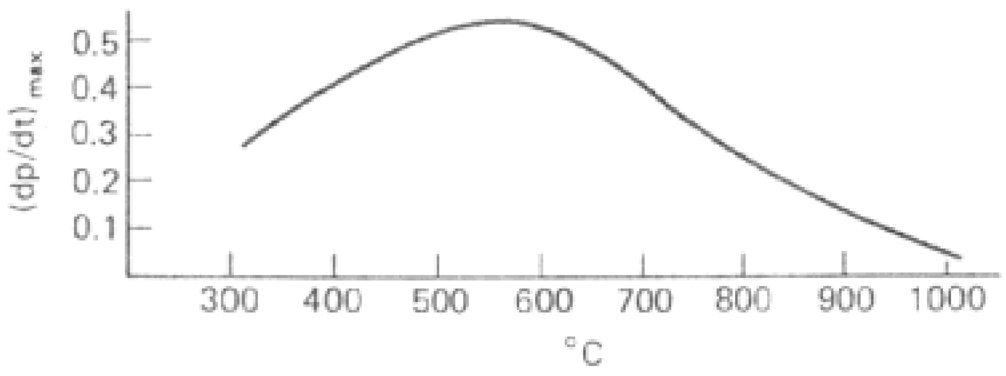

FIG. 87. Rate of burning ('coefficient of vivacity', dp/dt_{max}) of 'Ammonpulver' against the temperature of carbonization of cellulose, according to T. Urbański *et al.* [6].

One of the modifications consisted in partially (or completely) replacing potassium nitrate by sodium nitrate. Sodium nitrate changed some properties of the mixtures, in spite of the similarity to potassium nitrate. As pointed out previously (Vol. III, p. 329), sodium nitrate mixtures for mining (in Germany 'Sprengsalpeter') gave a better performance than potassium nitrate mixtures (in Germany 'Sprengpulver'). This has never been investigated and explained, but recently a few notes have appeared which point out the difference between sodium and potassium nitrate. Thus according to Towse [17] the difference between these two nitrates can be found in their behaviour at a temperature of *ca.* 900°C. Sodium nitrate decomposed mainly according to equation (1a) but *ca.* 8% reacted in the sense of equation (1b):

$$2\,\mathrm{Na\,NO_3}\begin{cases}\rightarrow 2\,\mathrm{NaNO_2} + \mathrm{O_2} & (1a)\\ \rightarrow \mathrm{Na_2O} + \mathrm{NO} + \mathrm{NO_2} + \mathrm{O_2} & (1b)\end{cases}$$

Reaction (1b) does not occur with potassium nitrate. In the light of the above it seems that sodium nitrate is more reactive than potassium nitrate at high temperature.

Various modifications of black powder are known. One of the most popular is sulphurless black powder (Vol. III, p. 331). Fedoroff and associates [18] mentioned over twenty different modifications of black powder.

Here are a few modifications introduced with the aim of lowering the rate of burning.

(1) Addition of silicate dust (e.g. brick dust) and graphite. Such mixtures do not burn uniformly and leave a considerable residue.

(2) Addition of resin, which reduces the rate of burning of black powder under atmospheric pressure *ca.* 20 times.

(3) Substitution of pitch for charcoal slows down the burning 4 to 10 times.

(4) Substitution of cuprene (acetylene polyermized on copper as a catalyst) for charcoal.

(5) Introduction of triphenyl phosphate, camphor substituted ureas (as suggested by F. Olsen).

(6) Mixing black powder with nitrocellulose dissolved in a usual solvent, with the ratio black powder/nitrocellulose being 60/40. The resulting dow was extruded in much the same way as cannon propellants. This was known as Benite, developed by Hassmann and improved by Huselton and Kaplowtiz according to [18]. The composition of Benite was: 40% Nitrocellulose (13.15% N), 44.3% KNO_3, 6.3% Sulphur, 9.4% Charcoal. Ethyl Centralite was added to this mixture in a proportion of 0.5%.

According to Stettbacher [19] the addition of 1–6% of $BaSO_4$ is strongly advised to slow down the rate of burning of black powder.

Among recent modifications of black powder a patent [20] should be mentioned. The mixture is composed of potassium perchlorate (60–80%), salts of benzoic acid (40–20%) and a small proportion of water (*ca.* 2%). Water is probably combined with benzoic acid salts in the form of hydrates.

By replacing charcoal with pit (fossil) coal an increase in the rate of burning can occur.

Considerable work is being carried out by Glazkova *et al.* [21, 22] on the burning of mixed explosives and the catalysis of burning. She considered sulphur in black powder to be a catalyst.

Here are the main conclusions of the work of Glazkova *et al.* [22] related to the burning of mixtures of inorganic nitrates with charcoal.

(1) Inorganic nitrates can play the part of catalysts and their effectiveness can be arranged in the following way:

$$\mathrm{Na} > \mathrm{Pb} > \mathrm{K} > \mathrm{Ba} > \mathrm{Al} > \mathrm{Ca,\ Mg,\ Cu.}$$

(2) A stoichiometric mixture of ammonium nitrate and charcoal reacts in the condensed phase and a similar mixture of sodium nitrate with charcoal in a gas phase (see above for the statement on burning a mixture of potassium nitrate).

(3) The burning rate of the mixtures depends mainly on the catalytic activity of cations and not on their concentration.

(4) The most effective catalytic action on the burning of mixtures with ammonium, potassium and sodium nitrate possess salts of Cr (VI), Cu(II), Pb (II) and sulphur. They are acting mainly on reactions in condensed phase, that is, with ammonium and potassium nitrate.

Explosive properties

A paper by Isaksson and Rittfeldt [23] described the examination of black powder of different origins. They came to the conclusion that samples of different origins can be identified on the basis of their combustion parameters.

Thus burning under atmospheric pressure can vary from 1.2 to 2.1 m/sec. In a closed vessel, the coefficient of vivacity $(dp/dt)_{max}$ can vary from 4000 to 10700 kg/sec.

The rate of burning of confined black powder can be as low as 170 m/sec for coarse powder [24] to 950 m/sec for fine powder [25]. For sulphurless powder the rate of burning is higher: 1500 m/sec according to Belyaev *et al.* [25].

Hygroscopicity of Black Powder

Potassium nitrate is non-hygroscopic, but black powder is relatively hygroscopic. Charcoal is responsible for the hygroscopicity of the mixture because of the high absorption power of charcoal. One of the methods of reducing the hygroscopicity is to mix charcoal with non-hygroscopic substances. This however may reduce the burning properties of the powder.

The method of mixing charcoal with sulphur (binary mixture) can be beneficial under the following conditions:

(1) all charcoal is mixed with sulphur,
(2) the temperature of mixing should be kept for a short time at approximately 120°C, that is, above the m.p. of sulphur,
(3) mixing is carried out in the air-tight container in an atmosphere of nitrogen, to prevent the oxidation of sulphur.

Manufacture of Black Powder

The classic method of manufacturing black powder comprises mixing the ingredients in a ball mill and finally in edge runners. The process has not changed in nearly a hundred years. However, recently an improvement has been introduced by Løvold [26] in the factory of Dyno industrier A.S., Nitedals Krudtvaerk, Nitedal in Norway. This method consists of mixing and milling all three ingredients in a single operation in a Jet-Mill (Fig. 88 [24]). The mill has no moving parts which is one of the safety factors. Compressed air is blown through a specially designed nozzle in the lower part of the mill and into the grinding chamber. The air leaves the nozzles with a very high velocity. The material to be crushed – a mixture of all three components as a continuous stream – is fed into the chamber where the collision of particles causes pulverization to the size distribution as follows [26]:

100% finer than 25 μm
95% finer than 15 μm
90% finer than 10 μm
83% finer than 5 μm

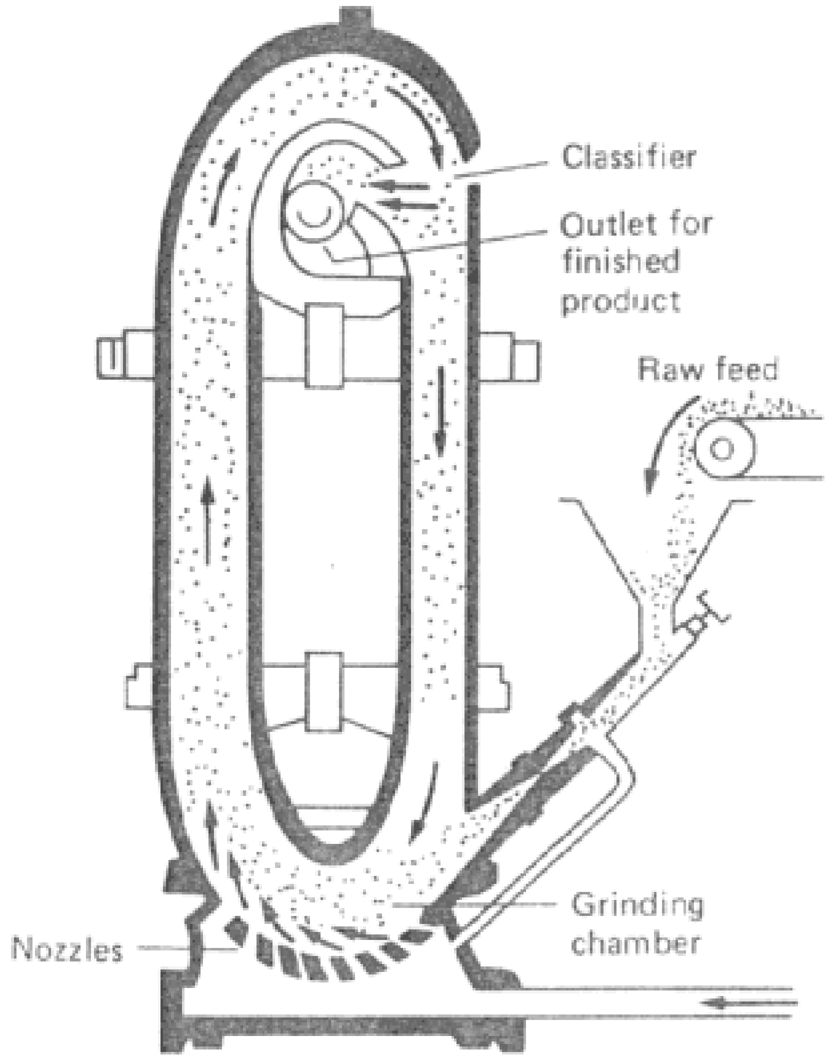

FIG. 88. Jet Mill of Nitedals Krudtvaerk, Norway for Compounding Black Powder according to Løvold [22] as given in S. Kaye, *Encyclopedia of Explosives*, Vol. 8, p. P517. ARRADCOM, 1978.

By changing the running conditions of the mill it is possible to get other particle sizes. The Jet-Mill is a central part of the new method of making black powder. However some old elements can be used. According to Løvold the process can be depicted by the scheme:

KNO_3+S+C → Weighing and Mixing Bin → Mixture bin (supplying continuously the required quantity of the mixture) → Jet-Mill → Cyclone → Press → Corning → Sieving → Polishing. The dust from the sieve goes back to the Cyclone.

Løvold has summarized the advantages of this new process as follows:

1. It is possible to operate the process automatically.
2. It is possible for one person to supervise the process by remote control.
3. The amount of explosive in the process is small.
4. The whole process can be carried out in one single room.

Although an explosion occurred at Nitedal in 1976, according to Biasutti [31] it was not connected with the manufacturing process. The explosion occurred outside the manufacture building.

The Use of Black Powder

1. Black powder with potassium nitrate and with sodium nitrate (the latter-German 'Sprengsalpeter') is widely used for mining when a low strength of explosive is required, for example in quarries where large and undamaged blocks are needed or when the material is soft (e.g. slate).
2. For slow burning fuses, delay charges.
3. For small rockets (signal, distress and life-saving at sea rockets), rockets for rain-making (Vol. III, p. 324).

Pyrotechnics

Pyrotechnics is strongly connected with black powder. This is however outside the scope of the present book. The existing literature is recommended [27–30].

Accidents with Black Powder

As mentioned earlier (Vol. III, p. 361) the manufacture of black powder is one of the most dangerous operations in the production of explosives. Before the advent of the manufacture of nitroglycerine it was considered to be the most dangerous type of manufacture. It still remains dangerous in spite of considerable improvement in the methods of production. In his book Biasutti [31] described an explosion in the edge runner at the factory in Modderfontein, South Africa in 1980. Nobody was injured thanks to the remote control operation.

History of Black Powder

The following are published monographs dealing specifically with the more recent history of black powder in various countries to complete the references in Vol. III, pp. 363–364: [32–36].

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CHAPTER 19

COMMERCIAL (MINING) EXPLOSIVES

(Vol. III, p. 395)

INTRODUCTION

The early history of the use of explosives in mines and in various branches of civil engineering has been described in Vol. III. The growing use of explosives for peaceful application has been described in a number of monographs. Here are some of them (in addition to those mentioned in Vol. III):

Assonov [1], Samujlo [2], Rossi and Pozdnyakov [3], Cybulski [4], Charewicz, Krawiec *et al.* [5], Dubnov, Bakharevich and Romanov [6], Fordham [7], *Mining Research*, Two Collective Vols (Ed. G. B. Clark) [8], the book on *Explosive Working of Metals* by Reinehart and Pearson [9].

According to the U.S. Statistics [10] the consumption of industrial explosives in the U.S.A. in 1979 and 1980 surpassed 4000 million pounds a year.

It should be added that in the U.S.A. commercial explosives can be classified as blasting agents and explosives [118]. The former are those which do not detonate from a detonator No. 8 but require a stronger initiator, while explosives detonate readily.

PRINCIPLES OF COMPOSITION OF COMMERCIAL EXPLOSIVES

The principles of the design of commercial explosives were described in Vol. III, pp. 420–440. Some of the principles will now be discussed in detail on the basis of more modern literature.

Oxygen Balance

The composition of commercial (mining) explosives should correspond to two requirements:

(a) production of non-toxic gases,
(b) full utilization of the energy of the reaction between the oxygen carrier and combustible ingredients.

The oxygen balance is usually calculated on the unwrapped explosive and, as Fordham [7] pointed out, only a part of the wrapper (waxed paper, polyethylene or other polymers) – usually a half – takes part in the chemical reaction. As pointed out in Vol. III (p. 424) both negative and positive balance can produce toxic gases: carbon monoxide and nitrogen oxides respectively. Dubnov *et al.* [6] pointed out that the explosive can also react with the medium surrounding the shot-hole.

Rossi [11] and Khudyakov [12] studied this problem and came to the conclusion that coal can react with CO_2 to yield CO, apatites and potassium salts can bind NO_2, molybdenum and some copper ores bind carbon monoxide. Some iron ores can catalyse the oxidation of carbon monoxide to carbon dioxide. Dubnov [6] pointed out that sulphur containing ore may be responsible for the formation of such toxic gases as SO_2 and H_2S.

Dubnov *et al.* gives the results of experiments in an apatite mine with Ammonit 6 as follows.

TABLE 76. Toxic gases produced by detonation of Ammonit 6 [6]

Combustible of the wrapper in g for 100 g of explosive		Oxygen balance %		Found in the atmosphere of the borehole l/kg	
Paper	Paraffin wax	Explosive	Cartridge	CO	NO_2
1.7	2.3	+0.3	− 9.8	30.1	3.4
1.7	4.8	+0.3	−18.3	34.1	3.4

Rossi, according to Dubnov reported that by replacing paraffin wax paper with polyethylene, the concentration of carbon monoxide was reduced from 39–42 to 12–20 l/kg, after the detonation of Ammonit No. 6.

Subsequently the official regulation in U.S.S.R. [13] reduced the amount of paper to 2 g and paraffin wax (or similar hydrophobic product) to 2.5 g/100 g of explosive.

Other factors influencing the formation of CO and nitrogen oxides:

The fineness of particles of ammonium nitrate reduces the amount of CO and NO, as given by Svetlov [11]: see Table 77.

Another factor influencing the composition of the products is the ratio between the diameter of shot-hole and the diameter of the cartridge. The following are data for Ammonit 6 Zh V [11]: see Table 78.

TABLE 77. Influence of the fineness of ammonium nitrate of the amount of toxic gases, according to Svetlov as reported by Rossi [11]

Explosive	Concentration of toxic gases, 1/kg CO	NO
Ammonit No. 6		
large particles	28	9.8
fine particles	23.9	2
Ammonit PZhV–20		
large particles	23.8	5.8
fine particles	21.4	0.9

TABLE 78. Influence of the diameter of shothole and of the cartridges [11] explosive: Ammonit No. 6 ZhV

Diameters in mm		Concentration of toxic gases, l/kg	
Shothole	Cartridges	CO	NO
42	32	49–57	1.4–3.6
34	32	30–31	1.4–1.9

The composition of fumes produced by detonation of explosives used in Poland: Barbaryt A and Metanit D2 (Vol. III, pp. 478–479) was examined by Cybulska and Sobala [14]. The fumes were analysed after the detonation in both laboratory conditions and in shot-hole underground. Samples of gases were taken 2 and 10 metres from the test site every three minutes for 30–40 minutes. The maximum concentrations were found as below:

CO	0.007–0.040%
NO_2	0.0055–0.010%

These concentrations decrease very quickly through the blowing ventilation. Overcharging of shot-holes produced a marked increase in the above gases. When fired in coal more fumes are produced than in stone.

Volk [15] examined the detonation fumes, between the detonation of Ammonit 1 in an atmosphere of air and argon. In the former case the amount of NO was higher than in argon, and the method of determining toxic gas products in the Federal Republic of Germany was described [16]. G. Persson and P. A. Persson [106] and Lindqvist and Johnson [107] found that experimental firing of charges of AN–FO explosives in steel-tubes gave results comparable with those in rocks. Similar results of firing charges in mortar were also reported [108].

HYGROSCOPICITY OF MINING EXPLOSIVES

The hygroscopicity of ammonium nitrate is a great drawback in explosives containing this salt. It limited the use of ammonium nitrate explosives, and only relatively recently methods were found of reducing the hygroscopicity of ammonium nitrate explosives.

One of the methods of protecting explosives against moisture consists in using a hydrophobic envelope, such as paper impregnated with hydrophobic substances more efficient than paraffin, such as paraffin with added substances containing polar groups – pitch, asphalt, petroleum tar etc. or using a polyethylene envelope.

A recent method of protecting ammonium nitrate against moisture, is mixing it with substances such as calcium or zinc stearate, petroleum tar, asphalt, barium sulphate and guar gum powder. According to Dubnov [6] stearates are in powder form of 5–20 μm size, whereas ammonium nitrate is of 70–120 μm. Owing to such sizes a very small proportion of stearates suffices to cover the surface of particles of ammonium nitrate. To evaluate the efficiency of the hydrophobic substances – Pozdnyakov in the U.S.S.R. [17] developed a hydrostatic apparatus which determines the pressure of water which is required to penetrate through a thin layer of explosive enclosed in a capsule. Dubnov [6] gives the figures for water pressure in centimetres needed to pass through a standard explosive composed of ammonium nitrate (80%), TNT (19%) and hydrophobic substance (1%). Some of his figures are collected in Table 79.

TABLE 79. Water column (in cm) needed to penetrate Poznyakov apparatus [6]

Calcium stearate	90 cm
Zinc stearate	88
Paraffin wax–petroleum tar (4:1)	85
Paraffin wax–asphalt (1:2)	82
Ferric stearate	78
Paraffin wax	70
Paraffin wax–calopheny (4:1)	68
Paraffin wax–soot (1:2)	67
Paraffin wax–graphite (1:2)	67
Paraffin wax–calopheny (3:1)	66
Paraffin wax–dinitronaphthalene (1:2)	64

Shestakov [18] introduced an original method of protecting ammonium nitrate which consists in mixing ammonium nitrate with $Fe_2(SO_4)_3$ (0.5%) and fatty acids (stearic, palmitic acid) (0.25%). A thin layer of ferric stearate or palmitate is formed on the surface of crystals of ammonium nitrate. It is now customary to use 0.3–0.4% fatty acids and 0.07% iron salts. Part of the fatty acids can be replaced by paraffins. Explosives containing fatty acids and iron salts are marked with symbol Zh V.

The mixing of ammonium nitrate with hydrophobic components is usually achieved in edge runners used extensively in black powder manufacture (Vol. III, p. 350, Figs 93, 94) or in disc mixers (Vol. III, p. 504, Fig. 166).

Water resistance of commercial explosives is examined in Germany at Test Station Dortmund – Derne [69].

A train of four cartridges is fixed in a file on a wooden board, the first of the cartridges is equipped with a detonator No. 8. Five longitudinal notches are cut into each cartridge. The train is immersed for 5 hours in 20 cm depth of water. After that they are detonated. The train must detonate entirely.

A similar test is used in the U.S.A. [69].

STABILITY OF COMMERCIAL EXPLOSIVES

Physical Changes

Ammonium nitrate commercial explosives are stable at a moderate temperature and dry atmosphere and should not be kept at temperatures above 32°C when a change in the crystal habit of ammonium nitrate occurs and the change of temperature may harden the cartridges. The same can occur if explosives are kept in a humid atmosphere and a change of temperature can produce cracking of ammonium nitrate.

Explosives with nitroglycerine should be protected from freezing and the thawing of frozen nitroglycerine can cause disasters (Vol. III, p. 518). Currently in most countries a non-freezing mixture of nitroglycerine with nitroglycol is used. The change of explosive properties on storage was discussed in Vol. III, pp. 436–438.

Chemical Changes

Ammonium nitrate is usually slightly acid owing to the loss of ammonia leading to the presence of free nitric acid. This can possess a deteriorating effect on nitrate esters present in the explosive. It is therefore advisable to include neutralizing agents, such as $CaCO_3$ and Centralites (Vol. III, p. 645). The latter in proportion of 0.5%. Diphenylamine can be used only in mixtures without aromatic nitro compounds, as diphenylamine reacts with higher nitrated aromatics. Ammonium nitrate explosives with nitrate esters and dynamites are usually subjected to the Abel-test at 80°C to verify their stability [19].

Apart from the reaction of the decomposition of nitrate esters some other changes can occur in mixed explosives, such as the reaction of the oxidation of aluminium, particularly marked in water–gel explosives. Also permitted (permissible) explosives containing ion exchange mixtures of sodium nitrate with ammonium chloride a double exchange reaction can occur:

$$NaNO_3 + NH_4Cl \rightleftharpoons NaCl + NH_4NO_3.$$

The reaction is reversible and ammonium nitrate can react with sodium chloride.

All the above considerations lead to imposing a limited storage time on mining explosives. In Poland ammonium nitrate permitted explosives should be used within 1½–3 months from the production date. Non-permitted ammonites and dynamites 2–4 months. In the U.S.S.R. ammonium nitrate explosives in cartridges should be used within 3 months.

RATE OF DETONATION AND CRITICAL DIAMETER

As is well known the rate of detonation of explosives depends on the density and diameter of cartridges. Figure 89 gives the rate of detonation against the diameter of cartridges of some mining explosives according to Cybulski [4].

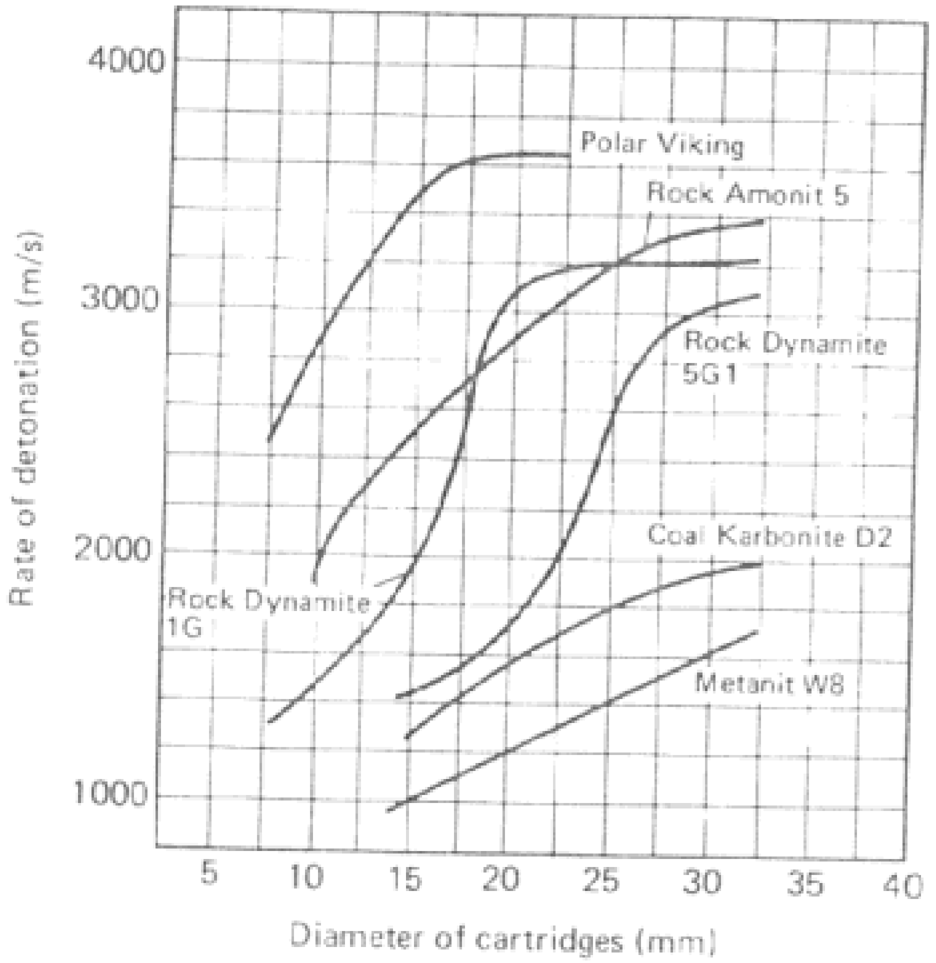

FIG. 89. Rate of detonation of typical mining explosives against diameter of cartridges [4].

Below a certain diameter detonation is not propagated. A definition of the critical diameter is as follows. The critical diameter is larger when the cartridges detonate in the open, and smaller when confined in metal tubes. Table 80 gives the figures according to Cybulski [4].

As is known, the rate of detonation depends on the confinement of the charges. Cybulski [4] gives some data collected in Table 81.

"GAP TEST" (TRANSMISSION OF DETONATION)

The gap test values depend, among different factors, on the density (see Vol. III, p. 436, Fig. 144), diameter (Table 82) and confinement (Table 83).

TABLE 80. Critical diameters of mining explosives according to Cybulski [4]

Explosives	Diameters in mm 100% detonation	Possible detonation	No detonation
Metanit powietrzny D2	20	15	10
Karbonit węglowy D2	25	15	13
Amonit skalny 5	10	–	8
Barbaryt powietrzny AG1	25	20	17
Dynamit skalny 1G1	12	8	6

TABLE 81. Dependence of the rate of detonation on confinement according to Cybulski [4]

Explosive	Diameter of cartridges mm	Density	Rate of detonation m/s In open	In a shothole
Metanit powietrzny D2	36	0.71	1620	1920
Karbonit węglowy D4	36	0.71	1960	2330

TABLE 82. Dependence of the gap-test on diameter (Dubnov [6])

Diameter mm	Explosive AM 8 gap in cm	AM 10 gap in cm
32	0–1	2–3
36	2–4	3–6
40	4–6	5–8
60	7–15	10–20
90	20–30	25–30

TABLE 83. Gap-test in open space and in a mortar. Initiation with detonator No. 8 according to T. Urbański [20]

Explosive	Density	Gap test, cm in open	in mortar
Bradyt powietrzny C*	1.08	18	25
Bradyt powietrzny F**	1.06	15	24
A 2***	1.00	1.5	2.5
Miedziankit****	1.70	0	40

Compositions:

* 64.7% NH_4NO_3, 4% nitroglycerine, 8% TNT, 2% charcoal, 20% NaCl.

** Vol. III, p. 475.

*** 85.5% NH_4NO_3, 5.5% TNT, 9% nitronaphthalene and in addition ca. 1.5% mineral oil.

**** 90% $KClO_3$, 10% Kerosene (Vol. III, p. 278).

Gap Test and Temperature

The gap test depends on the temperature of explosives. Thus for a permitted explosive with 10% nitroglycerine–nitroglycol the gap was found to be 5 cm at −10°C, 6 cm at 0°C, 8 cm at 10°C and 10 cm at 20°C (see Dubnov *et al.* [6]).

A remarkable difference exists between the gap test in the open and in a mortar with the chlorate explosive Miedziankit. When initiated in open space with detonator No. 8 the detonation died away 7–10 cm beyond the detonator. On the contrary, in a mortar, no limit was found owing to the short borehole.

The problem of the cause of such a difference between ammonium nitrate and chlorate explosive has not been examined but certainly merits a special study.

Potassium chlorate is no longer used in explosives and is limited only to pyrotechnic compositions and match-head formulation [21]. Sodium chlorate is produced to manufacture chlorine dioxide as a bleaching agent of wood pulp and cellulose fibres.

The transmission distance of picric acid charges was examined by Burlot [22]. This is however outside the scope of the present book. Also the method of determining the transmission detonation through an inert solid medium, such as a number of card-boards ('card–gap test') [116, 117], cellulose acetate [121, 122] or Plexiglas layer is discussed in the literature on the theory of detonation, for example [34].

CHANNEL EFFECT

T. Urbański in 1926 [20] described the phenomenon currently known as channel effect (Vol. III, pp. 435–436). He found that several ammonium nitrate explosives in a steel tube produce a shock wave which moves at a velocity higher than the detonation wave. This is summarized in Table 84.

The author expressed the view that in a long bore-hole 'end' cartridges can be compressed to a high density ('dead pressed') which detonate with difficulty.

TABLE 84. Shock wave in open space and in a steel tube.
Initiation with detonator No. 8
according to T. Urbański [20, 33].
Explosive Bradyt F (see Table 83), cartridge 30 mm diameter

	In the open	In a steel-tube 35/42 mm
Detonation velocity m/s	2740	3220
Shock-wave m/s		
0–50 mm	1815	–
50–100 mm	560	3830

An unfavourable opinion of this work was given in [23]. The phenomenon was described in 1965 by Ahrens [24], Woodhead and Titman [25], and by Johansson and Persson [26]. Tribute was paid to the priority of the author of the present book by Golbinder, Svetlova and Tyshevich [27]. The latter authors contributed a considerable number of experimental facts on channel effect.

POSSIBLE SPIRAL WAY AND DETONATION OF MIXED EXPLOSIVES

Photographs of the detonation of ammonium nitrate explosives with an open lens camera were taken by T. Urbański [28]. The image was composed of light and dark bands with a sinusoidal shape. An hypothesis was advanced by the author of the possible spiral way of the detonation. At the same period British authors – Campbell, Bone *et al.* [29, 30] published a number of papers in which they indicated the spiral way of the propagation of detonation of gas mixtures. Their results were substantiated by Laffitte *et al.* [31].

T. Urbański continued his experiments with a camera giving images at 10^{-4} s intervals [32].

The conclusion was [33] that only mixed explosives, for example ammonium nitrate – TNT give the described pattern.

The latter fact was also observed by P. A. Persson and G. Persson [34] and they claimed that the pattern on the photographs was due to glass cracking. An argument against such a suggestion is that if a glass-tube is filled with an homogeneous explosive, for example TNT, Picric Acid or PETN, no sinusoidal pattern is observed, although the cracking is the same.

Another experiment by T. Urbański [33, 34] throws some light on the detonation of explosives, if the detonation was carried out in a plastic tube put concentrically inside another tube made of glass and *suspended* in air (Fig. 90). If the inner tube was filled with homogeneous explosive not a mixture, the inner tube remained undamaged after the detonation. If the inner tube is filled with a mixture (e.g. NH_4NO_3 and TNT) the inner tube was covered with holes (Fig. 91).

FIG. 90. Detonation in two concentric tubes: T – outer glass tube, I – inner celluloid tube filled with an explosive, D – detonator [32, 33].

The success of the experiment depends on the choice of the correct dimensions of the outer (glass) and inner (plastic) tube.

The fact that the inner tube filled with mixtures is perforated indicates that

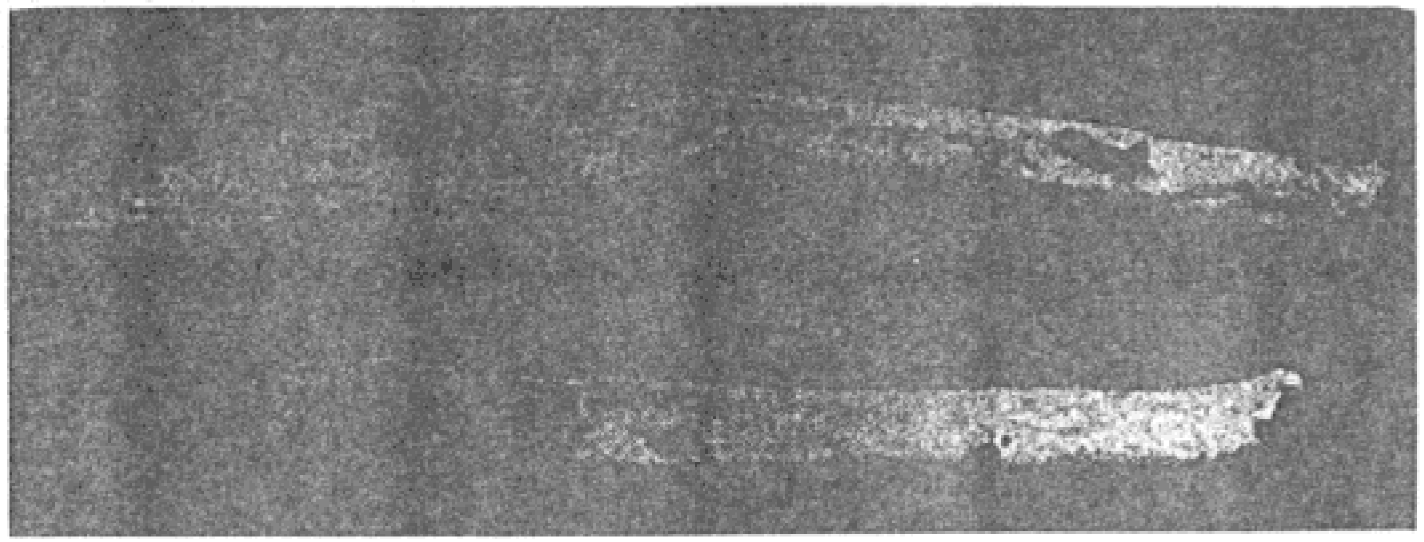

FIG. 91. Inner celluloid tube after detonation of TNT/Ammonium nitrate 78/22 mixture, according to T. Urbański [32, 33].

the two solid phases forming an explosive mixture do not detonate simultaneously and this fact has some bearing on the pattern seen in the photograph.

It should also be recalled that the slow explosion of nitroglycerine can manifest a spiral mode of propagation [35].

DEFLAGRATION OF EXPLOSIVES IN COAL-MINES (Vol. III, p. 417)

The deflagration of explosives in coal mines was examined for the first time by Audibert and Delmas [36] and independently by Cybulski (Vol. III, p. 418) and showed that the decisive factor is the admixture of coal-dust to the explosive particularly in the vicinity of the detonator. Explosives containing nitroglycerine are more liable to deflagration and particularly chlorate explosives can create such a danger.

The problem of deflagration of ammonium nitrate explosives was extensively investigated by Andreev and co-workers [37]. Their conclusion was that the presence of wood meal increases the ability of such explosives to deflagrate and reduces the critical diameter of burning. Also the replacement of NH_4NO_3 + NaCl by $NaNO_3$ + NH_4Cl (Vol. III, p. 421) in mixtures containing TNT and nitroglycerine slightly increased the ability to deflagrate. Andreev and Glazkova [38] found that the ammonium nitrate/TNT mixture 80/20 burned faster under the action of the addition of potassium nitrate or potassium perchlorate. Further experiments by Glazkova and Zhadan [39] suggested replacement of ammonium chloride by ammonium oxalate.

According to Dubnov [6] the conditions of shot-firing which lead to a deflagration of mining explosives were recently established by Galadzhii and co-workers [40, 41], Dubnov and Romanov [42]. In principle deflagration can occur when the gap between cartridges is larger than that required to produce the detonation. Thus Dubnov and Romanov [42] describe three gap regions:

(a) transmitting the detonation,
(b) producing the deflagration,
(c) refusing any action.

This is depicted in Fig. 92 based on experiments [6].

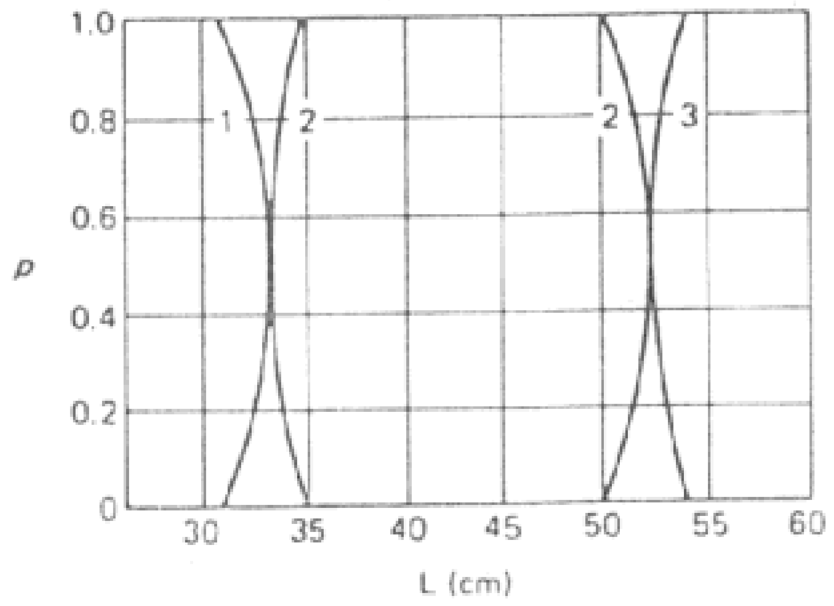

FIG. 92. Experimental curves of the probability *p* of detonation (1), burning (2) and no reaction (3) of a passive cartridge of cyclonite (dia. 35 mm, density ρ = 1.2) as a function of the distance *L* cm from the active cartridge of TNT (dia. 35 mm, ρ = 1.0) according to Dubnov *et al.* [6].

In the U.K. the ability of explosives to deflagrate is examined with the gap test by filling the gap with coal-dust.

The papers by Zimmermann [43] and Murray *et al.* [44] pointed out once more that the penetration of coal-dust into the explosive increases the danger of deflagration of the explosive. Further experiments on deflagration confirmed the influence of coal-dust on the ease of deflagration [102]. Some experiments were carried out to show the influence of deflagration on methane-air explosion [103].

EVALUATION OF THE STRENGTH OF MINING EXPLOSIVES

In addition to the laboratory methods which comprise mainly lead block expansion and the rate of detonation different methods of a more practical character are in use. Thus Cybulski [4] reported the method used in Poland which is essentially the method of bench firing and determining the burden which can be brought down by a charge of 200 g of explosive in a bore-hole of 80 cm length and stemming of 60 cm. This is presented in Fig. 93. In (a) the correct burden is shown and in (b) an overlarge burden is shown. The dimensions for a rock are referred to 200 g of Metanit D2 and stemming with lime.

Apart from such a practical method of determining the strength of explosives the following are the laboratory methods of examining the strength of explosives

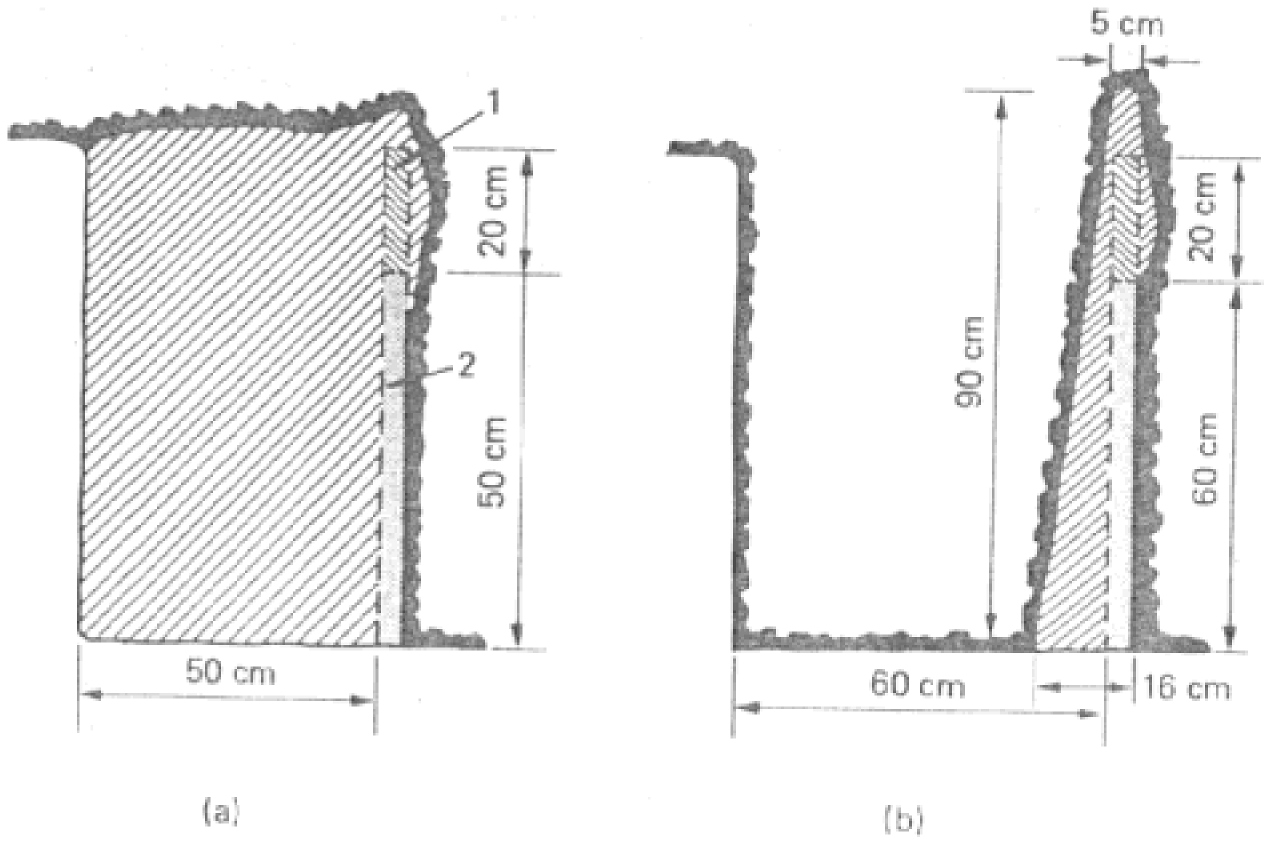

FIG. 93. Determination of the strength of an explosive by firing in a coal burden: (a) a correct burden (50 cm) (b) a burden too large (60 cm). Charge of 200 g Metanit powietrzny D2 (1), stemming (2), according to Cybulski [4].

(Fordham [7]): ballistic mortar, lead block expansion ('Trauzl block'), rate of detonation.

The International Study Group for the Standardization of the Methods of Testing Explosives, EXTEST has been in operation since 1960 (the original name was: The European Commission for the Standardization of the Methods of Testing Explosives). The early history of this organization has been presented by Ahrens [45]. The reader should consult this important paper which gives technical details for carrying out the testing of explosives, further developments have been reported by Persson [46].

Among the methods for determining the strength of explosives underwater detonation has been recommended. It was described for the first time by Sadwin, Cooley, Porter and Stresau [47]. The authors suggested that the method developed for testing military explosives [48] could be used for commercial explosives. Further examination of underwater detonation of explosives was described by Peterson and Begg [49], Fossé [50] and Bjarnholt [51]. All of these authors came to the conclusion that 'bubble energy' can be readily measured and forms the most useful criterion provided by the underwater test. It is not limited to gram quantities and can be used in charge dimensions comparable to those used in practical blasting, it is also simple and inexpensive. According to Fossé the charge is placed at a depth of 12.65 m in a basin 19 m deep and with a radius of 30 m. More recent experiments on underwater detonations have been reported [104]. Satyavratan and Vedam [105] found that a linear correlation exists between underwater energies and lead block expansion values.

SAFETY AGAINST METHANE AND COAL-DUST

This problem was fully discussed in Vol. III, pp. 409–491. A few more recent items of information will be given here.

The modern testing gallery in India is presented in Fig. 94.

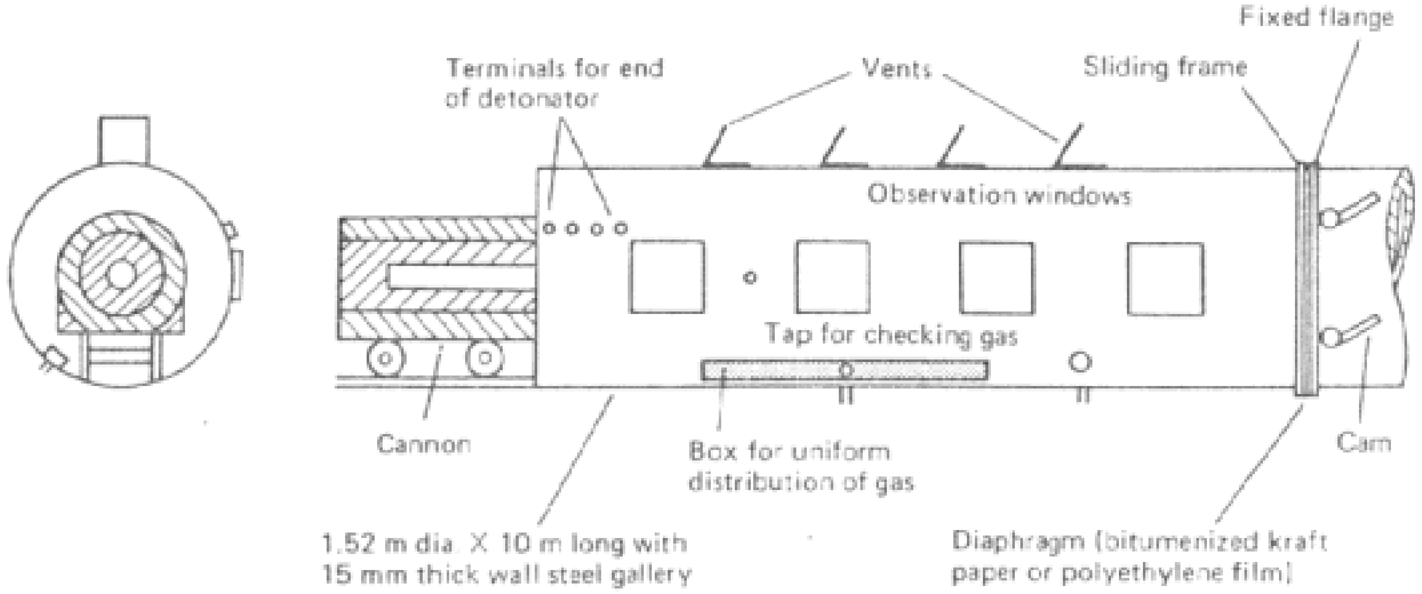

FIG. 94. Modern Cylindrical Steel Gallery for Testing Permitted Explosives (Courtesy IDL Chemical Ltd, Hyderabad, India).

As mentioned previously the result obtained in a gallery depends on the mode of initiation.

In the usual test the detonator is inserted last into the cannon, this is called direct initiation. If the detonator is placed at the opposite end of the train of cartridges and is inserted first into the cannon the initiation is called inverse and the probability of ignition of a methane–air mixture is very high. Figure 95, illustrates the difference between direct and inverse initiation according to Taylor and Gay [52].

More severe tests, known as 'Break Tests', exist in the U.K. a description of which was given in Vol. III, p. 419, Fig. 140. Here is the description according to Fordham ([7], pp. 79–82).

The tests were devised in the United Kingdom for studying the safety of explosives intended for use in ripping, i.e. increasing the height of roadways in mines after the coal has been extracted. The extraction of coal relieves stresses in the surrounding rocks and is therefore liable to cause breaks which can contain methane–air mixtures.

Break Test 1 consists of a shot-hole in which a break occurred across the hole in the middle of the explosive charge. It is simulated by placing a train of explosive across the gap between two steel plates in a test gallery.

Break Test 2 consists of a break parallel to the shot-hole in such a way that half of the shot-hole is in one piece of rock and the remainder of the explosive in the space between the rocks. It is simulated by two parallel plates of which the lower is grooved as a bore-hole – Fig. 96.

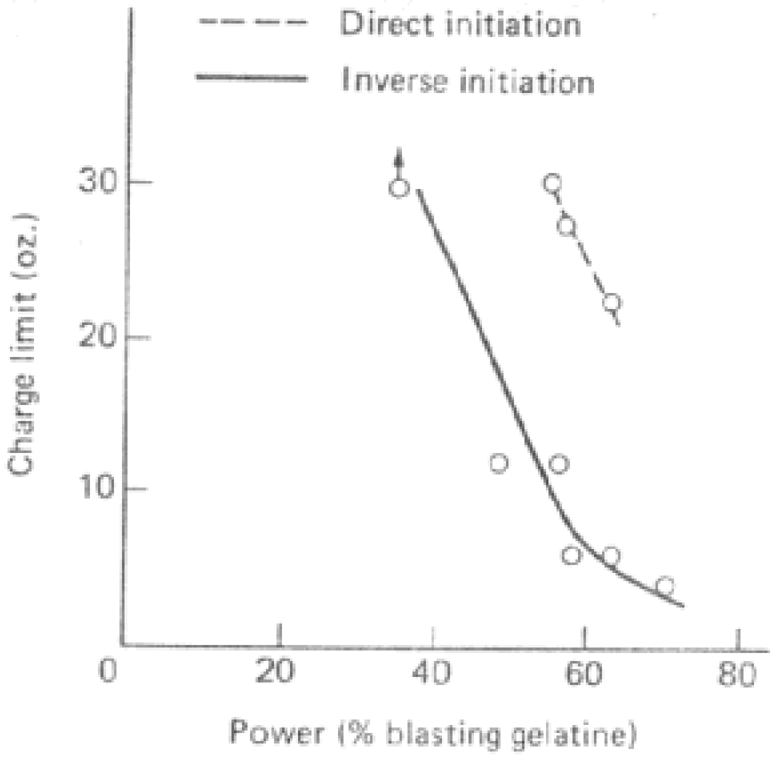

FIG. 95. Effect of initiation on gallery testing [7].

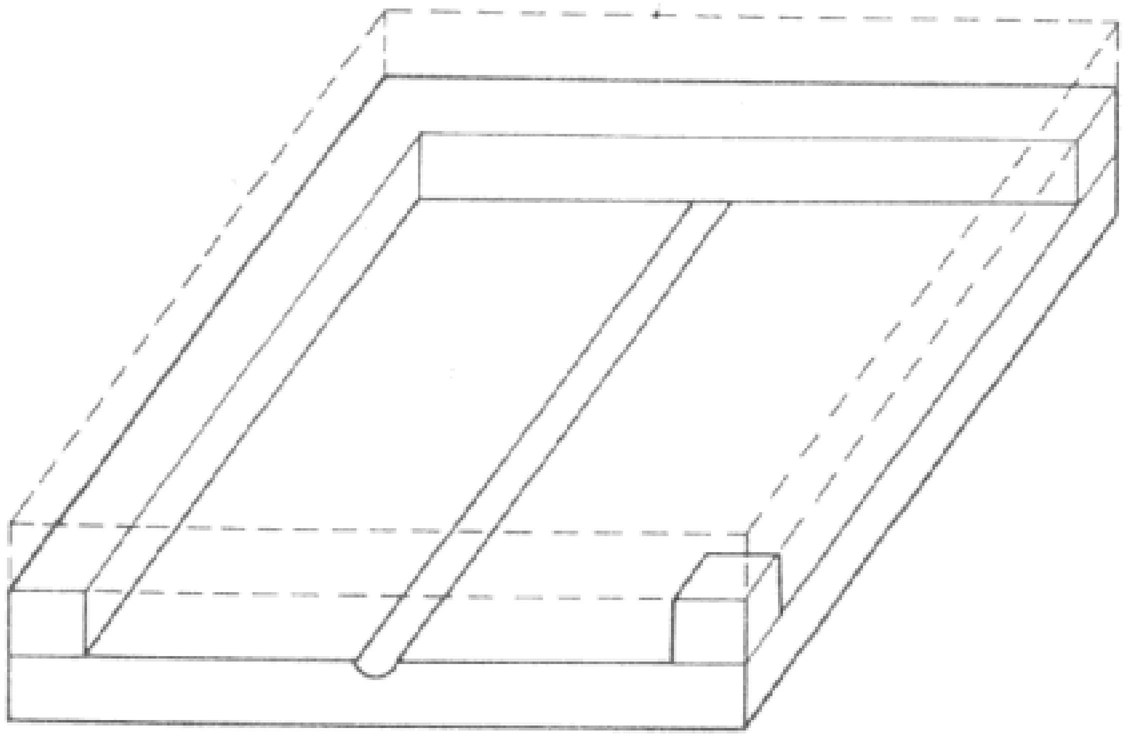

FIG. 96. No. 2 Break Test. The position of the upper plate is shown by the broken lines, according to Fordham [7].

Two heavy steel plates 1.8 m^2 are held 5 or 15 cm apart. The plates are in a gastight enclosure formed from steel sides with sheet polyethylene. The explosive cartridges are in the groove. The space inside the enclosure is filled with an explosive gas mixture. The ignition or non-ignition of the gas mixture is observed.

Break Test 3 consists of a break occurring at the end of a shot-hole. This is simulated by a cannon fired with the mouth in close proximity to a steel plate.

The most severe of these is Break Test No. 2.

In the U.S.S.R. a cannon spraying coal dust in quantity of 6 kg by means of a small (50 g) explosive charge. Coal dust of 400–600 g/m^3 is formed and the shot of the examined explosive is fired 2–10 s after spraying the dust.

The mechanism of the ignition of methane and coal-dust was summarized in diagram – Fig. 97 depicted by Cybulski [4].

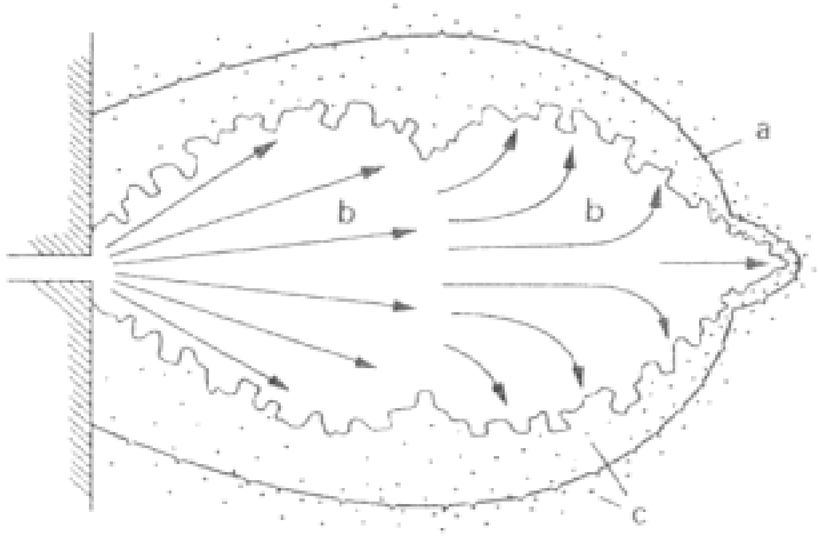

FIG. 97. Shock wave and products of detonation according to Cybulski [4]: (a) – shock wave, (b) gas products of detonation, (c) – solid particles of explosive.

Here three elements are shown of the projection from the mortar:

1. Shock wave,
2. Gas products of detonation,
3. Particles of the explosive mixture: undecomposed explosive, sodium chloride, metal parts of the detonator. Some of them are projected in front of the shock wave.

The necessity for standardization of gallery-tests as carried out in different countries has also arisen [109]. Gorol and Sobala [110] drew attention to their observation that the results against methane–air was a better practical criterion of the safety of explosives than the test against coal-dust.

Theory of Safety Against Methane and Coal-Dust

The theoretical aspect of inhibition of explosions of methane–air and coal dust–air is mainly regarded from the view point of the action of alkali metals in flame and particularly on the action of potassium ion [53–55].

Ashton and Hayhurst [56] rationalized it in terms of collisional ionization and recombination of electrons with alkali metal ions in flame, for example:

$$M + X \longrightarrow M^+ + e^- + X.$$

Where X is a flame species.

AMMONIUM NITRATE–FUEL OIL MIXTURES (AN–FO)

(Vol. III, pp. 482, 508)

As described in Vol. III, p. 482 the cheapest ammonium nitrate explosives (AN–FO) were introduced in opencast mines. Diesel fuel-oil was used as a cheap combustible ingredient – originally in 1954 and eventually on a larger scale in 1960 in the U.S.A. [57, 72] and almost simultaneously in Canada, Scandinavia and Germany [58], Japan and in U.S.S.R. [59].

The following are figures on the use of AN–FO explosives in the U.S.A. in 1979 and 1980: over 1300 and nearly 1400 million pounds respectively. Their use was mainly in quarrying, non-metal mining and construction work [10].

An International Symposium on Mining Research took place in 1961 [60] and was partly dedicated to AN–FO explosives. Hino and Yokogawa [61] described the action of surfactants on the detonation ability of ammonium nitrate and its mixtures with coal tar in proportions 93.3/6.2. The addition of 0.5% of surfactant increased the detonation ability of the mixtures. Particularly effective were sodium dinaphthylmethane disulphonate, sodium laurylsulphonate and sodium dodecylbenzene sulphonate.

Grubb [62] drew attention to the importance of the intimacy of mixing ammonium nitrate with fuel oil by using fine and porous particles of ammonium nitrate and Clark *et al.* [63] described the use of micro-prilled ammonium nitrate of less than 20 mesh size. They found the AN–FO made of such ammonium nitrate can readily detonate but the rate of detonation is limited by characteristic low bulk density – the consequence of micro-prills.

The possible use of AN–FO explosives for underground work was described by Henning [64] and Bullock *et al.* [65]. The authors came to the conclusion that AN–FO can replace dynamite in blasting operations even in small diameter holes (e.g. 23 mm [64]). An important problem for underground work is fumes produced by AN–FO. This was investigated by Van Dolah *et al.* [66]. Their main conclusions are in agreement with general rules: the negative oxygen balance favours the formation of CO but does not reduce the amount of NO_2. The positive balance appreciably increases the concentration of NO_2. The strength of the primer also has an influence on the composition of the products. The concentration of oxides of nitrogen increased as the strength of the primer decreased.

According to Schiele [58] the maximum rate of detonation is with 5.5% diesel oil. Chaiken, E. B. Cook and Ruhe [114] used the large closed gallery to examine both the rate of detonation of AN–FO and the composition of gaseous products. Figure 98 gives the rates of detonation of AN–FO made of prilled and powdered ammonium nitrate. Ammonium nitrate was catalysed by 4% of undisclosed catalyst. The formation of nitrogen oxides was favoured by inadequate initiation and propagation of detonation, as already known [115]. The rate of detonation against the diameter of cartridges is changing as depicted in Fig. 99.

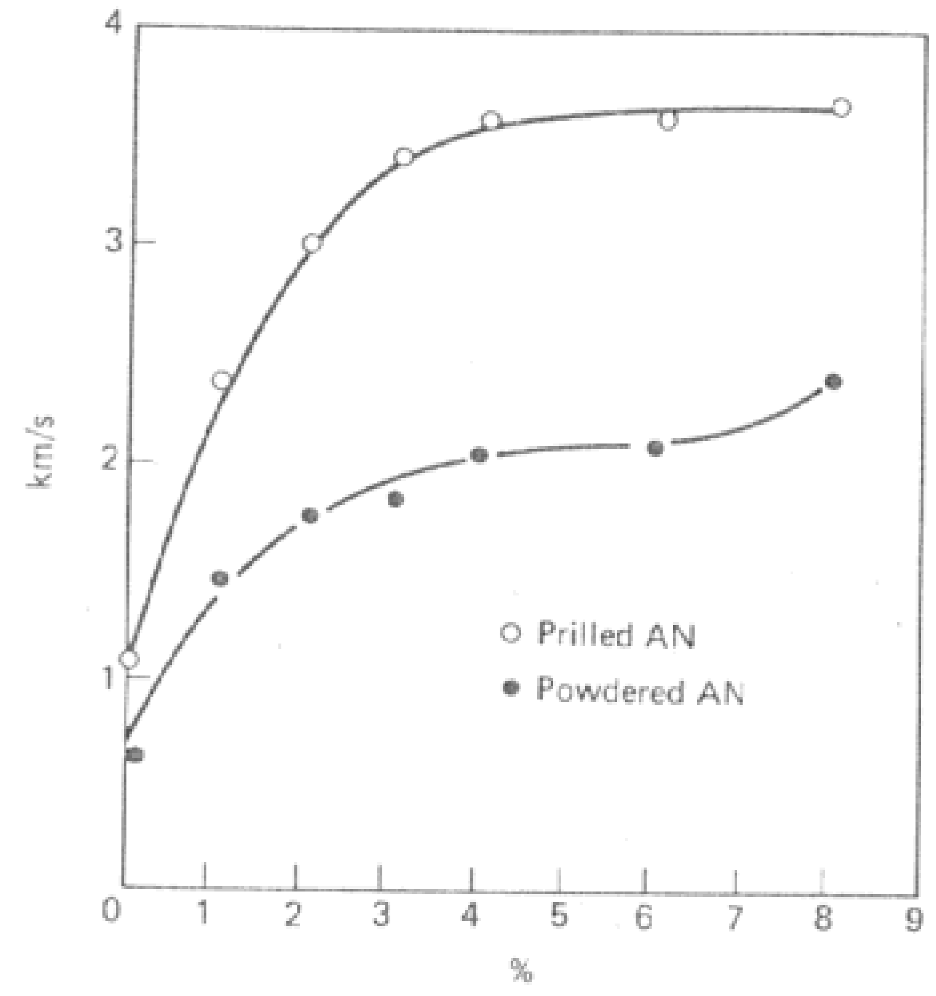

FIG. 98. Rate of detonation of AN–FO (with prilled and powdered AN) as a function of the proportion of Diesel oil diameter 14 cm [114].

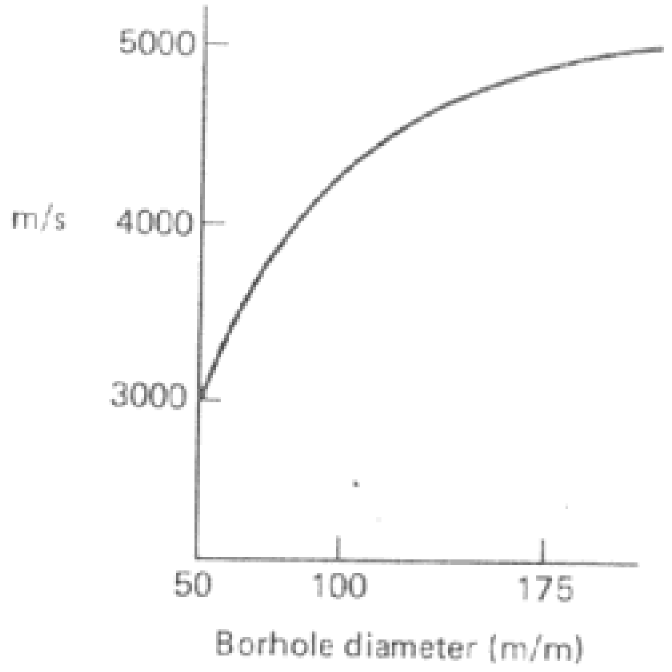

FIG. 99. Rate of detonation of AN–FO as a function of bore-hole diameter (Schiele [58]).

EXPLOSIVE WORKING OF METALS

A low rate of detonation is required for most operations connected with explosive working of metals. It is usually achieved by mixing explosives marked for their ease of detonation (such as PETN, Cyclonite) with a relatively large quantity of such oxygen carriers as $NaNO_3$, KNO_3, $Ba(NO_3)_2$.

Plastic explosives are particularly suitable for the working of metals.

Most problems connected with explosive working of metals are outside the scope of the present book and the monograph [120] should be consulted.

MINING EXPLOSIVES USED IN VARIOUS COUNTRIES

Below are listed mining explosives used in some countries which complete the list given in Vol. III, pp. 446–489. In addition to the list a separate group is described:

Water gel (Slurries), p. 545.

Bulgaria

Bulgarian Permitted Explosives are characterized by the presence of potassium sulphate as the agent giving safety to methane and coal-dust [68]: Table 85.

TABLE 85. Bulgarian permitted explosives

Components	Skalinit 1	Skalinit 2
NH_4NO_3	69	64
KNO_3	–	5
TNT	15	15
Charcoal	1	1
K_2SO_4	15	15
Oxygen balance %	+1.37	+2.63
Heat of detonation (calculated) Kcal/kg	720	685
Calculated temperature of explosion °C	2295	2295
Rate of detonation m/s	3435	3200
Lead block cm^3	300	280
Gap test cm	4	3

Germany (Vol. III, p. 455)

German Permitted Explosives are, as before, divided into three classes. Their composition still remains undisclosed and the method of manufacture is kept secret.

Two main groups of Permitted Explosives are known: those made by Vasagchemie Synthen GmbH: Wetter-Devonit A, Wetter-Roburit B, Wetter-Salit A, Wetter-Securit C, Wetter-Wasagit B, Wetter-Westphalit B, and made by Dynamit Nobel A.G.: Wetter-Carbonit C, Wetter-Energit B, Wetter-Nobelit B.

Their properties are collected in Meyer Dictionary [69].

Great Britain (Vol. III, p. 461)

Permitted explosives. The five groups of permitted explosives used in the U.K. are now called P explosives with numbers P1 to P5.

P1 Explosives should pass the following test [7]

(a) 26 shots fired of 142 g of explosive with inverse initiation, unstemmed should not give more than 13 ignitions of methane–air mixture

(b) 5 shots fired of 795 g with direct initiation, stemmed, should not ignite methane–air mixture

(c) 5 shots fired of 795 g with direct initiation stemmed, should not ignite coal dust–air mixture.

Their power should not be larger than 58–66% of blasting gelatine [7]. Polar Ajax and Polar Viking are typical representatives of this group of explosives (Vol. III, pp. 466 and 468 respectively).

One more explosive P1 should be mentioned: Hydrobel of the composition given in Table 86.

TABLE 86. British permitted explosives

Components	Hydrobel (P1)	Explosives Unipruf (P3)	Carrifrax (P4)
NH_4NO_3	20	53	10
$NaNO_3$	–	–	46.5
Liquid nitrate esters	40	8	9
Nitrocellulose	2	–	–
NaCl	27	29	–
NH_4	–	–	28
$BaSO_4$	9.5	–	–
Combustible (e.g. wood meal)	1	9.5	6
Others (e.g. hydrophobic compounds)˙	0.5	0.5	0.5

P2 Explosives are sheathed explosives (Vol. III, p. 431).

They have been almost entirely withdrawn owing to the danger of breakage of the sheath and therefore loss of safety. According to Fordham [7] they have been superseded by P3 explosives.

P3 Explosives are so called Eg.S. explosives – Vol. III, p. 429. Currently these explosives should pass the following [7] test:

(a) 26 shots fired of 397 g with inverse initiation, unstemmed should not give more than 13 ignitions of methane–air mixture.
(b) 5 shots fired of 1020 g with direct initiation stemmed should not give ignition of methane–air mixture.
(c) 5 shots fired of 567 g with inverse initiation unstemmed should not give an ignition of coal dust–air mixture.

Their power should not be higher than 42–50% of blasting gelatine. Unigel and Unigex are typical representatives of this group of explosives (Vol. III, p. 466).

One more explosive P3 should be mentioned: Unipruf (Table 86).

P4 Explosives were designed for ripping with delay detonators. They should satisfy the following tests [7]:

(a) as with P3 explosives,
(b) 5 shots fired of the maximum permitted charge weight in Break Test I should not give an ignition of methane–air mixture.
(c) 26 shots are fired in Break Test II in a gas mixture of 3.6% propane with air and nitrogen which is more easily ignited than methane–air. Preliminary shots determine the most hazardous charge of explosive not exceeding 227 g. No more than 13 ignitions may occur.
(d) 5 shots of a cartridge of 30.5 cm long and 3.7 cm diameter are fired in Break Test III and no ignition should occur.

Carrifrax is the typical explosive P4 (Table 86).

P5 Explosives are designed for blasting solid coal with millisecond delay.

26 shots of 567 g are fired into methane–air mixture and no ignition should occur. In addition the explosives should pass the second (b) and third (c) test applied to P3 explosives.

Italy

Italian mining explosives are described in the Encyclopedia by Fedoroff, Sheffield and Kaye [70].

Four groups of explosives are listed.

(1) *Mining explosives with nitroglycerine*. These contain 43–77.5% nitroglycerine with collodion cotton (1.5–5.0%) and oxygen carriers: NH_4NO_3, $NaNO_3$ or KNO_3. An exception exists with 7.0% nitroglycerine, 0.8% collodion cotton, 44% ammonium perchlorate, 32.2% sodium nitrate, 10% DNT, 5% TNT, 1% wood meal.

Another group consists of gelatinous explosives with 82.5–92% nitroglycerine and 5.5–8% collodion cotton. The former contains sodium nitrate (8.5%) and wood meal (3%).

(2) *Mining explosives with 4–14% nitroglycerine, and 0.1–1.5% collodion cotton*. A characteristic feature is the presence of a large quantity of ammonium picrate: 51–89% and one of the mixtures has 65% cyclonite.

(3) *Mining explosives without nitroglycerine with ammonium nitrate and TNT*. The aromatic nitro compounds are sometimes replaced with 10–30% PETN or Cyclonite. The names are: Ager, Vulcania, Vulcanite.

(4) *Mining explosives with ground smokeless powder*. These are mainly ballistite mixed with oxygen carriers, mainly ammonium nitrate.

Novel Mining Explosives used in Poland

As previously described (Vol. III, p. 475), mining explosives in Poland are divided into four groups:

I. Rock explosives (wrapped in red paper) (Tables 85–87)
II. Coal Explosives (Karbonits) (wrapped in blue paper)
III. Permitted explosives (Barbarits, Metanits) (in yellowish paper)
IV Permitted special explosives (Special Metanits) (in yellowish paper with two black bands) (Tables 87–91).

TABLE 87. AN–FO type Polish explosives

Ingredients	Saletrol A	Amonit Skalny I H
NH_4NO_3 (prilled)	94.5	90
Lubricating oil	5.5	–
Petroleum tar	–	2
Wood meal	–	8
Oxygen balance %0	0.0	+0.06
Lead block expansion cm^3	205	235
Rate of detonation m/s	3560	2630

According to their composition they are marked with letters:

G – denotes the presence of glycol dinitrate ('nitroglycol'),

J – means that they are ion exchanging mixtures (Vol. III, p. 421) containing $Na^+NO_3^- + NH_4^+Cl^- \rightarrow Na^+Cl^- + NH_4^+NO_3^-$,

H – denotes hydrophobic properties of the ingredients, particularly that ammonium nitrate contains hydrophobic compounds, such as calcium stearate.

Most of the explosives described overleaf were introduced between 1975 and 1978.

TABLE 88. Polish rock explosives (Amonits)

Ingredients	Explosives: Amonit Skalny					
	6 G	11	11 G	12 GH	14 GH	15 GH
NH_4NO_3	81	85	85	81.4	86.5	82
Nitroglycerine	2	5.5	2.75	3.5	2.25	2.88
Nitroglycol	2	–	2.75	3.5	2.25	2.87
DNT	–	1.5	1.5	–	–	–
TNT	8	–	–	4	–	–
Petroleum tar	–	–	–	–	1.8	1.25
Wood meal	2	7.5	7.5	2	7.2	4
Al	5	–	–	5	–	7
Ca Stearate	–	0.15*	–	0.5	–	–
Lubricating oil	–	0.5	0.5	–	–	–
Fe_2O_3	–	–	–	0.1	–	–
Oxygen balance %0	+3.35	+3.97	+3.61	+4.92	+2.0	+0.85
Lead block expansion cm^3	420	330	310	370	315	400
Rate of detonation m/s	3030	2480	2000	3000	2600	2800
Gap test cm	13	9	5	14	4	8

* Over 100%

TABLE 89. Polish rock explosives (Dynamites)

Ingredients	Dynamit Skalny			
	3 GH2	5 G1	5 G3	8 GH
NH_4NO_3	47.9	50	50	47.4
$NaNO_3$	–	14.8	15.5	–
Nitroglycerine	22.5	11	11.5	22.5
Nitroglycol	22.5	11	11.5	22.5
DNT	2	4	10	2
TNT	–	7	–	–
Collodion cotton	2	0.8	1.0	2
Wood meal	3	1	0.5	3
Ca Stearate	–	–	–	0.5
Glycol	–	0.3	–	–
Fe_2O_3	0.1	0.1	–	0.1
Oxygen balance %0	+3.5	+5.87	+5.3	+2.02
Lead block expansion cm^3	430	320	320	420
Rate of detonation m/s	2370	2120	2800	2200
Gap test cm	7	6	8	11

TABLE 90. Polish coal and permitted explosives (Karbonits and Metanits respectively)

Ingredients	Karbonit weglowy D6G	Metanit powietrzny D5G	Metanit powietrzny W2A	Metanit powietrzny specjalny J1
NH_4NO_3	77	63.5	56	–
$NaNO_3$	–	–	–	53.8
Nitroglycerine	4	2	2.5	7.8
Nitroglycol		2	2.5	2.2
DNT	5	3.5	3	–
Wood meal	3.5	3	4	2.2
NaCl	10.5	26	25	–
NH_4Cl	–	–	7	34
Soot	0.1*	–	–	–
Dyestuff	–	–	0.1	–
Oxygen balance %0	+5.3	+4.96	+0.4	+7.55
Lead block expansion cm^3	265	200	180	100
Rate of detonation m/s	2150	2035	1900	1700
Gap test cm	7	4–6	3	5

* Over 100%

TABLE 91. Polish permitted explosives (Dynamite type)

Ingredients	FGH	Barbarit FGH 2	KG
NH_4NO_3	14.2	12.2	15
$NaNO_3$	–	–	15
Nitroglycerine	26.5	28	11
Nitroglycol	7.5	5	11
Centralit II	0.5	0.5	–
Collodion cotton	1	1	0.4
NaCl	40	43	34.5
NH_4Cl	–	–	10
$BaSO_4$	10	10	0.5
$CaCO_3$	0.3	0.3	–
H_2O	–	–	0.6
Oxygen balance %0	+2.15	+1.8	+3.56
Lead block cm^3	175	160	150
Rate of detonation m/s	2250	2000	2150
Gap test cm	12	4–5	4–5

Spain

According to Fedoroff and Sheffield [71] original types of explosives were developed during World War II by Ottaolauruchi: Esplosivo F.E.1, F.E.2 and F.E.3.

They were composed of 65–70% NH_4NO_3, 17–25% TNT and 10–15% $Na_2HPO_4 \cdot 7H_2O$.

Sweden

A few AN–FO Type explosives used in Sweden are given in Table 92 [67].

TABLE 92. AN–FO explosives used in Sweden [67]

Components	AN–FO–0	AF–FO–2	AN–FO–4	AN–FO–8
NH_4NO_3	94.5	92.9	91.4	88.2
Fuel Oil	5.5	5.1	4.6	3.8
Al	–	2.0	4.0	8.0

U.S.S.R. Mining Explosives [6]

Mining explosives in U.S.S.R. are divided into six groups.

I. For open cast work: Akvatols, Igdanit (AN–FO), TNT, TNT + Al (Table 93).
II. For open-cast and underground work, where no dangerous coal-dust and methane are present (Tables 94, 95).
III. Permitted explosives safe to methane but not for coal mines. (Table 96).
IV. Permitted explosives safe to methane and coal-dust (Table 96).
V. High safety permitted explosives (Table 97).
VI. Highest safety permitted explosives in particularly dangerous coal mines (Table 97).

Ammonits and ammonals. These are used in cartridges of 32 and 90 mm diameter. Most popular is Ammonit 6Zh V with ammonium nitrate protected by fatty acids and iron salts.

Some of the most popular compositions are given in Table 94.

The density of the explosives is comprised between 0.95 and 1.15 Ammonit Skalnyi No. 1 is also manufactured in compressed cartridges of density 1.43–1.53.

A modification of Ammonits are Zernogranulits. They contain ammonium nitrate in prills mixed with molten TNT. Those with a negative oxygen balance are used obviously in open-cast work only. Thanks to a high TNT content they are relatively hydrophobic. Some of Zernogranulits are described in Table 95.

TABLE 93. AN–FO type explosives used in U.S.S.R. [6]

	Dynamon		Granulit		Igdanit
	AM–10	AC–8	AC–4	C–2	
NH_4NO_3	87.7	89	91.8	92.8	94.5
Mineral Oil	2.3	–	–	–	–
Diesel Oil	–	3	4.2	4.2	5.5
Al	10	8	4	–	–
Wood meal	–	–	–	3	–
Oxygen balance %0	+0.25	+0.34	+0.41	+0.06	+0.14
Heat of detonation kcal/kg	1295	1240	1080	915	920
Volume of gases l/kg	800	845	910	985	980
Lead block cm^3	425–460	410–430	390–410	320–330	320–330
Rate of detonation m/s = 1–1.3 40 mm dia. in steel 10 g booster	4100–4300	3000–3600	2600–3200	2400–3200	2200–2800
Gap test cm dia. 32 mm	2–3				
40	5–8				
90	25–30				
100	–	0–4	0–2	–	–
Moisture % H_2O in open pit		5	3	5	
underground		2–3	1–2	2–3	

Dynamon AM–8 differs from Dynamon AM–10 by a lower aluminium and higher mineral oil content: 8% and 3% respectively.

The density is comprised between 0.80 and 0.95.

Permitted explosives are described in Tables 96 and 97.

Detonits and dynamites. Detonits are rock explosives used in the U.S.S.R. which contain 6–15% nitroglycerine and nitroglycol. Particularly popular is Detonit M of the composition:

NH_4NO_3 mark ZhV 78%
(hydrophobic)
Low freezing nitrate esters 10%
Collodion cotton 0.3%
Al 10.7% and
Ca or Zn stearate in addition (over 100%) – 1%.

Oxygen balance is +0.18%, lead block expansion 460–500 cm^2, rate of detonation in cartridges of

TABLE 94. Ammonium nitrate explosives in U.S.S.R. [6]

Components	Ammonits No. 6 ZhV	No. 10 ZhV	Ammonal VA–4	Ammonit Skalnyi (rock) No. 1	Skalnyi (rock) Ammonal No. 3
NH_4NO_3 (hydrophobic)	79	85	80.5	66	72
TNT	21	8	15	5	5
Wood meal	–	7	–	–	–
Al	–	–	4.5	5	8
Cyclonite	–	–	–	24	15
Oxygen balance %0	−0.42%	+1.53%	+0.18	−0.79	−0.78
Lead block expansion cm^3	360–380	300–320	410–430	450–480	450–470
Rate of detonation m/s	3600–4800	3200–3600	4000–4500	4800–5300	4000–4500
Critical diameter in open m/m	10–13	15–20	12–14	5–6	8–10
Gap test cm for diameter 32 mm	3–6	2–5	5–8	10–14	8–12

TABLE 95. Zernogranulits and Grammonals in U.S.S.R. [6]

Components	Zernogranulits 79/21	30/70	50/50–V	30/70–V	Grammonals A–8	A–45
NH_4NO_3	79	30	50	30	80	40
TNT	21	70	50	70	12	45
Al	–	–	–	–	8	15
Oxygen balance %0	+0.02	−0.45	−27.15	−45.9	−0.24	−38.65
Lead block expansion cm^3	360–370	330–340	340–350	330–340	420–440	440–460
Rate of detonation m/s	3000–3600		3600–4200	3800–4500	3800–4000	5800–6300
Critical diameter in open mm	50–60	40–60	40–50	40–60	30–40	60–80

TABLE 96. Permitted explosives in U.S.S.R. [6] Class III and IV

Components	Ammonit AP–4ZhV	Class III Ammonit AP–5ZhV	Pobedit VP–4	Class IV Ammonit PZhV–20	T–19
Ammonium nitrate ZhV	68	70	65.5	64	61
TNT	17	18	12	16	19
Nitrate esters	–	–	9	–	–
Wood meal	–	–	1.5	–	–
NaCl or (KCl)	15	12	12	20	20
Oxygen balance %0	+0.45	+0.16	+0.48	+0.4	−2.47
Lead block expansion cm^3	285–300	320–330	320–340	265–280	270–280
Rate of detonation m/s	3600–4200	3600–4600	3800–4600	3500–4000	3600–4300
Gap test: cm diameter	5–10	5–10	6–25	5–10	5–10
36 mm diameter after 1 hr in water	4–6	4–7	5–20	4–7	2–4

Density: 1.0–1.2.
They do not ignite methane when 600 g fired with stemming of 1 cm.
Class IV: in addition they do not ignite coal dust when 700 g fired without stemming.

TABLE 97. Permitted, Class V and VI [6]

Components	Uglenit E–6	Class V Selectit granulated	Uglenit No. 5	Class VI Uglenit No. 7
NH_4NO_3 Zh V		66.5	14	–
$NaNO_3$ or (KNO_3)	46.3	–	–	(57)
Nitrate esters	14.2	10	10	10
Wood meal	2.5	8.5	1	2
NaCl or (KCl)	(7)	15	75	–
NH_4Cl	29	–	–	30
Stearates	1	–	–	–
Diatomite or PCV	–	–	–	1
Oxygen balance %0	+0.53	−0.2	+0.13	+4.94
Lead block expansion cm^3	130–170	220–240	60–90	100–120
Rate of detonation m/s	1900–2200	1800–2000	1750–1900	1600–1800
Gap test– cm diameter 36 mm	5–10	5–7	3–10	3–10

They do not ignite methane when the cartridge of 200 g of Uglenit E 6 or Selectit is suspended in experimental gallery.

The same with cartridges of: Uglenit No. 5 (500 g) and Uglenit No. 7 (1000).

24 mm diameter 3900–4300 m/s
32 mm diameter 4800–5000 m/s.
Critical diameter (in open) 8–10 mm
Gap test: 24 mm diameter 6–12 cm and
32 mm diameter 16–22 cm.

After keeping under water the figures are 4–8 cm and 10–15 cm respectively.

Density 1.1–1.3.

Dynamites which contain a higher proportion of nitrate esters, for example 62% are very little used in U.S.S.R. and form only 0.2–0.3% of the total production of explosives. The main objection is low shelf life and misfiring which have produced a number of accidents.

Permitted in Sulphur Mines and Oil Fields

In sulphur mines Sulphur Ammonit No. 1 ZhV and in oil fields Neftyanoi Ammonit No. 3 are used. Their properties were given in Vol. III, pp. 488–489 and the composition is given below (Table 98).

TABLE 98 [6]

Components	Sulphur Ammonit No. 1 ZhV	Neftyanoi Ammonit No. 3
NH_4NO_3, ZhV	52	52.5
TNT	11.5	7
Nitrate esters	5	9
Wood meal	1.5	–
KCl	–	30
NH_4Cl	30	–
Stearates	–	1.5
Oxygen balance %0	−1.0	−0.7
Lead block expansion cm^3	200–220	220–240
Rate of detonation m/s	2500–3000	2800–3200
Gap test: cm	5–10	3–7
after storage in water for 1 hour	3–7	2–5
Ignition test in an experimental gallery	400 g in a mortar does not ignite sulphur dust suspension	400 g in a mortar does not ignite methane with petroleum vapour

Modern Japanese Mining Explosives [*] (Vol. III, p. 468).

Recent information about some Japanese mining explosives are given in Tables 99–104.

TABLE 99. Rock explosives

Ingredients			Explosives		
	Sakura dynamite	Tokugiri dynamite	No. 3 Kiri dynamite	No. 2 Enoki dynamite	Akatsuki† dynamite
Nitroglycerine/nitroglycol mixture 60/40 gelatinized with nitrocellulose	48–55	35–54	18–24	20–27	5–20
Nitro Compounds (DNT, DNX, TNT)	–	–	0–9	2–9	0–10
NH_4NO_3 and sodium and potassium nitrate	34–42	39–60	65–75	50–72	60–85
Sawdust	8–12	2–8	1–11	4–8	1–5
Properties					
Density	1.45–1.55	1.40–1.50	1.30–1.45	1.30–1.45	1.25–1.45
Lead block cm^3	320–360	430–480	380–430	270–430	370–430
Detonation velocity m/s	5500–6100	6500–7200	5500–6500	5800–6500	5000–5500
Gap test (as the multiple of charge diameter)	5–7	6–8	4–6	4–6	2–6

† For open-pit work.

* According to: Kogyo Kayaku Handbook, The Industrial Explosives Society of Japan, Tokyo, 1977, Makoto Kimura, Sumitomo Corporation in Tokyo, and K. Yamamoto of Nippon Kayaku Co. Ltd.

TABLE 100. Japanese permitted explosives containing nitrate esters (more than 7%)

Ingredients		Explosives		
	No. 1 Toku-Ume dynamite	No. 3 Shiza-Ume dynamite	No. 3 Toku-Shiraume dynamite	EqS Bakuyaku
Nitrate esters (as in Table 99)	18–23	18.7	18–20	9–12
Nitro Compounds (as in Table 99)	4–8	3.0	–	–
Inorganic nitrates (ammonium, sodium potassium)	50–55	49.5	50–46	50–55
Sawdust	1–3	3.8	2–4	5–10
Sodium chloride	20–26	25.0	25–27	30–34
Properties				
Density	1.35	1.40	1.35–1.45	0.95–1.05
Lead block cm^3	290–310	280–300	300–320	170–230
Detonation velocity m/s	5500–6000	5500–6000	5500–5800	2700–3300
Gap test (as in Table 99)	5–7	5–7	5–7	3–6

TABLE 101. Japanese permitted explosives containing less than 7% of or no nitrate esters

Ingredients			Explosives		
	No. 5 Shouan-Bakuyaku	G Shouan-Bakuyaku	No. 105 Shouan-Bakuyaku	No. 2 Kurotaka Shouan-Bakuyaku	EqS–1 Bakuyaku
Nitrate esters (as in Table 99)	–	6.2	5–6	–	–
Nitro Compounds (as in Table 99)	5–8	–	–	4–6	5–7
Inorganic nitrates (as in Table 99)	75–80	69.8	67–73	76–80	63–71
Sawdust	4–6	9.0	6–11	4–7	10–14
Sodium chloride	11–13	15.0	14–16	4–7	25–30
Properties					
Density	1.0	1.0	0.95–1.05	1.0	1.0
Lead block cm^3	270–290	280–300	280–300	270–290	205–215
Detonation velocity m/s	4500–5000	3300–3800	3400–3600	4500–5000	3000–3500
Gap test (Table 99)	2–4	3–5	3–5	>2	>2

TABLE 102. Japanese perchlorate explosives (Vol. III, p. 474, Table 136)

Ingredients		Carlit Explosives	
	No. 5 Kuro Carlit	Akatsuki Carlit	Ao Carlit
Ammonium perchlorate	73–78	22–27	17–22
Nitro Compounds	–	2–7	2–7
Inorganic Nitrates	–	60–70	60–70
Sawdust	6–11	8–13	8–13
Ferro-Silicon	13–18	2–7	2–7
Properties			
Density	1.10–1.15	1.10–1.15	1.05–1.10
Lead block cm^3	440–470	390–440	380–440
Detonation velocity m/s	4000–4500	4000–4500	3700–4200
Gap test (Table 99)	4–6	3–5	3–5

TABLE 103. Miscellaneous Japanese commercial explosives

Ingredients		Explosives	
	Urbanite	Dai Happa yo Bakuyaku	Akatsuki Bakuyaku
Nitrate esters	50–54	5–7	–
Nitro compounds	2–6	10–15	6–8
Inorganic nitrates	36–44	75–78	81–84
Sawdust	2–6	3–6	6–8
Al	–	–	2–4
Properties			
Density	1.30–1.40	0.98	1.0
Lead block cm^3	420–470	380–400	380–400
Detonation velocity m/s	2000–2500	3800–4300	4400–4600
Gap test (Table 99)	6–8	–	2–3
Used in	Urban blasting	Large blasting	Open pit

TABLE 104. Japanese 'TNT commercial' explosives

Ingredients		Explosives	
	No. 2 Kohzumite	No. 12 Kohzumite	No. 31A Kohzumite*
TNT	15–30	6–15	100
RDX	0–10	11–20	–
Inorganic Nitrates	50–80	43–85	–
Ammonium perchlorate	0–8	–	–
Al	0–5	0–6	–
Sawdust	0–15	1–3	–
Properties			
Density	1.10	1.03	1.12
Lead block cm^3	450–480	380–400	310–350
Detonation velocity m/s	5300–5500	4800–5000	5500–5600
Gap test (Table 99)	5–6	4–5	

* For open pit work.

Belgium

The composition of typical permitted explosives made in Belgium are given overleaf (Table 105), according to Goffart and Waterlot [119]. The explosives belong to ion exchange group with potassium or sodium nitrate and ammonium chloride.

TABLE 105.

Components	Explosives		
	Charbrite 418	Charbrite 4/50	Kempoxite 1
Nitroglycerine and Nitroglycol	9.5	9.5	12.0
KNO_3	58.25	55.25	–
$NaNO_3$	–	–	48.0
NH_4Cl	30.0	28.0	30.3
Ammonium Oxalate	–	5	6.5
Hydrophobic compounds	2.25	2.25	–
Calcium stearate	–	–	0.35
Guhr	–	–	2.0
Cellulose	–	–	0.7
Oxygen balance %0	+8%	+5.5%	+4.3%

WATER–GEL (SLURRY) EXPLOSIVES

The last twenty years have shown a rapid increase in the use of Water–gel (Slurry) Explosives in commercial explosives.

The consumption of 2·5 millions of pounds in 1958 grew to over 460 and 400 millions of pounds in 1979 and 1980 respectively [10] in the U.S.A. They were originally used in metal mining (iron-ore open-pit operations) on a large scale, and until now metal mining, quarrying and non-metal mining remain the main consumers of water–gel explosives.

Two excellent reviews have appeared: on the earlier history [72, 73] and recent development of slurry (water–gel) explosives [74].

History

Abel as early as 1874 [75], Kast [76] and T. Urbański *et al.* [77, 78] proved that the presence of water in high explosives increased the rate of detonation (see Fig. 43 and Tables 50 and 62). This found limited practical application in the use of nitrocellulose with water in demolition cartridges [75, 76]. Streng and Kirshenbaum [79] obtained a patent for an explosive composed of ammonium nitrate aqueous solution with aluminium powder. In Sweden Wetterholm *et al.* [80] obtained a patent in 1957 which claimed: 'an oxygen balanced plastic safety explosive characterized by its main ingredients being 20–45% of a high velocity, high brisant explosive, oxygen delivering inorganic salts mixed in a gel of water and a hydrophilic colloid with an amount of water between 3–25%'. The explosive 'Securit' contained 34% DiTEU (*N,N*-bis-β, β, β-trinitroethyl) urea (Chapter VIII, p. 247) 54% NH_4NO_3 and $Ca(NO_3)_2$, 0.8% rice starch, 5.2% glycol and 6.5% water. The explosive showed the rate of detonation 6100 m/s, gap test of diameter, 25 mm was 4–5 cm, critical diameter in a glass tube was 11 mm. Industrial manufacture was not fulfilled (1950) owing to the introduction of the successful AN–FO explosives.

On the contrary, in the United States the 'slurry explosives' developed by Cook [81, 82] and tested in the Iron Ore Co., in Canada in 1957 was quickly accepted in open pit work. The original composition by Cook and Farnam [81] was 25% coarse TNT, 55% NH_4NO_3 or NH_4NO_3 (35–45%) and $NaNO_3$ (10–20%) 20% H_2O with added guar gum as a thickening agent. The addition of the thickening agent was a considerable improvement as it prevented segregation of the ingredients. Guar gum is a polysaccharide: galacto-mannan [83].

Also another patent appeared at the same time by Hardel and Bjork [84] who used aluminium powder as a sensitizer (instead of TNT).

It was soon recognized that the presence of tiny air-bubbles in the slurry was a very good sensitizer. The bubbles adhere to TNT particles or Al powder and help detonation by creating hot spots by adiabatic compression.

Another kind of early slurry was that developed by Gehrig of Atlas Chemical Industries [85]. It consisted of a saturated solution of ammonium nitrate in nitric acid of 60–70% HNO_3 and some organic substances which are not attacked by nitric acid, for example, vinyl polymers. However handling of the solution with nitric acid is difficult and can be dangerous. A fire occurred in a factory in Rourkela (India) in 1972 through spilling nitric acid slurry on wooden boards [86].

The advantages of slurry explosives were summarized by Mahadevan [74] as below:

1. By dissolution, water brings the ingredients into close contact with each other.
2. It provides a continuous medium through which a detonation wave passes.
3. It desensitizes the explosive against fire, sparks, impact and friction thereby decreasing hazards associated with storage and handling.
4. Water is believed to increase the energy of the explosive by taking part in the reaction at the time of explosion especially when Al is present in the composition.
5. It affects the products of detonation and suppresses the formation of toxic gases: carbon monoxide and oxides of nitrogen.
6. It has a pronounced effect on the 'Coke Oven' reaction $2\,CO \rightarrow C + CO_2$ which is very important in preventing dissociation of energetic products of detonation such as H_2O and CO_2.
7. Low percentage of water presents problems on storage: the explosive becomes hard and grainy due to the crystallization of inorganic oxidizer salts on the contrary a higher percentage of water decreases the sensitivity as well as the strength. According to Cook, 1% increase in water lowers the strength of the slurry by *ca.* 1.7%. Thus an optimum percentage of water is in the range of 8–20%.

9\. Water acts as a coolant and offers a perspective of using water–gel explosives in underground gassy coal mines.

Cross-linking Agents

One of the draw-backs of early compositions was the low viscosity of the solution and hence the ease of segregation and loss of air-bubbles. A deterioration in performance was observed on storage. A significant achievement consisted in increasing the viscosity of guar gum by adding cross-linking gel forming agents.

The first cross-linking agents were borax and other boron compounds, antimony compounds e.g. ammonium pyroantimonate, potassium antimony tartrate followed by adding a dichromate, that is oxidation of trivalent to pentavalent antimony was found to give an efficient cross-linking agent [74].

Semi-synthetic and synthetic polymers are also used as thickening agents. Such are carboxymethyl cellulose [87, 6] and polyacrylamide [73] respectively.

Surface Active and Emulsifying Agents

Surface active agents (surfactants) improve the dispersion of ingredients and consistency of slurry. According to Hiroshi *et al.* [88] by adding small amounts of alkali metal salts of alkyldiphenyl ether disulphonic acid a slurry explosive was obtained which can be initiated with a No. 6 cap without adding sensitizers. Also alkali metal salts of sulphuric acid esters of higher aliphatic alcohols, of aromatic sulphonic acids are good surfactants and improve the detonability of slurry explosives. Sorbitol monooleate was recommended [74] as the emulsifier.

Oxygen Carriers

In addition ammonium nitrate, sodium nitrate and calcium nitrate are added to slurry explosives. A mixture of calcium nitrate and sulphur [89] seems to be particularly efficient. Calcium nitrate makes slurry more resistant to low temperature and the explosive can withstand the temperature of −12°C. Ammonium perchlorate can also be used [72], but does not seem to get a wider application.

Aluminium

The addition of aluminium powder in a form of foil, flakes or granules can make slurry without nitro compounds. The patent by Davis, Fassnacht, Kirst and Noran [90] gives slurry explosives composed of ammonium and sodium nitrate, aluminium and water. An emulsifier is added to help the presence of air bubbles. The fact that aluminium can react with the strongly oxidizing ingredients of the explosive mixture can be dangerous.

Aluminium in the presence of water in a strongly oxidizing medium can make the explosive deteriorate and also create danger through heating and gassing. To avoid the reaction of aluminium coating is recommended of Al particles, with stearic, palmitic and oleic acids [74]. Flakes and dust of aluminium posed handling problems as it resists wetting of aqueous medium. Mahadevan and Varadarajan [91] solved the problem by wetting aluminium with ethylene glycol and adding such paste to the mixture.

Alkylamine Nitrates

A number of patents (e.g. by Dunglinson [92]) disclosed that by adding alkylamine nitrates to slurry a great increase in sensitivity could be achieved. Particularly efficient is methylamine nitrate, as disclosed by Frederic [93] and at present Du Pont Co. and I.C.I. are using methylamine nitrate as an ingredient of their slurry explosives [74]. Du Pont issued the explosive under the trade name 'Tovex' [73]. Methylamine nitrate is made by reacting methylamine with concentrated nitric acid (66%) free of nitrous acid (Vol. II, p. 465). It is important that nitric acid is free of nitric oxides which would give side reactions (e.g. diazotization) of methylamine.

There are no remaining problems in formulating water–gels which will perform well in any construction or mining operations under all climatic conditions. Although water-gels are not cheaper than NG-based explosives, manufacturers and customers prefer to use these explosives because of lesser hazards involved in manufacture, storage, transportation and handling.

The slurries can be 'tailor made' to suit individual strate conditions, thus enabling maximum burden to be achieved with the best fragmentation resulting in the reduction of the overall cost of mining. Maximum coupling and hence maximum utilization of energy released to break the rock can be achieved by using water–gels especially pourables. At present the only advantage of NG-based explosives is their greater shelf-life as compared to slurries. To a greater or smaller extent, water–gels have replaced NG-based explosives. The present trends indicate that the former may replace the latter.

Compositions of a few slurry explosives in different countries are given in Tables 106–109.

In Germany Wasag Chemie Sythen G.m.b.H. factories are producing Wasagel explosives with 12% or more water. Mark IK is a non-freezing gel.

Dynamit Nobel AG are making Dynagel mark 1, 2, 3, P1 and P2. All the above explosives are with negative oxygen balance and can be used for open-cast work only. For their properties – see Meyer [69].

Slurry explosives for open-cast work in U.S.S.R. comprise also granulated TNT ('Granulotol') and a granulated mixture of TNT with 15% Al ('Alumotol').

Table 108 gives a comparison of the properties of Granulotol dry and with water.

The heat of detonation of 'Alumotol' is by *ca.* 35% higher than of 'Granulotol' and so is lead block expansion.

TABLE 106. Water-gel blasting agent (SBA) and Slurry Explosives (SE) made in U.S.A. [72]

Components	SBA A1	SE	SE
NH_4NO_3 } $NaNO_3$ }	49	39	–
$NaClO_4$	–	–	39
Al	35	25	25
H_2O	15	15	15
Thickener	1	1	1
Density	1.45	1.60	1.88
Relative crater volume (TNT/Al 80/20 = 1)	1.22	1.22	1.73

TABLE 107. Water-gel (slurry) explosives made by Du Pont of Canada [73]

Components	Trade Names			
	Tovex 20	Tovex 40	Tovex A–4	Tovan 30
TNT	20	40	20	–
NH_4NO_3	49	27	37	48
$NaNO_3$	12	15	10	15
Al	–	–	15 (granules)	15 (flake)
Water	15	15	15	17
Other (Thickening, surface active agents etc.)	4	3	3	5
Properties				
Density	1.40	1.40	1.42	1.27
Rate of detonation V m/s				
unconfined, 5 in. dia	4600	5500	4730	
Confined in steel 5 in. dia	4680	5865	5350	
Calculated: V m/s	5000	5850	5500	5000
Heat of explosion kcal/kg	760	780	1125	1210
Gas volume l/kg	830	850	740	670

Japanese slurry explosives are all based on Du Pont, Hercules or IRECO Chemicals.

Sunvex 100A, 200 and 220 contain methylamine nitrate. Energel MA-7 contains ethanolamine mononitrate. IRECO explosives are sensitized with Al.

The following are slurry explosives used in Sweden [67]: Reomex A (aluminized and methyl nitrate sensitized), Reomex B (methyl nitrate sensitized) and Reolit C (TNT sensitized) gels. Their oxygen balance is –0.35, +1.43 and –1.75 respectively, and the rate of detonation 4000–5000 m/s, however no exact composition was given. Methylamine nitrate is a very good sensitizer of slurry explosives. Owing to this fact T. Urbański suggested, and took part in, developing at IDL Chemicals Ltd, Hyderabad, India [94] the manufacture of methylamine nitrate by the Plöchl reaction, that is, by reacting ammonium nitrate solution with formaldehyde. A small proportion of dimethylamine and a still smaller proportion of trimethylamine nitrate is produced in this reaction, and the reaction requires special conditions because it occurs in an oxidizing medium of ammonium nitrate.

Relatively recent information [112] is that Du Pont de Nemours stopped its dynamite manufacture at the end of 1976. Dynamites have been replaced by

TABLE 108. Akvatols, Akvanals and Akvanits (Slurry explosives used in U.S.S.R. [6])

Components	Akvatol				Akvanal		Akvanit	
	65/35	AB	MG	M–15	No. 1	2	3L	16
NH_4NO_3	63	51	26.5	58.5	57	44.2	25.5	53
$NaNO_3$	–	–	20	–	–	–	32	–
$Ca(NO_3)_2$	–	–	–	–	10	7.4	–	10
TNT	34	28	–	25	20	5	30	29
Cyclonite	–	–	–	–	–	35	–	–
Al	–	–	–	15	5	–	–	–
Alumatol 75/25	–	–	40	–	–	–	–	–
Na-carboxy-methylcellulose	3	–	–	1.5	1.0	1.1	0.5	1.0
Borax	–	–	–	0.02–0.04*	–	–	–	–
Polyacrylamide	–	2	–	–	–	–	–	–
Guar gum	–	–	1.5	–	–	–	–	–
Mineral Jelly	–	–	–	–	–	0.8	–	–
Water	15*	14	12	15*	6	6.5	12	6
Antifreeze	–	5	–	–	–	–	–	–
Sulphite cellulose extract	–	–	–	–	1.0	–	–	–

* Over 100%

Lead block expansion of the above explosives is from 310 cm^3 (Akvanit No. 1) to 480 cm^3 (M–15) and the rate of detonation is 4500–5500 m/s. The density: 1.30–1.55.

TABLE 109. Properties of dry and slurried TNT (U.S.S.R.) [6]

	Dry	Slurried
Heat of detonation kcal/kg	825–870	1000
Volume of gases l/kg	745	895
Lead block expansion cm^3	285–295	320
Rate of detonation m/s	4500–5000	5500–5700
Critical diameter mm in open	60–80	–

cartridges of 'Tovex' explosives with amine nitrate sensitizer and without nitroglycerine.

Although methylamine nitrate was considered to be a relatively safe and – in addition – is present in an aqueous solution precautions should be taken with regards to the problem of safety of handling the solution. The explosion of two tank cars loaded with 86% solution of methylamine nitrate occurred in Potomac River (U.S.A.) in 1976. The explosion was probably due to friction in a pump [86]. An important paper by Persson, Jerberyd and Almgren [111] established that methylamine nitrate slurry explosives of the Swedish type of pumpable water–gel (Bulkreomex) could decompose when piston velocity increased above 20 m/s.

Gas Bubbles

The role of gas bubbles in explosives has already been discussed (pp. 298, 547). Goffart [96] described the importance of gas bubbles which increase the cup sensitivity of slurry explosives containing aluminium dust. However, the presence of gas bubbles of course reduces the density and subsequently the rate of detonation, for example a density of 1.33 falls to 0.83 and the rate of detonation from 3600 m/s to 2710 m/s (for a diameter of 36 mm).

The critical diameter of slurry explosives was determined by Michot and Bigourd [97]. The smallest critical diameter (22 mm) is shown by slurry with Al (density 0.95) and with methylamine nitrate (density 1.00). Also the method of determining the critical diameter has been given [98].

Permitted Slurries

Van Dolah, Hay *et al.* [99, 100] developed permitted slurry explosives with sodium chloride. Mahadevan [101] studied the stability and performance of permissible slurries, and Mahadevan and Varadarajan [91] described the commercial production of permitted slurries of small diameter cartridges.

Slurries with High Explosives

TNT was a common ingredient of slurry explosives of the 'Tovex' type made by Du Pont of Canada (see Table 107) [73]. PETN and RDX slurries were developed by T. Urbański [95]. The method consisted in dissolving pentaerythritol and hexamethylene-tetramine in nitric acid (d. 1.50) and neutralizing with ammonia or ammonium carbonate the solution containing some suspended PETN and RDX. A solution of ammonium nitrate in water with suspension of the above explosives resulted.

There is however a tendency to avoid incorporating typical high explosives into slurries owing to their high cost and sensitivity to impact and friction. Ethylene glycol mononitrate was in use in Canada and an accident occurred in Beloeil in 1975 [86]. As glycol mononitrate was considered to be safe to handle no special precautions were taken and it was pumped with two Moyno pumps. The detonation which destroyed the factory probably started through friction in a pump.

Composition of Slurries with Nitroglycerine based Explosives

A comparison was made by Mahadevan [74] of slurries with 'classical' nitroglycerine explosives as follows:

> "At present the only advantage of nitroglycerine-based explosives is their greater shelf-life as compared to slurries. To a greater or smaller extent, water–gels have replaced nitroglycerine-based explosives."

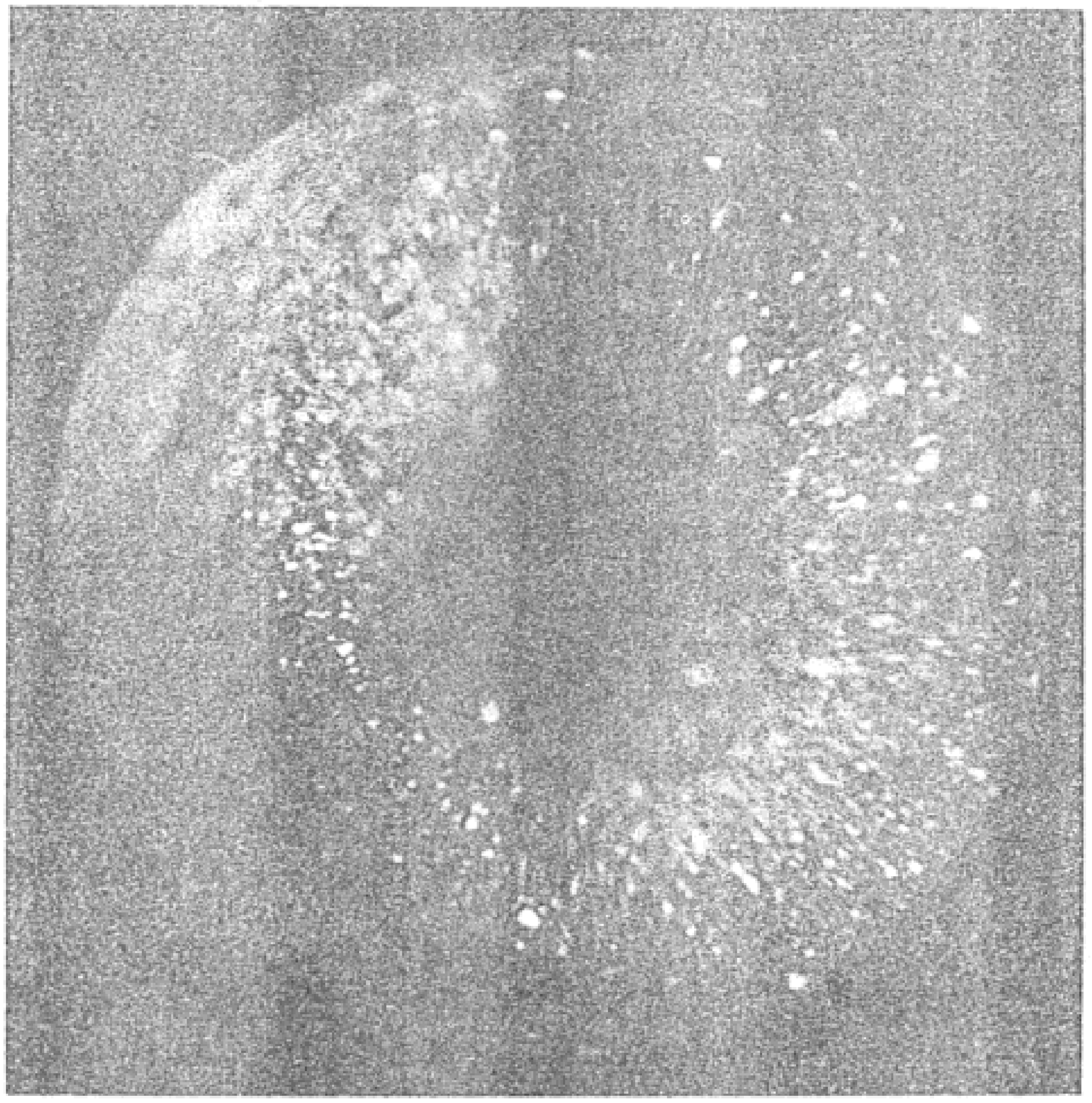

FIG. 100. Nonel 1-tube (detonating fuse) showing a thin layer of explosive inside the plastic tube (Courtesy Nitro Nobel A.B., Gyttorp, Sweden).

NONEL DETONATING FUSE

Among the most important inventions in the field of accessories to mining explosives is the Nonel Detonating Fuse ingeniously invented by P. A. Persson at Nitro Nobel A.B. [113].

It is composed of a thick walled polyethylene tube sprayed inside with a small amount of a highly sensitive and strong explosive such as Octogene (HMX), Cyclonite (RDX) or PETN. It is based on the fact that a shock wave travels along the tube with a higher velocity than the detonation wave. Figure 100 gives a cross-section of the Nonel tube.

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APPENDIX

METHODS OF DETERMINING THE ABILITY OF EXPLOSIVES TO DEFLAGRATE

Methods of determining the ability of explosives to deflagrate were introduced in 1934 by Audibert and Delmas [1]. It consisted determining whether an explosive can be subjected to burning or exploding under the flame produced by ignition charges.

A general scheme was developed in different countries which consists in the following method: an explosive is confined in a steel tube of different dimensions, viz.:

length	200–1370 mm
diameter	38–90 mm
wall thickness	3–20 mm

The tube is closed on both sides. One of the closing plaques is provided with a nozzle of different diameters, e.g. from 1 to 20 mm. Another one is covered inside by an inert substance, such as sand. The initiation of the explosive is usually made by black powder or an explosive mixed with coal-dust.

The minimum diameter of the nozzle which produces a deflagration is determined and serves as a measure of the ability of the explosive to deflagrate.

Another criterion is the proportion of coal-dust added to the examined explosive. In Poland the explosive is mixed with coal-dust (up to 55%). The minimum addition of coal-dust which gives a deflagration is 17–28%. Pure ammonium nitrate explosives do not deflagrate.

Further description of the methods of determining a deflagration is outside the scope of this book. They are fully described by Charewicz [2].

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CHAPTER 20

THE MANUFACTURE OF COMMERCIAL (MINING) EXPLOSIVES

(Vol. III, p. 498)

Little can be added to first steps of manufacturing mining explosives, such as drying, milling and mixing of ingredients of mining explosives (Vol. III, pp. 498–503). Disk mixers (Vol. III, p. 504, Fig. 167), edge runners (Vol. III, p. 350, Figs 93, 94) and Werner-Pfleiderer kneaders (Vol. III, pp. 586–7, Figs 206–209) are still in use for mixing ammonium nitrate explosives without nitroglycerine.

Those with a small amount of nitroglycerine (4–6%) can be mixed in Werner-Pfleiderer and in Drais kneaders (Vol. III, pp. 512–514, Figs. 173–175). The latter are particularly suitable for making explosives with a higher content of nitroglycerine.

PLANETARY MIXERS

The typical planetary mixer is a Drais kneader the most commonly used type is with two bowls pivoting around an axle. While one of the bowls is being emptied or filled, the other one is under the stirrers. The capacity of the bowl is of about 500 kg of dynamite. More recently Drais has built a machine of 500 l useful capacity consisting of four instead of two pillars (Fig. 101).

Another kind of planetary mixer of a smaller capacity (250 kg) was developed by Biazzi S.A., Vevey (Fig. 102) [1]. The main characteristics are the light structure of aluminium, the particular disposition of blades which makes it possible to avoid a foreign body being caught into the mass and wedged between the blades and the interior of the bowl.

The stirrers revolve one around the other at 17 rpm and rotate around their own axis at 45 rpm. The speed can be changed and the mixing time can be kept between 4 and 8 min. At a lower speed the danger of explosion is smaller. The stirring can be clockwise or anticlockwise. The machine is stopped and the stirrers are raised automatically by means of a timing device.

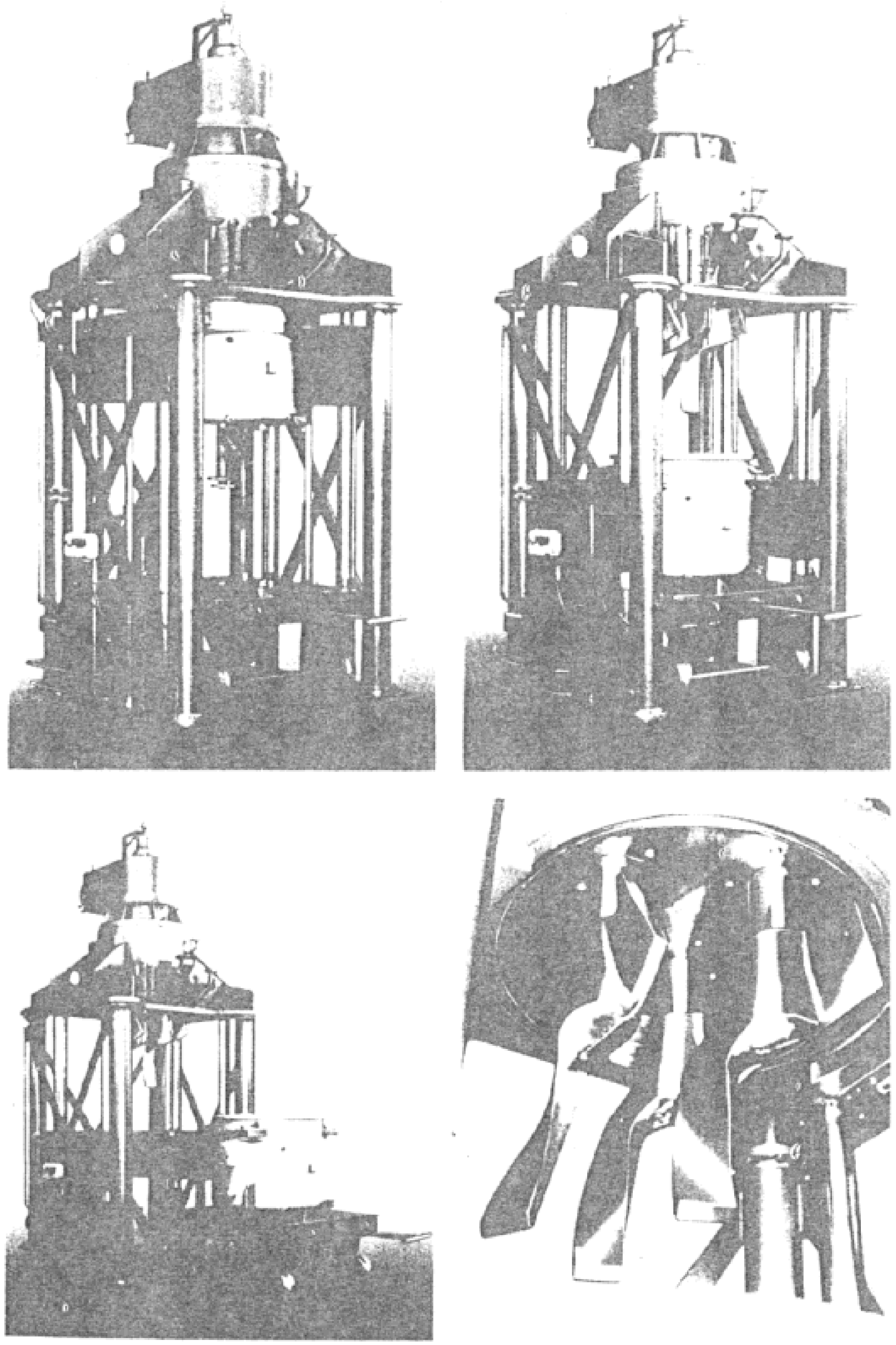

FIG. 101. New design for a Drais Planetary Mixer (Courtesy Draiswerke Maschinenfabrik G.m.b.H., Mannheim-Waldorf, FRG).

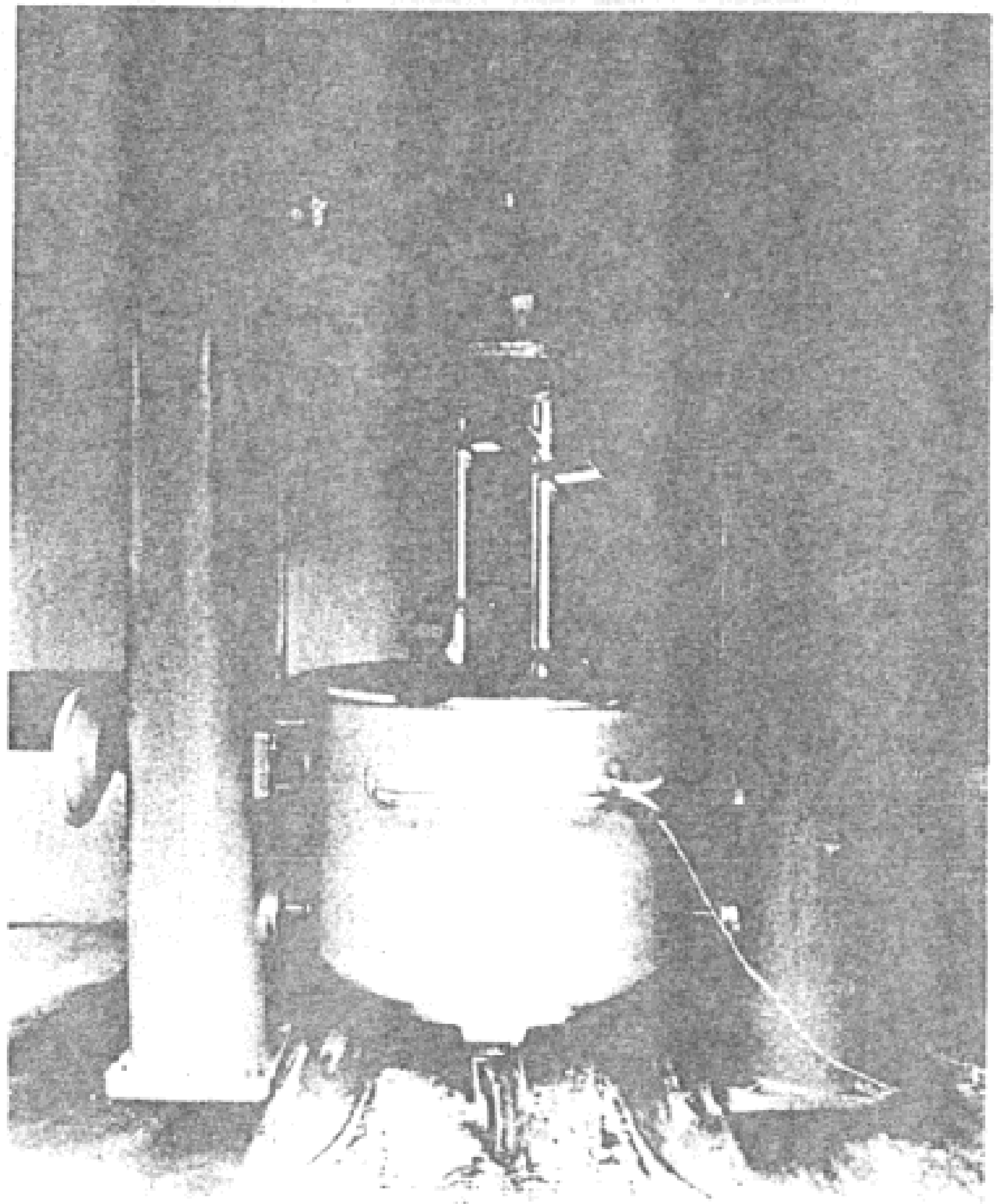

FIG. 102. Planetary mixer by Biazzi (Courtesy Biazzi S.A., Vevey, Switzerland). Earth connection of the bowl can be seen.

Although the design of planetary mixers excludes friction, a few explosions have occurred [2]. Most of them were due to the presence of foreign bodies in the bowl, and a few accidents were due to hand stirring the mixtures, contrary to instructions.

Also a few accidents with Werner-Pfleiderer mixers have been described [2] mostly due to the accidental presence of foreign bodies.

Another kind of explosives mixer 'Tellex Mixer' has recently been developed by Fr. Niepmann, G.m.b.H., Gevelsberg, FRG [3]. The mixing bowl is of steel alloy and consists of two troughs in which mixing can be made of powder, semi-gelatinous and gelatinous explosives, as well as AN–FO and slurry mixtures. The capacity of the troughs is 180–700 kg.

Two spiral stirrers guarantee good mixing (Figs 103a, b).

Mixing lasts 8–10 min and remote control assures the safety of personnel (Fig. 104).

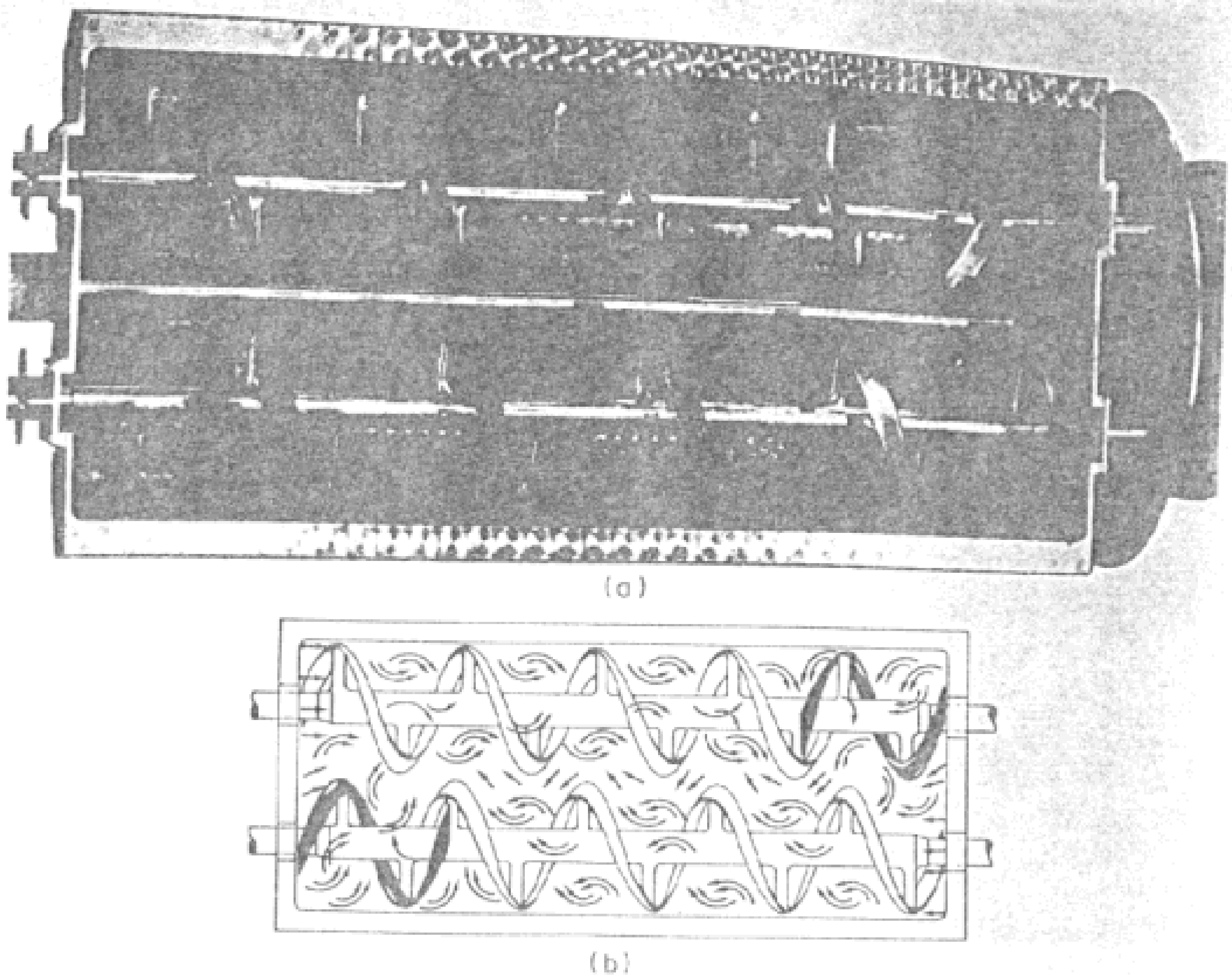

FIG. 103. Tellex explosives mixer by Niepmann (Courtesy Niepmann A.G. Maschinenfabrik, Walchwill/ZG., Switzerland) (a) View from above; (b) Diagram of functioning of stirrers.

CARTRIDGING

Maschinenfabrik Fr. Niepmann G.m.b.H. & Co., Gevelsberg, FRG specializes in making cartridging machines for explosives. A diagram of an early version of a cartridging machine is given in Vol. III, pp. 517–8, Fig. 179. Two modern Niepmann cartridging machines will be described here.

Figure 105 depicts 'Cartex' for cartridging powder-explosives, a cartridging machine which makes 9 cartridges (there are also models making 12 cartridges) [4].

The explosive is fed by screws into the open end of the paper tubes. When shells have been filled, the screws stop automatically, then a brief reverse rotation prevents a surplus feed. The filled tubes travel to the folding machinery where they are closed before being conveyed to the paraffining station, if necessary. The operation is controlled at two points: by manual control inside the cartridging room and by a remote control panel in the control room.

Machines of this type can make cartridges of 20–40 mm diameter and 90–254 mm length, with a yield of 100–180 cartridges per minute.

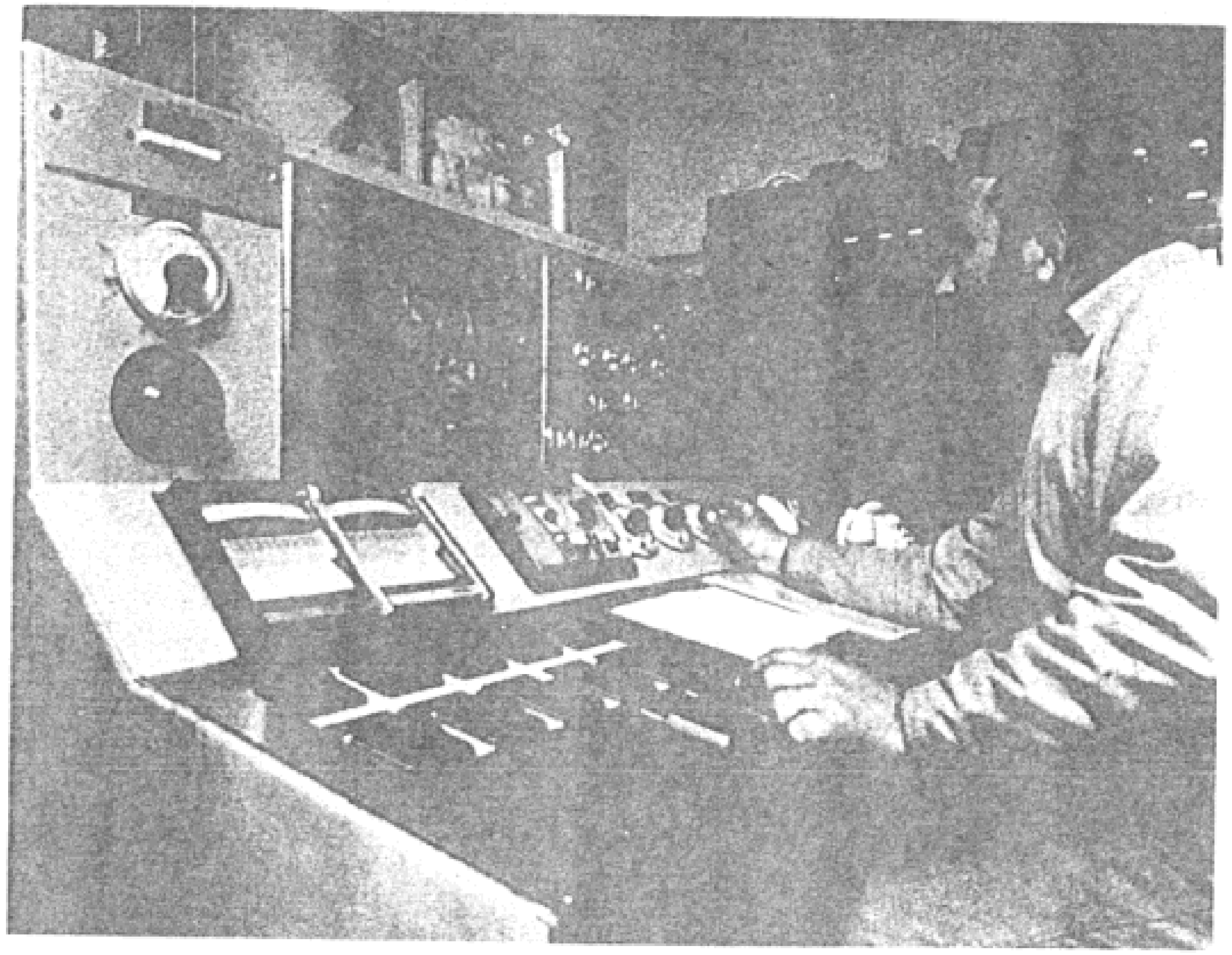

FIG. 104. Control room of mixing explosives at Kemira (Courtesy Kemira OY, Vihtavuori, Finland).

Figure 106 depicts a cartridging machine LD-Ex 701 for gelatinous explosives [5]. Large diameter cartridges can be made: 50–125 mm diameter and 300–800 mm length. The hopper is loaded with an explosive. Feed rollers and transfer screws convey the material to the filling station. Plastic film from a supply reel is formed into tube, and the longitudinal seam is sealed. The explosive is fed into the casing until a desired length has been reached. The filling screw is stopped, the tube is pulled away and wire clips are applied to close the cartridge and the film is cut between the two clips. Cartridge length is adjustable. The machine can make 10–15 cartridges/minute.

Although the Niepmann machines are safe to handle, an accident occurred as described by Biasutti [2] in Rego da Amoreira, Portugal. As is usual in such accidents, it was due to the presence of a foreign metal object in gelatinous explosive with 33% nitroglycerine.

AN–FO

The methods of making AN–FO mixtures were described in Vol. III, pp. 508–510. In the early stages of AN–FO manufacture no necessary precautions

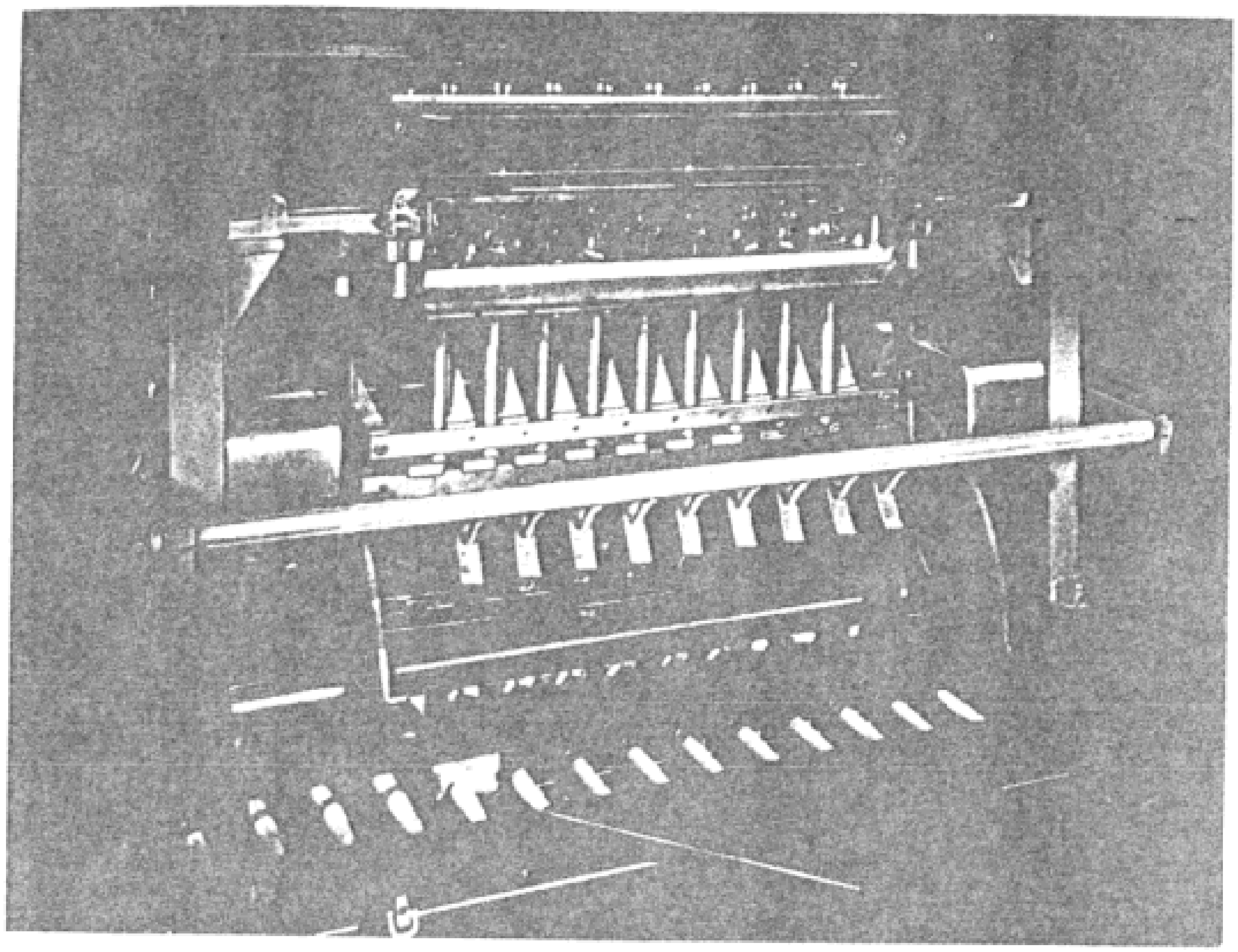

FIG. 105. Niepmann automatic filling and closing machine with 9 filling tubes (Courtesy Maschinenfabrik Fr. Niepmann G.m.b.H. and Co., D-582 Gevelsberg, FRG).

were taken AN–FO being erroneously considered to be a safe mixture. A huge accident at Norton, Virginia, U.S.A. (Vol. III, p. 508) compelled the authorities to issue instructions on the manufacture and handling of AN–FO, a detailed description of the accident can be found in the book by Biasutti [2]. The accident started when the mixture caught fire, probably from welders working in the premises. The fire was followed by several explosions which produced extensive damage. Since then AN–FO has been recognized as a conventional explosive and all regulations valid for explosives, should be applied as regards manufacture, handling, transportation and storage of AN–FO.

The methods for making and applying AN–FO for blasting have been given by Schiele [6].

Two modern methods developed by Nitro Nobel in Sweden are depicted in Figs 107 and 108. Portanol (Fig. 107) is a pneumatic ejector developed for the efficient charging of AN–FO made from ammonium nitrate prills. It is based on the ejector principle, that is, the blasting agent is sucked from the container and blown through a hose into the bore-hole.

Anol (Fig. 108) is a compressed air unit for charging AN–FO into shot-holes of 25–150 mm diameter.

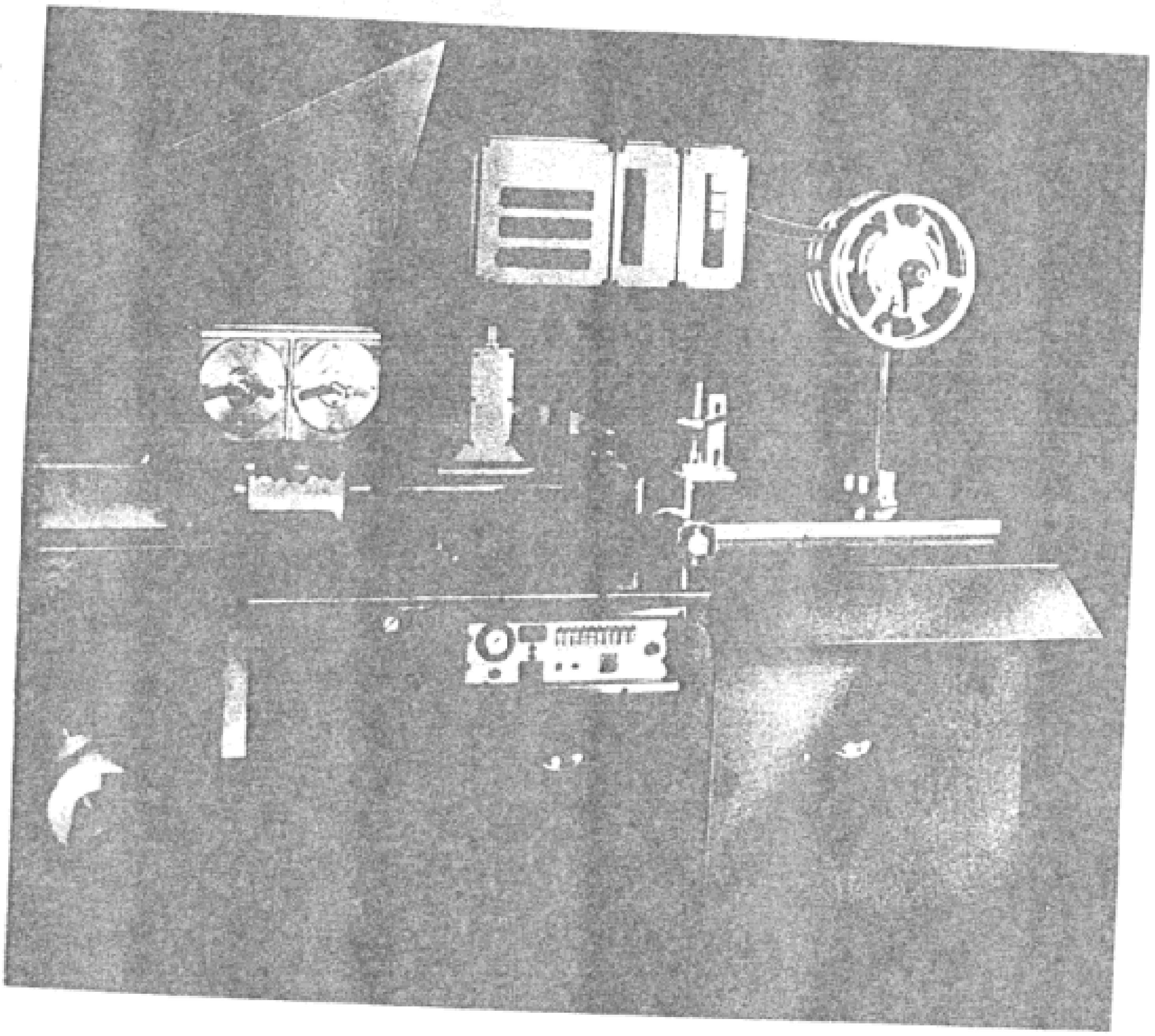

FIG. 106. Explosives packing machine for large diameter cartridges (Courtesy Maschinenfabrik Fr. Niepmann G.m.b.H. and Co., D-582 Gevelsberg, FRG).

FIG. 107. 'Portanol' ejector charger for prilled AN–FO (Courtesy Dr J. Hansson and Mr Bengt Ljung of Nitro Nobel Mec. Stockholm).

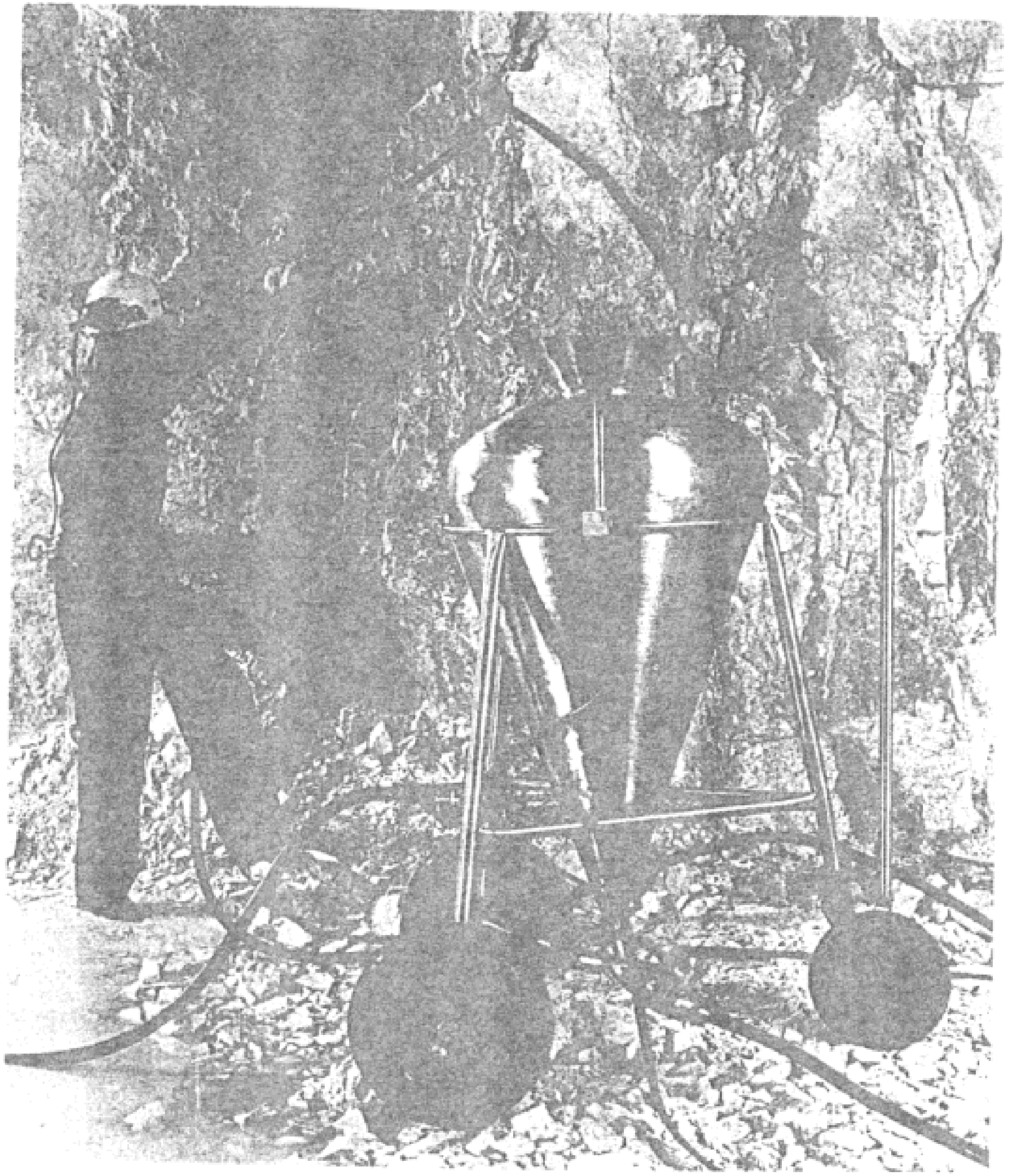

FIG. 108. 'Anol' for charging AN–FO (Courtesy Dr Jan Hansson and Mr Bengt Ljung of Nitro Nobel Mec. Stockholm)

It is important that the vital parts of the apparatus are made of stainless steel owing to the fact that AN–FO is highly corrosive. The charging hose is antistatic and electrically semi-conductive to avoid charging with static electricity.

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CHAPTER 21

LIQUID EXPLOSIVES

LIQUID OXYGEN EXPLOSIVES (OXYLIQUITS) (LOX) (Vol. III, p. 491)

Liquid oxygen explosives were widely used in Germany during World War I owing to a shortage of nitric acid and hence – aromatic nitro compounds. Shortly after World War I (Vol. III, p. 493) their use was limited. This was partly due to a number of fatal accidents, these explosives are little used today in most countries [1]. The use of LOX declined because of the introduction of AN–FO and Slurry explosives [2].

LIQUID ROCKET PROPELLANTS–PROPERGOLS (Vol. III, p. 291)

A few monographs and collective volumes have been published and should be consulted for further information on this expanding and very wide subject [3–9, 35]. The history of liquid propellants is given by Roth [7] based on the description by Malina and Truaux in a collective volume [8]. The scope of the science of Liquid Propellants is not limited to rocket propulsion but also embraces jet propulsion of engines and their design. This is outside the scope of this book. Subsequently only the information strictly connected with rocket propulsion will be given here.

Mono- and Bipropellants

a. Monopropellants are composed of substances which contain in one molecule both combustible and oxidizer moiety and possess explosive properties. Such are: nitromethane, methyl nitrate described already in Vol. I and II respectively and in Chapters VIII, X (this volume). They will not be discussed here.

b. Bipropellants are composed of two components: a fuel and a liquid oxidizer. Separately neither of them is explosive, but their mixture possesses burning and explosive properties. The liquids can be individual compounds or mixtures, and usually belong to hypergolic mixtures (Vol. III, p. 291), that is, they react spontaneously after a short induction period followed by mixing. The term 'Hypergolicity' is now in use for 'self-ignitability'. Non-hypergolic systems are not currently much in use [9].

The following were groups of compounds used as fuels: hydrocarbons, amines, hydrazines, boranes and as oxidizers: nitric acid, nitrogen oxides, hydrogen peroxide, liquid oxygen, halogens.

A few requirements are posed with regard to the stability of the components, their toxicity, ease of handling and cost of manufacture. From that point of view some ingredients originally suggested could not be accepted, such as liquid ozone which proved to be too sensitive to handle.

Cryogenic and Storable Components

Liquid hydrogen is a typical cryogenic fuel and oxygen and fluorine are cryogenic oxidizers. The latter is a more energetic oxidizing agent than oxygen and also oxidizers containing active fluorine atoms. Thus oxygen difluoride (OF_2) and chlorine trifluoride (ClF_3) (Vol. III, p. 312) are more energetic and reactive than oxygen containing oxidizers such as nitric acid, hydrogen peroxide (98%), dinitrogen tetroxide.

The energetic advantages of cryogenic fuel and oxidizers are visible from their performance in terms of specific impulse I_s as compared with storable components:

	I_s
Cryogenic	
hydrogen and fluoride	410
hydrogen and oxygen	391
Storable	
hydrazine and nitrogen tetroxide	292
methylhydrazine and chlorine trifluoride	284

Storable liquid propellants now receive greater attention than cryogenics. Storability refers to a liquid which can be kept for a long time at ambient temperature in standard containers without any significant loss of material.

The following are requirements applied to storable liquids [10]:

1. the freezing point should be sufficiently low to assure the liquid state under different climatic conditions. Also they should possess:
2. high density,
3. low vapour pressure,
4. relatively low viscosity.

They should not be excessively toxic, corrosive, reactive with air or thermally unstable. Their performance should be as high as possible and this is obviously limited to particular chemical structures. Subsequently blends were introduced for example, 50/50 hydrazine/unsym-dimethylhydrazine (UDMH), or UDMH with acetonitrile and diethylenetriamine (DETA). On UDMH see Vol. III, p. 308.

Most storable energetic oxidizers are very reactive, toxic and not very stable (e.g. ClF_3, N_2O_4, H_2O_2). The corrosive properties of nitric acid: RFNA and WFNA (85 and 97% HNO_3 respectively) are greatly removed by adding 0.5–1.0% HF thus forming IRFNA and IWFNA (inhibited acids) – as pointed out in Vol. III, p. 293 and in Chapter I of the present book. Sometimes a small proportion (*ca.* 1%) of phosphoric acid is also added.

Hypergolic Systems

The above described systems with compounds containing amino groups are hypergolic systems.

Kulkarni [11] gave a list of various compounds hypergolic with WFNA and their induction period according to [12] (Table 110).

The data for hydrazine [13] and UDMH [14] are given in Table 111.

TABLE 110.

Compound	Induction period sec.
Ethylamine	2.03
Propylamine	1.73
iso-Propylamine	0.94
sec-Butylamine	0.63
Diethylamine	0.45
Dipropylamine	0.17
Di-iso-Propylamine	0.15
Triethylamine	0.07
Tripropylamine	0.05
Ethanolamine	0.43
Ethylenediamine	0.09

TABLE 111.

Compound	Agarmond	Induction period sec	Reference
Hydrazine	RFNA	0.003	
Hydrazine	HNO_3 (98%)	0.005	[13]
UDMH	HNO_3 (98%)	0.012	[14]

Capener [9] and other sources [7, 24] give a wide list of hypergolic systems which can be summarized as follows:

Oxidizers: RFNA, WFNA, N_2O_4, N_2O_4 + NO (MON), Liquid oxygen (LOX, LO_2), Ozone, H_2O_2, Fluorine, Oxygen/Fluorine (Flox 30 and 70 with 70% of fluorine respectively), Fluorine chloride (ClF_3 – Vol. III, p. 312), Perchloric acid (Vol. III, p. 313), Perchloryl Fluoride (ClO_3F – Vol. II, p. 488, Vol. III, p. 313), Tetrafluorohydrazine (N_2F_4), Oxygen difluoride OF_2 [21–23], Bromine pentafluoride (BrF_5), Tetranitromethane (Vol. I, p. 588 and Chapter VIII, this volume).

There is currently a tendency to use oxygen fluorine and its compounds more widely.

Fuels: Diethylenetriamine (DETA), $(NH_2C_2H_4)_2NH$, Hydrazine, Monomethylhydrazine (NHM), Unsymmetrical Dimethylhydrazine (UDMH, Vol. III, p. 308), Terpenes, also non-hypergolic fuels JP-4 and JP-5 are in use.

Other composite fuels which are in use are:

MAF 1 a mixture of 50% DETA, 40% UDMH and 10% Acetonitride, MAF 3: 20% UDMH and 80% DETA, MAF 4 (Hydyne or U-DETA): 60% UDMH + 40% DETA, N_2H_4-UDMH: a mixture 50/50 of two components. Hydrodyne V: 75% hydrazine and 25% MMH, JP-X: 60% JP-4 and 40% UDMH.

Practical applications have been found for most of these compounds with some exceptions such as: liquid ozone as it is considered to be too difficult to handle, the only probable form of ozone safe enough is its mixture with oxygen (Vol. III, p. 309).

Intensive research is still being carried out to find the best oxidizer and fuel. Capener [9] gives a few examples of the most promising systems, they are collected in Tables 112–116. Roth [7] reported the most commonly used liquid propellants – Table 117.

Further information has been presented by Silverman and Constantine [24], who have described non-hypergolic mixtures of liquid oxygen with RP-1 (a hydrocarbon blend), hydrogen, ammonia, ethanol; hydrogen peroxide with hydrocarbons JP-4 and JP-5; IRFNA with JP-4. They also described hypergolic mixtures, such as: IRFNA with JP-X, UDMH, MAF-1, -3 and -4, aniline and furfurol; IWFNA with turpentine; N_2O_4 and hydrazine with UDMH, MMH, hydrazine with MMH, MON with MMH and UDMH.

TABLE 112. Propellants with RFNA
(composition: 84.6% HNO_3, 13.4% N_2O_4, 2% H_2O)

Enthalpy of formation RFNA – $\Delta H_f = 41.0$ kcal/mol
Density 1.57 at 25°C
m.p. −49°C
b.p. 66°C

Fuel	Oxidizer wt %	Specific impulse I_s max sec
B_5H_9	77	298
Hydrazine	60	278
MMH	71	278
UDMH	76	272

TABLE 113. Propellants with N_2O_4

Enthalpy of formation N_2O_4 $-\Delta H_f = 5.4$ kcal/mol
Density 1.43 at 25°C
m.p. −11.2°C
b.p. 21°C

Fuel	Oxidizer wt %	Specific Impulse I_s (max) sec
H_2	84	342
B_5H_9	77	306
Hydrazine	57	291
MMH	68.5	288
UDMH	72	286
DETA	74	278

TABLE 114. Propellants with H_2O_2 (100%)

Enthalpy of formation H_2O_2 $-\Delta H_f = 44.8$ kcal/mol
Density 1.44

Fuel	Oxidizer wt %	Specific Impulse I_s (max) sec
H_2	88	322
B_5H_9	73	316
Hydrazine	67	286
UDMH	81	283

TABLE 115. Propellants with fluorine

Enthalpy of formation of F_2 $-\Delta H_f = 3.47$ kcal/mol at −188°C
Density 1.51 at −188°C
m.p. −219.6°C
b.p. −188°C

Fuel	Oxidizer wt %	Specific Impulse I_s (max) sec
H_2	89	410
B_5H_9	82	360
Hydrazine	69	363
UDMH	71	344
NH_3	77	357

TABLE 116. Chlorine trifluoride

Enthalpy of formation of ClF_3 (liquid), $-\Delta H_f = 44.4$ kcal/mol
Density 1.81 at 25°C
m.p. −82.6°C
b.p. 11.3°C

Fuel	Oxidizer wt %	Specific Impulse I_s (max) sec
H_2	92	318
B_5H_9	88	290
Hydrazine	73	293
MMH	74	283
UDMH	75	280
DETA	75	267

TABLE 117. Most commonly used liquid propellants (according to Roth [7])

Oxidizer	Fuel	Oxidizer: Fuel ratio	Specific Impulse I_s sec
99% H_2O_2	Hydrazine	1.0	245
LOX	Ethanol	1.5	242
LOX	JP-4	2.2	248
Fluorine	NH_3	2.6	288
Fluorine	Diborane (B_2H_6)	5.0	291
Fluorine	Methanol	2.37	296
Fluorine	Hydrazine	1.98	2.98

Although considered as being storable, oxidizers such as N_2O_4 and ClF_3 are less in use owing to their low boiling points: 21° and 11°C respectively and hence difficulty in handling.

Novel Trends in Liquid Rocket Fuel

In the search for efficient hypergolic fuel various derivatives of furfuryl alcohol have been suggested [14–16]. Some of them have an induction period of the order of 0.020–0.025 sec with 98.5% nitric acid.

Among the fuels reacting with RFNA the following showed hypergolic properties: Schiff's bases [17], furfurylidene aniline and furfuramide [18], Δ^3-carene [19]. Particularly important are the findings of Panda and Kulkarni [20] who described aliphatic, alicyclic and aromatic furfurylidene ketones which are hypergolic with RFNA. The latter had the following composition: 76% HNO_3, 21% N_2O_4, 1% H_3PO_4, 0.3–0.5% HF and 1.7% H_2O.

OXIDIZERS

Oxygen Difluoride (OF_2)

As previously mentioned, oxygen fluorine and fluorine compounds are infrequently used as oxidizers. Oxygen difluoride is a particularly attractive oxidizer. It is denser than the stoichiometric mixture O_2/F_2 and consequently should give a better performance. It was first identified as a product of electrolysis of wet HF as early as 1927 [26]. A detailed description is given by Donohue, Nevitt and Zletz [21] with a yield of 45%, although a yield of 60% was also claimed [27]. Donohue *et al.* found that the yield varies with concentration.

The reaction [21] can be represented by the diagrammatic equation:

$$HF + nH_2O \longrightarrow OF_2 + O_3 + O_2 + H_2. \qquad (1)$$

According to Donohue *et al.* the conversion of HF to OF_2 is 100%.

Oxygen difluoride is a colourless gas of m.p. −224°C, b.p. −145°C [28, 25]. Its density is 1.52 at −145°C [25]. Bisbee, Hamilton, Rushworth, Houser and Gerhauser [23] determined thermochemical parameters of the compounds: the standard $-\Delta H_f^0$ was found to be 4.06 kcal/mol and of O–F bond energy −50.7 kcal/mol.

EPR spectrum of OF_2 was also examined [22].

Nitrogen Fluorides

Four nitrogen fluorides are known: NF_3, N_2F_4, N_2F_2 and N_3F, but only NF_3 and N_2F_4 [25, 29] are of real interest in rocket propulsion. They are both cryogenic with b.p. −129° and −73°C respectively. They are relatively resistant to the hydrolytic action of water. So far there is little prospect of practical use owing to the high cost and the yield of toxic decomposition products.

Multicomponent Fuel

Multicomponent systems usually contain aluminium as a component which increases the combustion energy. The stabilization of the system with an insoluble component and aluminium requires that insoluble phases (an insoluble combustible and metal) are uniformly suspended through the liquid phase. According to Beighley, Fish and Anderson [25] two methods were promising:

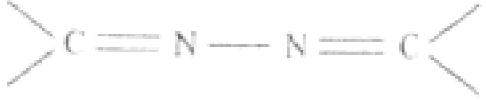
(1) by forming an emulsion,
(2) by forming a gel.

The latter method proved to be more successful. Two types of gelling agents were in use:

(a) silica and acetylenic black,
(b) natural and synthetic hydrophilic polymers.

There is an increasing demand for hydrazine as an excellent fuel. It is commercially made by the Raschig method and has been known since 1907. Its main drawback consists in yielding dilute (2%) solution. The monograph by Audrieth and Ogg (Vol. III, p. 307) is also dedicated to the problem of concentrating the solution. The problem still exists although the classical method was improved by Bayer in Germany. There are environmental problems in disposing of large quantities of by-products and a consumption of large quantities of energy.

According to the Encyclopedia [2] Usine Kuhlmann in France developed a new method which consists in a sequence of reactions: ammonia, hydrogen peroxide and carbonyl compounds (e.g. propione) react in the presence of an amide and a catalytic quantity of phosphate to form an azine intermediate:



The latter hydrolysed quantitatively to hydrazine and carbonyl compound which is recycled. A yield of 75% was claimed.

For gelling hydrazine, MMH, UDMH and their mixtures were used: natural gums, guar gum (applied extensively in slurry explosives – Chapter XIX), gum arabic, locust bean gum, alginates, gelatin, carboxymethyl- and hydroxymethyl cellulose, polyvinyl alcohol, polyvinyl pyrrolidone etc. The solid phase should be of course, compatible with the carrier fuel.

The rheological properties of such gels are of importance [10, 25].

The methods of examining the chemical and mechanical stability of propellant systems are described by Tannenbaum and Beardell [10].

POLYMERIZATION OF HYPERGOLIC FUEL

Trent and Zucrow [30] (while studying the hypergolicity of bicyclopentadiene with WFNA) advanced a hypothesis of polymerization reaction of the diene as a pre-ignition reaction. This was substantiated by Panda and Kulkarni [20, 31] through their experiments on self-ignition of several furfurylidone ketones and amines with RFNA. The same authors discovered hypergolicity of unsaturated phenols with RFNA and N_2O_4 [32]. The phenols are able to polymerize. In a series of recent papers Panda and Kulkarni [33] supported their hypothesis experimentally.

ANALYSIS

The analysis of liquid rocket propellants has been described in a monograph by Malone [34]. This is however outside the scope of the present book.

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CHAPTER 22

SMOKELESS POWDER

(Vol. III, p. 528)

Little can be added to the general description of smokeless powder given in Vol. III, although its use is wider than originally described and is not limited to firearms but is extensively used for rocket propulsion.

From the point of view of composition three kinds of smokeless powder can be described: single, double and triple-base powder.

The general characteristics of these groups of powder are summarized in Tables 118–120, according to Roth and Capener [1]. Potassium salts are added (Tables 118 and 119) as flash reducing agents. Lead salts (Table 119) are decomposition 'moderators' which play a role in producing low temperature coefficients of burning propellants and a low exponent n in the expression

$$\nu = k\,p^n,$$

where

ν – is the rate of burning
k – a coefficient
p – pressure under which the propellant is burning.

A low exponent n assures a 'plateau' burning, that is, there is little change in the rate ν with pressure (Preckel [39]).

STABILITY OF SMOKELESS POWDER (Vol. III, p. 559)

The stability of smokeless powder remains one of the major problems connected with the storage of propellants containing nitrate esters. It also forms the main subject matter of an International Symposia which has been organized in Sweden by J. Hansson for over ten years [2].

Tranchant [3] points out that three types of stability can be considered:

(a) chemical stability
(b) mechanical stability
(c) ballistic stability

However (b) and (c) depend on the chemical stability. The same author [4] suggested that the term 'Chemical Stability' should be replaced by a more pre-

TABLE 118. Typical single base powder in U.S.A. [1]

	M6	MIO	IMR	EC–NACO
Nitrocellulose (13.15%N)	87	98	100	91.4
Ethyl Centralite	–	–	–	3.8
Basic Lead Carbonate	–	–	–	1.0
Volatile (ethanol + dibuthyl ether)	–	–	–	3.8
K_2SO_4	–	1	1 (added)	–
Diphenylamine (DPA)	1 (added)	1	0.7 (added)	–
DNT	10	–	8 (coating*)	–
Dibutyl Phthalate	3	–	–	–

* See Vol. III, p. 627.

TABLE 119. Common double-base solid propellant in U.S.A. [1]

	M2	M5	M8	M21	N5	MDM
Nitrocellulose (13.25%)	77.45	81.95	52.15	53.0	50.0	48.6 (12.6% N)
Nitroglycerine	19.50	15.00	43.00	31.0	34.9	27.0
KNO_3	2.15	2.15	1.25	–	–	–
Ethyl Centralite	0.6	0.6	0.6	2.0	–	1.1
Graphite	0.3	0.3	–	–	–	–
Triacetin	–	–	–	11.0	–	18.7
Lead Salicylate	–	–	–	2.5	–	–
Lead Stearate	–	–	–	0.5	–	4.6
Carbon Black	–	–	–	0.03 (added)	–	–
Diethyl Phthalate	–	–	3.0	–	10.5	–
2-Nitrodiphenylamine	–	–	–	–	2.0	–
Lead Salts*	–	–	–	–	2.4	–
Candelilla Wax	–	–	–	–	0.2	–

* Composition undisclosed.

TABLE 120. Triple-base propellants in U.S.A. [1]

	M15	M17	M31
Nitrocellulose (13.15%)	20.0	22.0	20.0
Nitroglycerine	19.0	21.5	19.0
Nitroguanidine	54.7	54.7	54.7
Ethyl Centralite	6.0	1.5	
Sodium Aluminium Fluoride	0.3	0.3	0.3
Dibutyl Phthalate	–	–	4.5
2-Nitrodiphenylamine	–	–	1.5

TABLE 121. French smokeless powders [38]

Name	Composition		Calorimetric value cal/g	Gas volume cm^3/g	Force *f*
Poudre B épaisse	Nitrocellulose 12.8% N Diphenylamine	98 2	909	925	10 500
Poudre SD épaisse	Nitrocellulose 11.7% N Nitroglycerine Centralite	66 25 9	762	1012	9 800
Balistite CI	Nitrocellulose 12.5% N Nitroglycerine Centralite (to add)	58 42 1	1243	833	12 200

cise expression 'Measure of chemical evaluation of propellants'. However the term 'Chemical Stability' will be used for short.

The stability of smokeless powder depends on many factors, not only on the purity of the used nitrate esters, or the presence of a stabilizer, but also on the web thickness of powder grains (Vol. III, p. 55).

Currently the stability tests are directed towards the determination of changes of the stabilizers present in the propellant. The most important methods currently used to evaluate the change of the stabilizer are chromatographic methods.

The pioneering work of Schroeder (Vol. III, p. 563) and [5, 6] should be mentioned.

With the progress of chromatography techniques various methods were used, such as thin-layer chromatography (TLC) which started in 1962 by Hansson and Alm [7] followed by other papers [8, 9] including those on high velocity chromatography [10, 11].

Current research on stability and changes of stabilizers are published in volumes of Symposia [2].

Thus thin layer chromatography (TLC) was extensively used by Volk [12]. TLC and liquid chromatography by Ammann and co-workers [13], gas-chromatography (GC), TLC and high pressure chromatography (HPLC) by Ammann [14]. HPLC was in use by Lebert, Stephen and Zeller [15], Brook, Kelso, Neil and MacLeod [16], Lindblom [17], Sopranetti and Reich [18], Volk [19]. Gas chromatography was used by Sopranetti and Reich [20]. To obtain different retention times for derivatives of diphenylamine, they *N*-acylated the products with heptafluorobutyric anhydride and obtained a high resolution.

Microcalorimetry was also tried as a method of determining the beginning of decomposition of propellants [21–26]. It should be recalled that the first experiments on measuring the heat evolved during the decomposition of nitrocellulose powder were carried out by W. Świętosławski, T. Urbański and co-workers [27] (Vol. III, p. 552, 556).

Brook *et al.* [16] summarized the widely-used stability tests in Table 122 (see also Vol. III, p. 558).

TABLE 122. Most common stability tests [16]

Test	Temperature °C	Time of Test	
Abel Heat	65.5	10–30 min	KI starch paper
Methyl Violet	120	40 min	Methyl Violet paper
Dutch	105	72 hrs	Decomposition monitored by weight loss of sample
Surveillance	80	150 hrs	Brown fumes
Small Vessel	100	5 days	Decomposition by weight loss of sample
NATO	65.5	60 days	Loss in stabilizer determined spectroscopically
Woolwich	80	3 weeks	Loss in stabilizer determined by gas–liquid chromatography

In France and U.S.S.R. the stability test of Vieille is widely used. It consists in heating the samples at 110° or 106.5°C in the presence of litmus paper for a minimum of 70 hours (Vol. III, p. 558).

As pointed out in Vol. III quantitative methods such as Bergmann and Junk, pH measurement of heated samples, Taliani (Vol. II, pp. 26–28) are rarely used for control in magazines.

Volk [12] reported the results of his examination of the products of the changes in diphenylamine (DPA) and ethylcentralite during the storage of single and double base propellants respectively at temperatures between 60 and 95°C until the moment that NO_2 appears (a temperature 65.5°C for 60 days has been approved by NATO [3, 16]). According to Volk the nitrogen dioxide was evolved after more than 800 days.

He established the presence of 28 derivatives of DPA as follows:

> 2-nitro-, *N*-nitroso-, *N*,4-dinitroso-, *N*-nitroso-4-nitro-, 3-nitro-, 2,6-dinitro-, 2,4-dinitro-, *N*-nitroso-2,4-dinitro, 2,2-dinitro-, 2,4,6-trinitro-, 2,4′-dinitro-, *N*-nitroso-2-nitro-, *N*-nitroso-4,4′-dinitro-, 4-nitroso-2-nitro-, 4-nitro, 2,2′-4, 4′-tetranitroso-, *N*-nitroso-2,4′-dinitro-, *N*-nitroso-2,2′-dinitro-, 2,2,4-trinitro-, *N*-nitroso-2,2′,4-trinitro-, *N*-nitroso-2,4,4′-trinitro-, 2,4,4′-trinitro-, 2,4,4′,6-tetranitro-, 2,2′,4,4′-tetranitro-, 2,2′,4,4′,6-pentanitro, 4-nitroso-, 4,4′-dinitro-, 2,2′,4,4′,6,6′-hexanitro-diphenylamine, and picric acid.

Similar results were obtained by Brook *et al.* [16].

Ethylcentralite gave 24 products as follows:

> Nitro-, 1,3-dinitro-, 1,3,5-trinitro-benzene; ethyl-, 2-nitroethyl-, 4-nitroethyl-, 2,4-dinitroethyl-, 2,4,6-trinitroethyl-, *N*-2,4,6-tetranitroethyl-, *N*-nitroso-ethyl-, *N*-nitroso-2-nitroethyl-, *N*-nitroso-4-nitroethyl-aniline; 2-nitro-, 4-nitro-, 2,4-dinitro-, 4,4-dinitro-2,2,4,4-tetranitro-ethylcentralit; 4-nitro-, 2,4-dinitro-, 2,6-dinitro-phenol and picric acid.

It is important to note which compounds were formed in single and double base powders during long storage at normal storage temperature.

In 1976 Ammann [14] examined nitrocellulose powder manufactured in 1927 and found derivatives of diphenylamine as follows by TLC: 2-nitro, 2,2′-, 2,4-, 4,4′-dinitro-, 2,2′,4-, 2,4,4′-trinitro and tetranitrodiphenylamine. Also trace quantities of *N*-nitroso-4-nitro and *N*-nitroso-4,4′-dinitrodiphenylamine were detected.

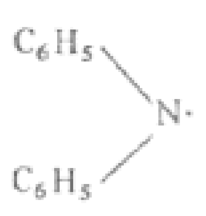
In a 15-year old single base powder Brook *et al.* [16] found 0.77% DPA, 0.23% *N*-nitroso-DPA, 0.02% 2-nitro and 0.04% 4-nitrodiphenylamine. Similar products in much the same quantities were found in nitrocellulose powder subjected to heating at 105°C (Dutch Test) for *ca.* 24 hours and at 65.5°C (NATO Test) for *ca.* 24 days.

FREE RADICALS IN THE CHANGE OF DIPHENYLAMINE

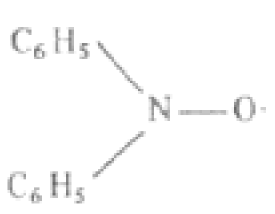
A new and original approach has been given by Mrzewiński [28] to the problem of the change of diphenylamine in single-base powder. He applied ESR technique to follow the transformation of the stabilizer and came to the conclusion that the charge–transfer phenomenon occurs in the first instance at room temperature between nitrocellulose (acceptor) and diphenylamine (donor) in agreement with the finding of T. Urbański *et al.* [29] that nitrate esters give charge–transfer with amines.

The ESR signal was recorded in nitrocellulose powder at room temperature. The intensity of the signal increased at 106.5°C (Vieille test) and reached a maximum after 20 hours.

According to Mrzewiński [30] this was due to the formation of a free radical of diphenylamine (I) a transient free radical of diphenylamine *N*-oxide (II). Free radical I is known to the literature [31]. It yielded *N*-nitrosodiphenylamine (which, as is known possesses stabilizing properties), *N*-nitrosonitro-, dinitro- and higher nitrated diphenylamines. According to Mrzewiński free radical I is



I



II

the active species of the formation of nitroso and nitro derivatives of diphenylamine when single base powder is heated. Short lived free radical II also participated in the formation of nitro compounds, but its role is much less pronounced.

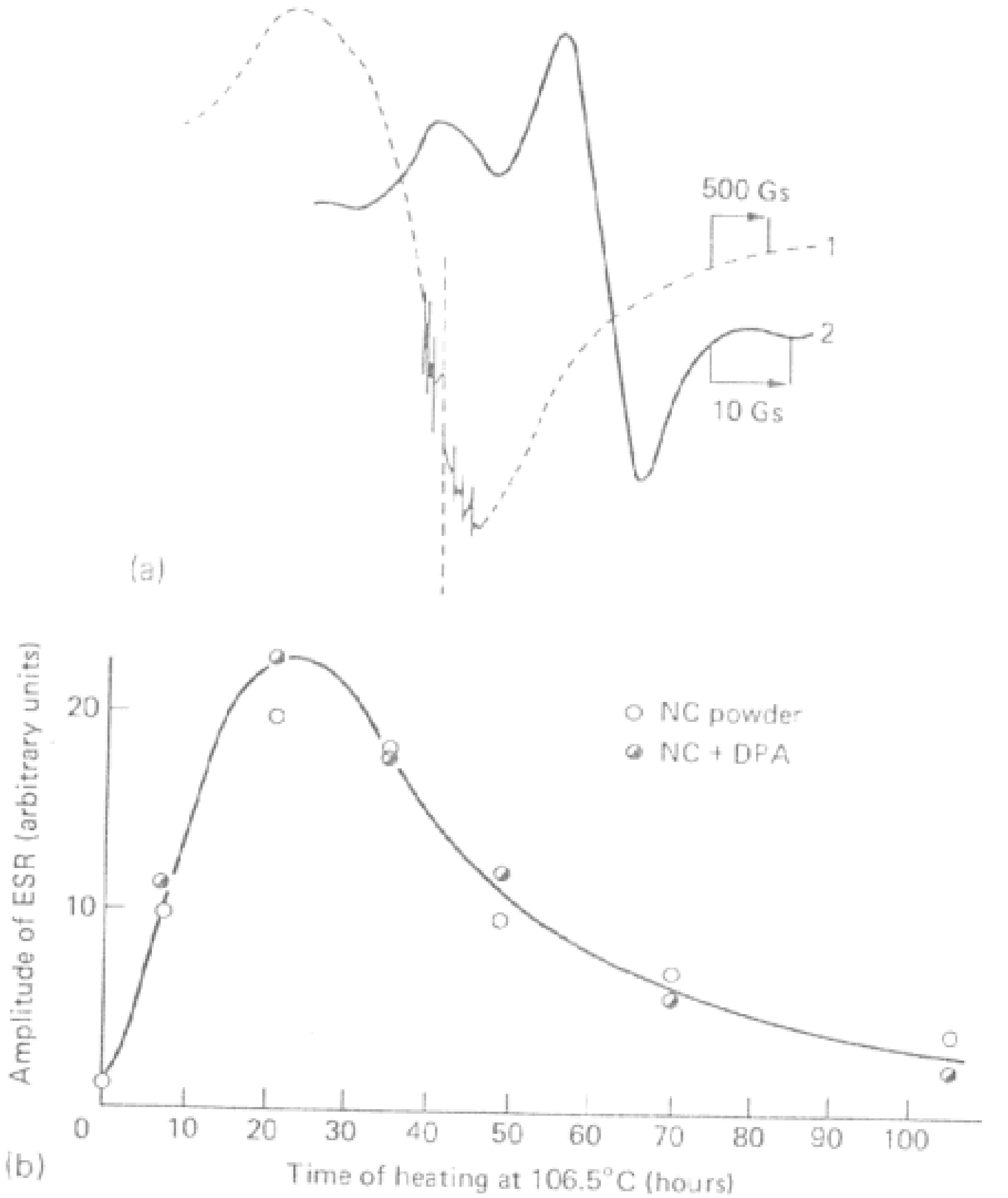


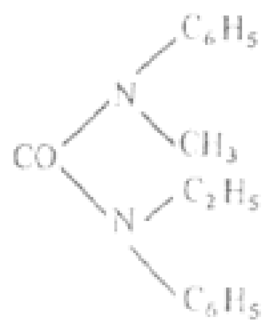
FIG. 109 (a) ESR signal in single-base propellant. 1 – broad line of metal impurities (Mn, Ni, Fe in quantity of *ca.* 10^{-4}%), 2 – narrow line of radical species [28, 30]. (b) Intensity of ESR signal against time (hours) of heating single base powder and Nitrocellulose with Diphenylamine at 106.5°C, according to Mrzewiński [28, 30].

STABILIZERS

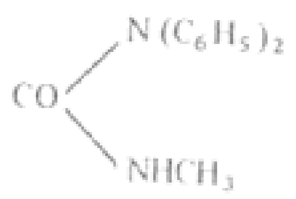
It is well known that diphenylamine (DPA) is too basic as a stabilizer of nitroglycerine and DEGDN (diethylene glycol dinitrate) containing powder. To reduce the basicity of DPA, 2-nitrodiphenylamine (2-NDPA) was introduced into propellants, particularly double base powders, as a successful stabilizer.

A similar action shows *p*-nitro-*N*-methylaniline (*p*NMA).

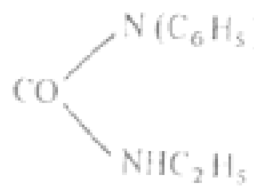
Centralites I and II (Vol. III, p. 645), Centralite III were successful as both stabilizers and 'non-volatile solvents' of nitrocellulose along with urethanes which seem now to be less used. Unsymmetrically substituted urea: unsym-diphenylurea (Vol. III, p. 645) named Acardite I is currently employed as also are its homologues–diphenylmethyl and diphenylethyl urea: Acardite II and Acardite III respectively.



Centralite III
m.p. 60.5°C



Acardite II
m.p. 171°C

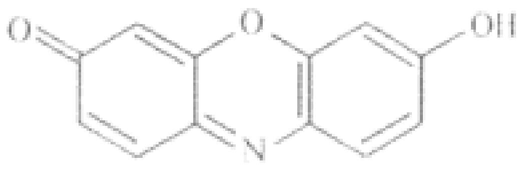


Acardite III
m.p. 73°C

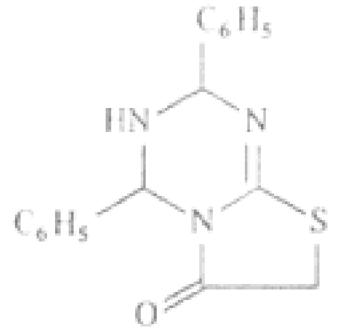
More recently a use has been found for resorcinol as a stabilizer. It readily reacts with nitrogen dioxide to yield nitroso- and nitroresorcinol which can further react with resorcinol molecules yielding various heterocyclics among them resorufin.

The action of this stabilizer was extensively discussed by Blay [32] and Volk [33].

Soliman [42] recently suggested a new stabilizer for double base propellants. This is 5,6,7-trihydro-5,7-diphenyl-thiazolo-[3,2-b]-*s*-triazin-3(2H)-one (III)



Resorufin



III

It gave good results when incorporated, in proportion of 3%, into a double base powder containing, 56% nitrocellulose (12.0% N), 27% nitroglycerine, 9% dinitrotoluene, 4% dibutylphthalate and 1% mineral oil.

When the propellant was kept for 12 days at 100°C, compound III was transformed in mononitro- and dinitrophenyl derivatives of III.

The substance was found to be unsuitable for stabilizing simple base powder due to its insolubility in etier or ether–ethanol.

Volk [33] also described the stabilizing action of a number of compounds. Some lead-salts such as lead salicylate and stearate appear to possess good 'moderating' properties, that is, moderating the decomposition process. As mentioned previously lead salts improve the ballistic properties of propellants lowering the temperature coefficient of burning propellants and helping a 'plateau' burning.

Kinetics of Decomposition

The kinetics of decomposition of single base powder have been studied by Mayet and Lucotte [34]. They found the activation energy $E = 27.5$–36.3 kcal/mol for the temperature range 80–100°C.

The kinetics of decomposition have also been examined by Mrzewiński [28] who rationalized it on the basis of the change of diphenylamine. He came to the conclusion that free radical II does not play a role in the kinetics of the decomposition of powder.

Electric Susceptibility of Single Base Powder

Mrzewiński [28] examined the electric susceptibility of a single base powder to detect whether decomposition of nitrocellulose and changes of diphenylamine of ionic character. First the change of dielectric constant with temperature was examined. It showed a trend presented in Fig. 110, typical for dielectric polymers. There is an abrupt increase of the dielectric constant with the increase of temperature around −12°C. The change in the dielectric constant with the age of the powder is given in Fig. 111. A similar trend was observed with laboratory ageing of powder at 106.5°C: there is a slight fall of the dielectric constant with a minimum after *ca.* 24 hours of keeping at this temperature. This is probably connected with the change of rational movements of fragments of functional groups.

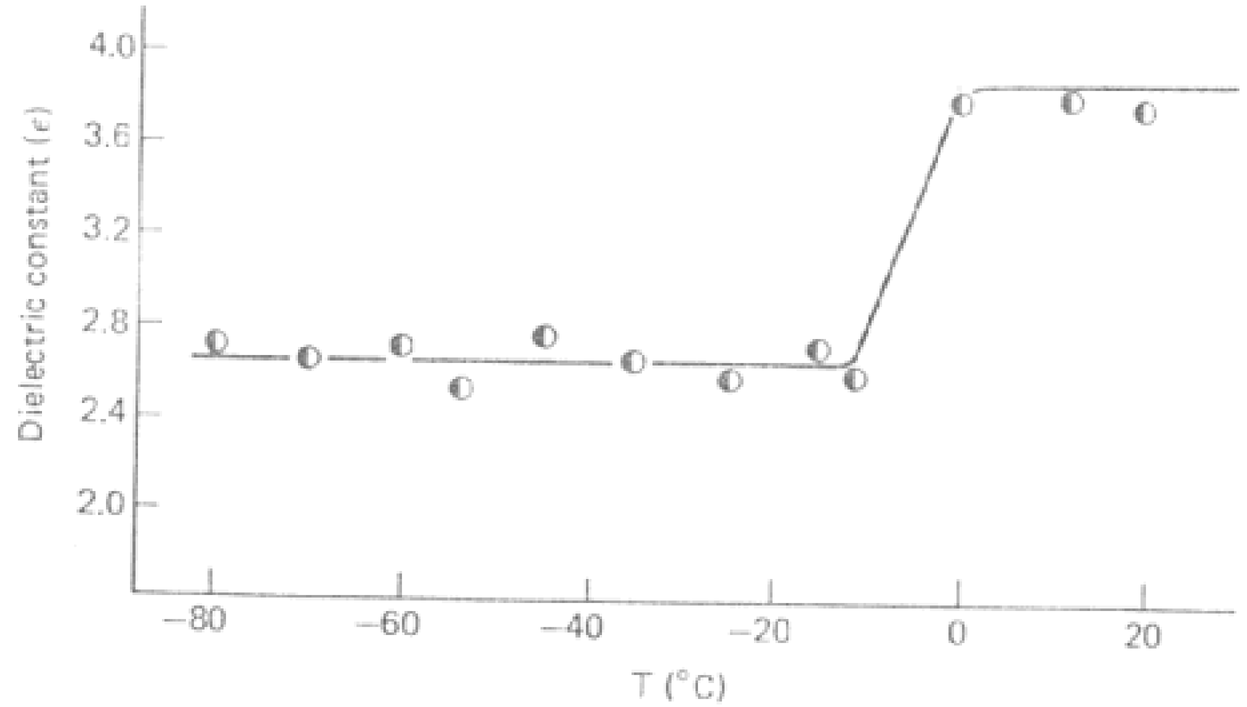


FIG. 110. Dielectric constant of single-base powder against temperature, according to Mrzewiński [28].

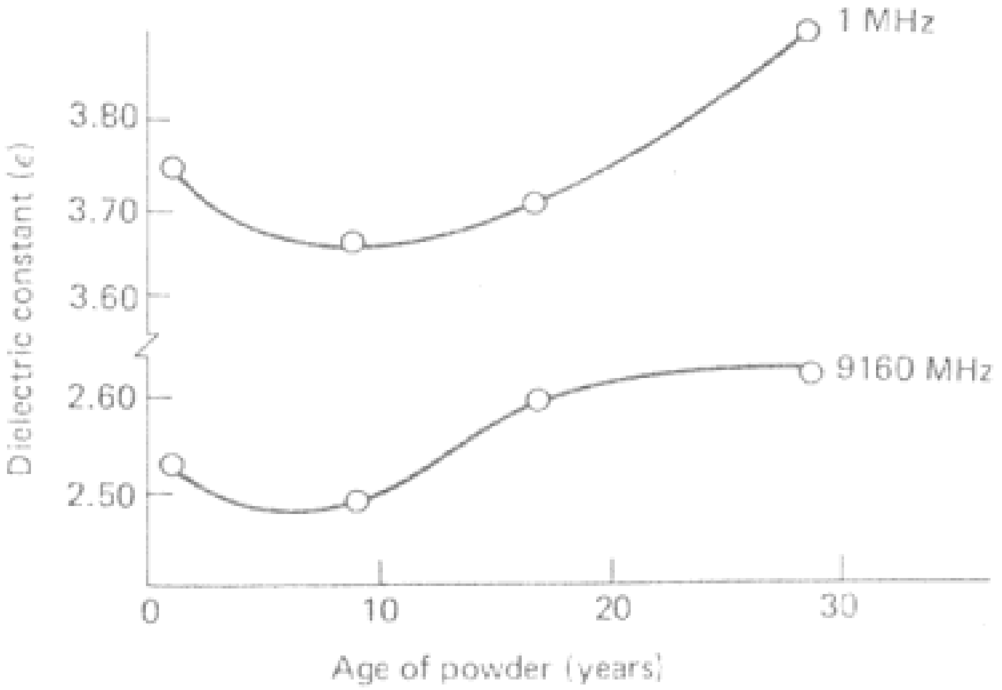


FIG. 111. Change of dielectric constant of single-base powder with the age of powder (Mrzewiński [28]).

Erosiveness of Smokeless Powder (Vol. III, 531, 548)

Lowering of the erosiveness of smokeless powder can be achieved by lowering its calorific value. Such is nitroguanidine containing powder (Vol. III, Tables 187, 191). Recently the addition of titanium dioxide and silicon dioxide were suggested as erosion reducing agents [47].

MANUFACTURE OF POWDER

Single Base Powder

Very little can be added to the description in Vol. III, pp. 571–641 and pp. 663–664 on the methods of manufacture of single base propellants.

On the other hand great progress can be seen in the manufacture of double base powder, particularly for rocket propulsion.

Double Base Powder (Vol. III, p. 641)

A few monographic descriptions exist, such as that by Sarner [35], collective volume [36], Encyclopedia [1] and [37], Tavernier [38].

Traditional Double Base Powder

Little can be added to the description of the manufacture of traditional double base powder of the ballistite type (Vol. III, pp. 647–651) where hot rolling is the essential operation for manufacture (Vol. III, Figs 259, 260). Hot rolling is also the central part of the manufacture of solventless powder (Vol. III, p. 654) prior to pressing. Hot rolling in the Kemira factory (Finland) is depicted in Fig. 112.

FIG. 112. Hot rolling of double-base powder in Kemira factory (Courtesy of Kemira OY, Vihtavuori, Finland).

Rocket Double Base Powder

Monographs [36, 37] and Encyclopedia [1] are mainly dedicated to double base rocket propellants. One of the trends of making large 'grains' of rocket propellant charges consists in making charges by casting. The principles of the methods were given in Vol. III, pp. 675–682.

During World War II the Germans used TNT/nitrocellulose cast propellant (Vol. III, p. 681). A similar propellant was developed by T. Urbański [41] in Great Britain during World War II. It was composed of TNT, low viscosity nitrocellulose, potassium nitrate and aluminium.

As previously mentioned (Vol. III, p. 675) two methods of making cast propellants charges are known:

(1) Cast propellant,
(2) Slurry cast propellant.

CAST PROPELLANTS

Some information based on the description by Steinberger and Drechsel [40] is given here. They give the composition of single base, double base and composite cast propellants in Table 123.

TABLE 123. Cast propellants composition [40]

Ingredients	Single Base		Double Base		Composite propellant	
	Casting powder	Finished propellant	Casting powder	Finished propellant	Casting powder	Finished propellant
Nitrocellulose	88	59	75	50.2	30	22.3
Nitroglycerine	—	—	17	44	10	32.8
Plasticizer	5	36				
Lead salts (e.g. lead stearate)*	5	3.4	6	4	—	—
NH_4ClO_4	—	—	—	—	28	20.8
Al	—	—	—	—	29	21.6
Stabilizer	2	1.6	2	1.8	3	2.5

* 'Ballistic Additives'.

Method of Manufacture

Casting powder is composed of small cylinders of *ca.* 1 mm diameter and length. The manufacture of casting powder consists in the operations as follows typical for smokeless powder [40]:

1. Mixing in the presence of solvents (alcohol/ether),
2. Extrusion by cutting the threads,
3. Drying to remove the volatile solvent at 60°C,
4. Finishing by polishing and covering with graphite, screening.

Propellant manufacture from casting powder and solvent consists of the following steps:

1. Filling a mould with casting powder, to occupy *ca.* 68% of the volume,
2. Evacuation by reducing the pressure below 10 mmHg,
3. Casting to fill the interstitial space with casting solvent – a mixture of nitrocellulose and plasticizers (Vol. III, p. 677, Fig. 270).

The casting solvent may be introduced from the top, from the bottom or radically from perforated cores.

Some types of casting powder are best cast *in vacuo*, and some under atmospheric pressure.

4. Curing under pressure: the solvent is introduced under pressure *ca.* 4 kg/cm^2 and a pressure of *ca.* 14 kg/cm^2 with a piston is applied on the solid (Fig. 113).

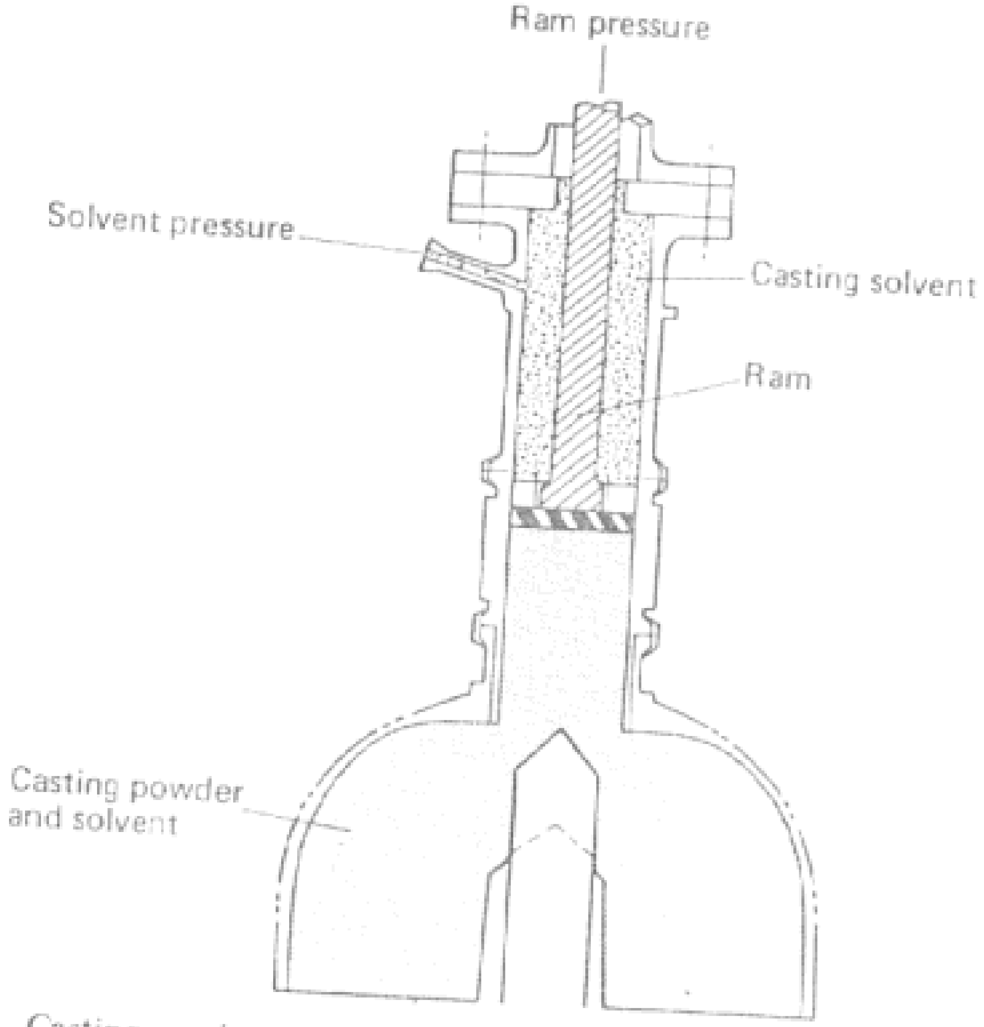


FIG. 113. Casting, curing and applying ram and solvent pressure of double-base rocket propellant [40].

Finished propellant grain has different shapes assuring the best ballistic performance – Fig. 114, according to Steinberger and Drechsel [40]. (See also Fig. 130 in Chapter XXIII).

There is however a problem of the migration of nitroglycerine into the lining which is an inhibitor of combustion. It is usually made of polyesters (Vol. III, p. 677, Fig. 270 and Fig. 115 this volume). Caire-Maurisier and Tranchant [43] examined modifications of the composition of lining and came to the conclusion that by introducing electron accepting groups into the composition of the lining migration could be inhibited. The electron accepting groups would repell the electron acceptor which is nitroglycerine. Practically all polymers were effective in containing chlorine, for example, polymers with units of octochlorodiphenyl. On the migration of nitroglycerine in ballistite propellants – see also Vol. III, p. 651.

SLURRY-CAST PROPELLANTS (PLASTISOL PROPELLANTS) (Vol. III, p. 677)

A new description of slurry-cast propellants ('Plastisol Propellants') has been given by Camp [44]. Fine particle spheroidal nitrocellulose is the base of the slurry-cast propellant. Olin Mathieson ball powders of various sizes (Vol. III, pp. 632–639) form a good basis for slurry cast propellants. They have been known and used for this purpose since 1947. A novel method of producing spherical nitrocellulose with an average particle size of *ca.* 10 μ was developed in 1959 by Naval Ordnance research units. The method consists in complete solution of nitrocellulose in nitromethane and dispersion in water with the aid of a colloid mill and an emulsifying agent.

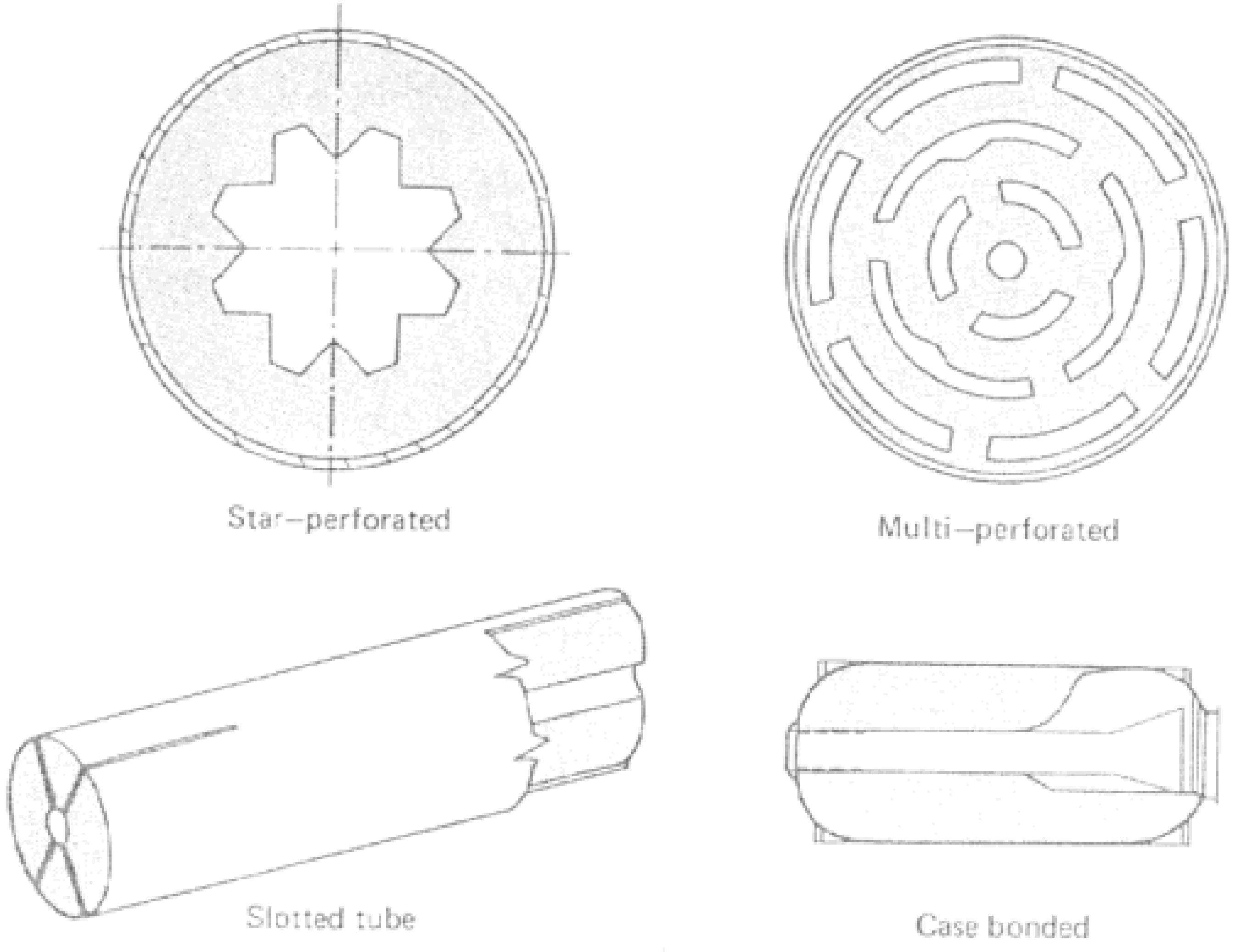


FIG. 114. Cast grains of rocket propellants. Cellulose acetate inhibitor is shown on the periphery of grains [40].

A typical composition of the propellant is as follows [45]:

Spheroidal nitrocellulose (12.2 or 12.6% N)	5–20%
Nitrate esters (nitroglycerine, DEGDN etc.)	25–40%
Desensitizing plasticizers (e.g. dibutyl phthalate)	0–10%
Stabilizers (centralite or 2-nitrodiphenylamine)	0.5–2.0%
Oxidizers (NH_4ClO_4, RDX)	40–50%
Metallic fuel (Al, Be)	0–20%

Mixing is carried out in air-powered or jet in inert liquids or in planetary mixers.

Spheroidal nitrocellulose is first dispersed in a solution of plasticizers and stabilizers followed by adding metal powder (if used) and oxidizers. The temperature of mixing is maintained below 30°C to avoid an excessive gelatinization and an increase of viscosity. After forming the charge it is cured at 40–60°C for a few days. Rubber lining with a cross-linked adhesive system was used to protect the outer surface of the charge.

SCREW-EXTRUSION PROCESS

The worm screw extrusion process (Vol. III, p. 659) is a new and original method for the production of double base powder developed in Germany at Dynamit Nobel A.G. A detailed description appeared recently [46]. The main part of the apparatus is a twin screw extrusion apparatus with two shafts rotating in the same direction – see the monograph by Janssen [46] – Fig. 115.

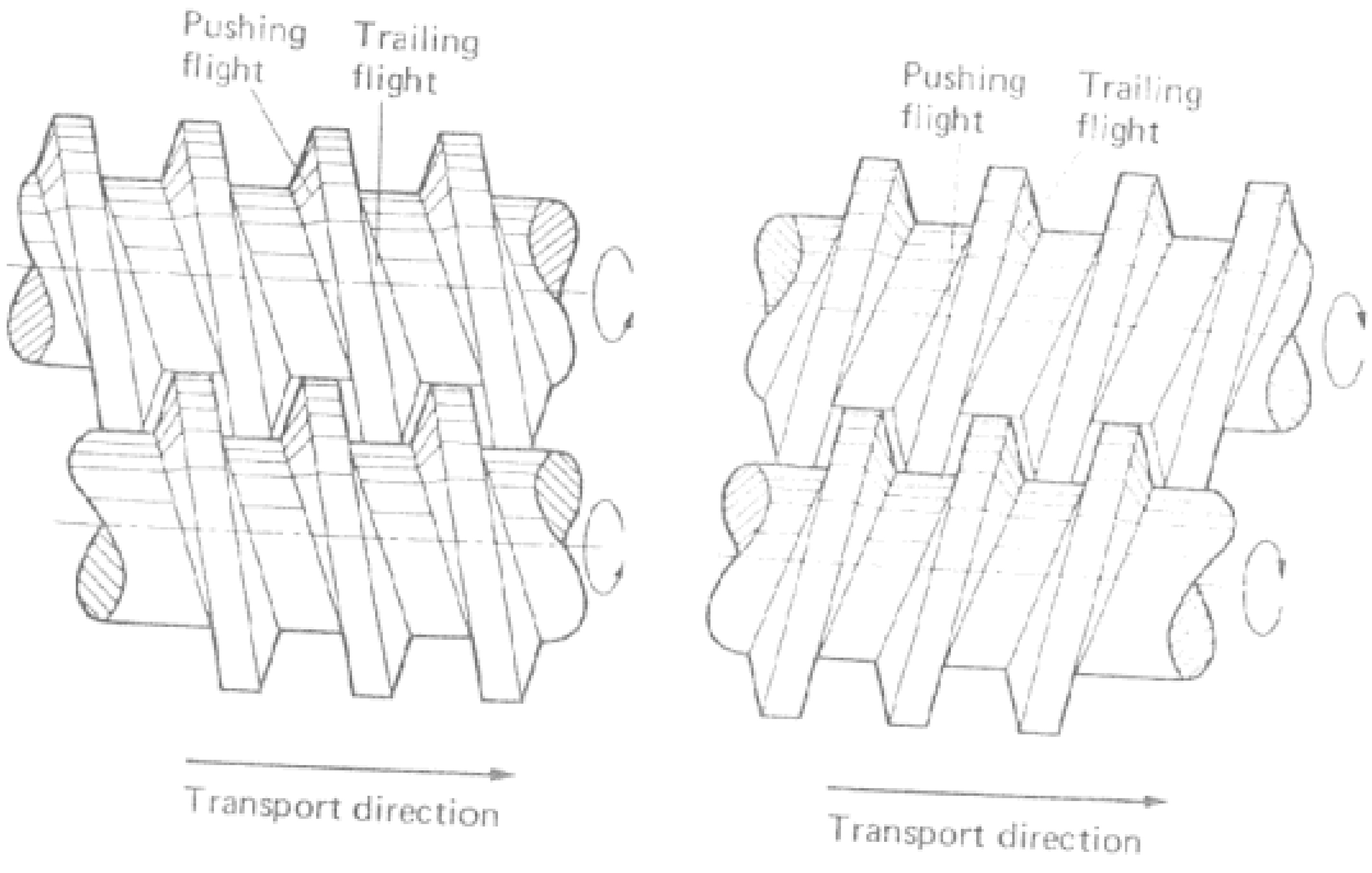


FIG. 115. Twin extrusion, according to Janssen [46].

This is a perfection of the original single screw extrusion apparatus (Vol. III, p. 658, Fig. 266).

The paper by Homburg and Brachert [45] describes the steps as follows:

(1) Mixing of ingredients under water,
(2) Dehydration to 15–20% water and gelatinizing the propellant charge by kneading,

(3) Granulation of the kneaded material for further dehydration and gelatinization in the granulating plant (I),
(4) Blending of the granulate,
(5) Second granulation in granulation plant (II),
(6) Drying the granulate in the drying plant,
(7) Shaping of the pellets into the raw grain, in the extrusion plant.

Kneading is a double-disc screw, that is, an eccentric disc mounted on two shafts rotating in the same direction, the screws are water cooled. Feeding of kneader is continuous. The water is thus separated from the material.

Granulation consists of steps: granulation (I) of lumpy material which returns to the mixing unit and back to granulation and to a twin-screw extruder.

Granulate I passes to the blending unit and then to granulation unit II. The material is dried and shaped in the extrusion plant with a twin-screw extrusion extruder with two shafts rotating in the same direction.

The propellant is plasticized in the twin-screw extruder and the final shape is eventually given.

The propellant is composed of nitrocellulose, nitroglycerine, plasticizer and stabilizers. The method is used to make tubes or cigarette burning cylinders.

The advantage of the described process is in it being continuous, with minimum personnel at a remote control.

Figure 117 shows a roller conveyer of the finished tubular product [45].

Bofors Nobel Chematur [48] have recently described a novel method of making a double-base powder as depicted in Fig. 118. Nitrocellulose, nitroglycerine and additives (e.g. centralite and a solvent) is to pelletize the powder paste, this is done in batches. All the ingredients are charged in the form of a slurry together with a solvent, to a pelletizer (1). The slurry is heated and the solvent makes the nitrocellulose fibres stick together in pellets of about 1 mm size. The heating continues until all the solvent is driven off and recovered. The upper and lower parts of the pelletizer are shown in Figs 119 and 120 respectively. The slurry in the pelletizer is cooled and pumped to a storage tank (2), where the pellets are settled in water. The water in that tank is used for the next pellet batch.

The pelletized material is transported as a water suspension to a screw extruder (3). The extruder drains the pellets, kneads them to a homogeneous material and extrudes through a slotted tube of propellant. The slotted tube is cut into granules (Fig. 121) by a rotating knife and stored under water in another storage tank (4). When enough material has been produced the granulate is agitated to form a uniform mixture and transferred to the second tank (5).

In an extrusion the granulate of the second storage tank is transformed into the finishing propellant by the same type of extruder as in the first extrusion step. The propellant tubes, single or multiperforated are extruded through the dies (60 directly into flowing water which transports them to a cutter. They are

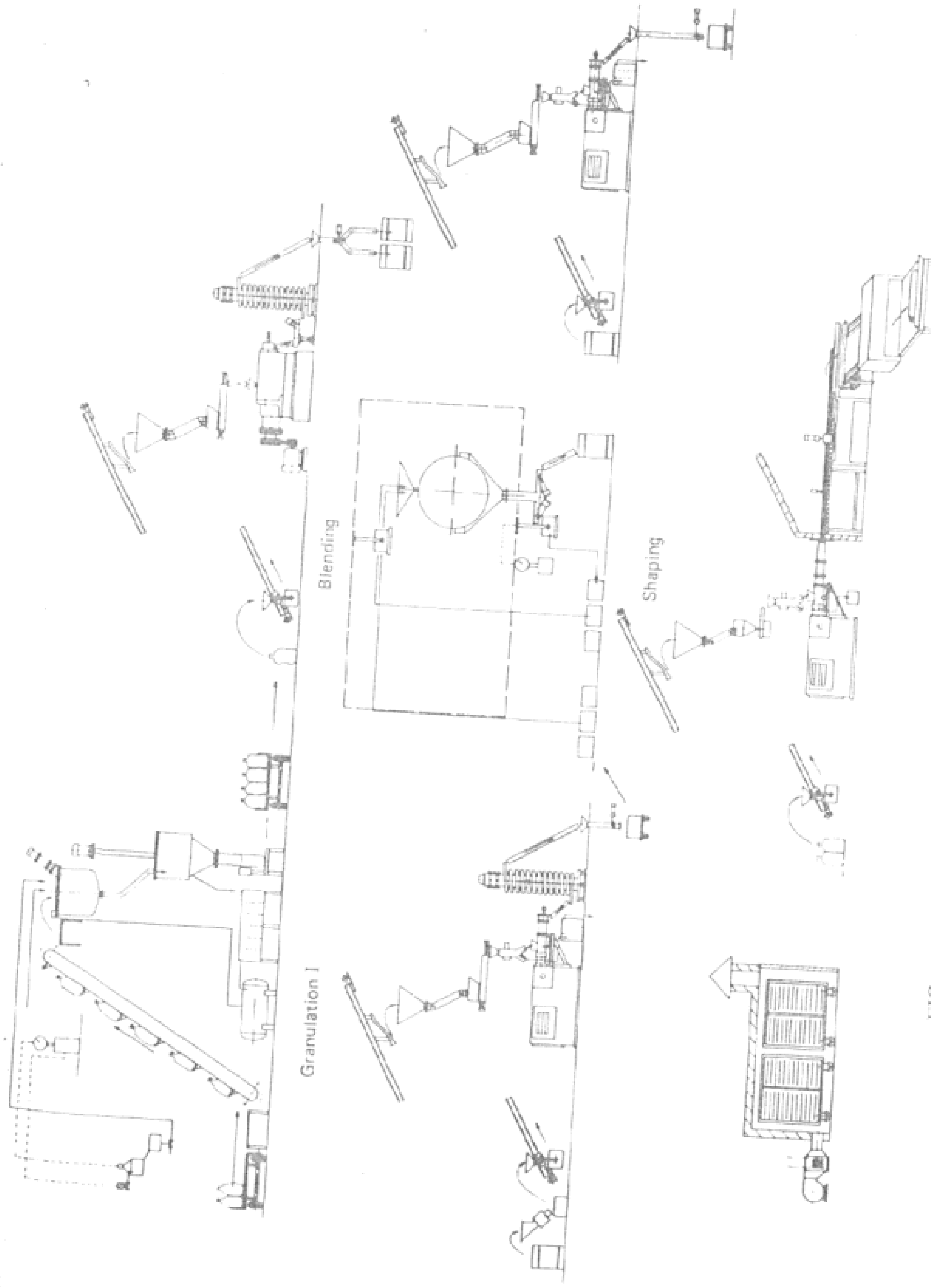


FIG. 116. Twin extrusion process of manufacturing double-base rocket propellants, according to Homburg and Brachert [45].

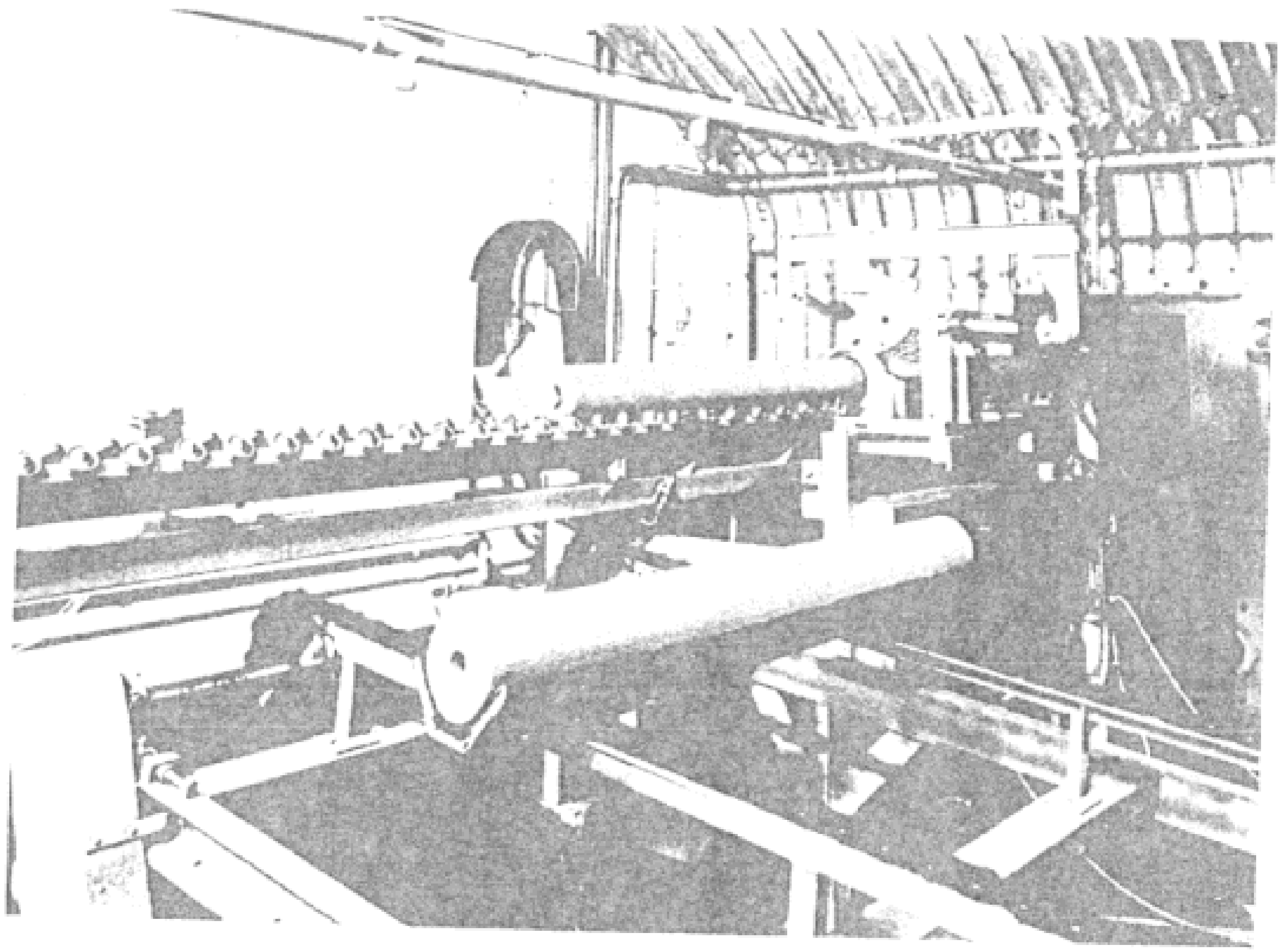


FIG. 117. Roller conveyer of finished tubular product Courtesy Dynamit Nobel A.G., D-5000 Köln (Dellbrück).

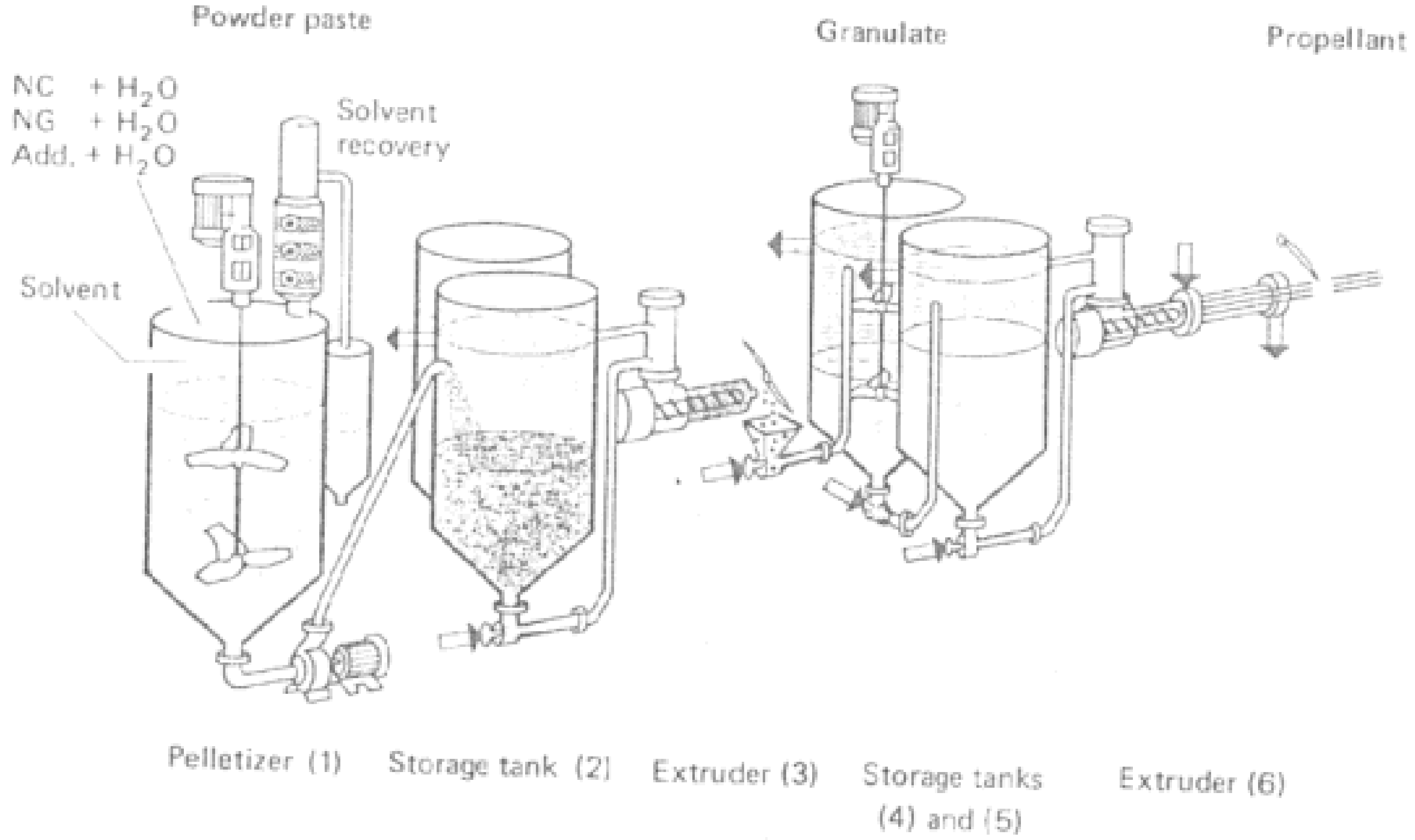


FIG. 118. Novel method of making a double-base powder of Bofors Nobel Chematur.

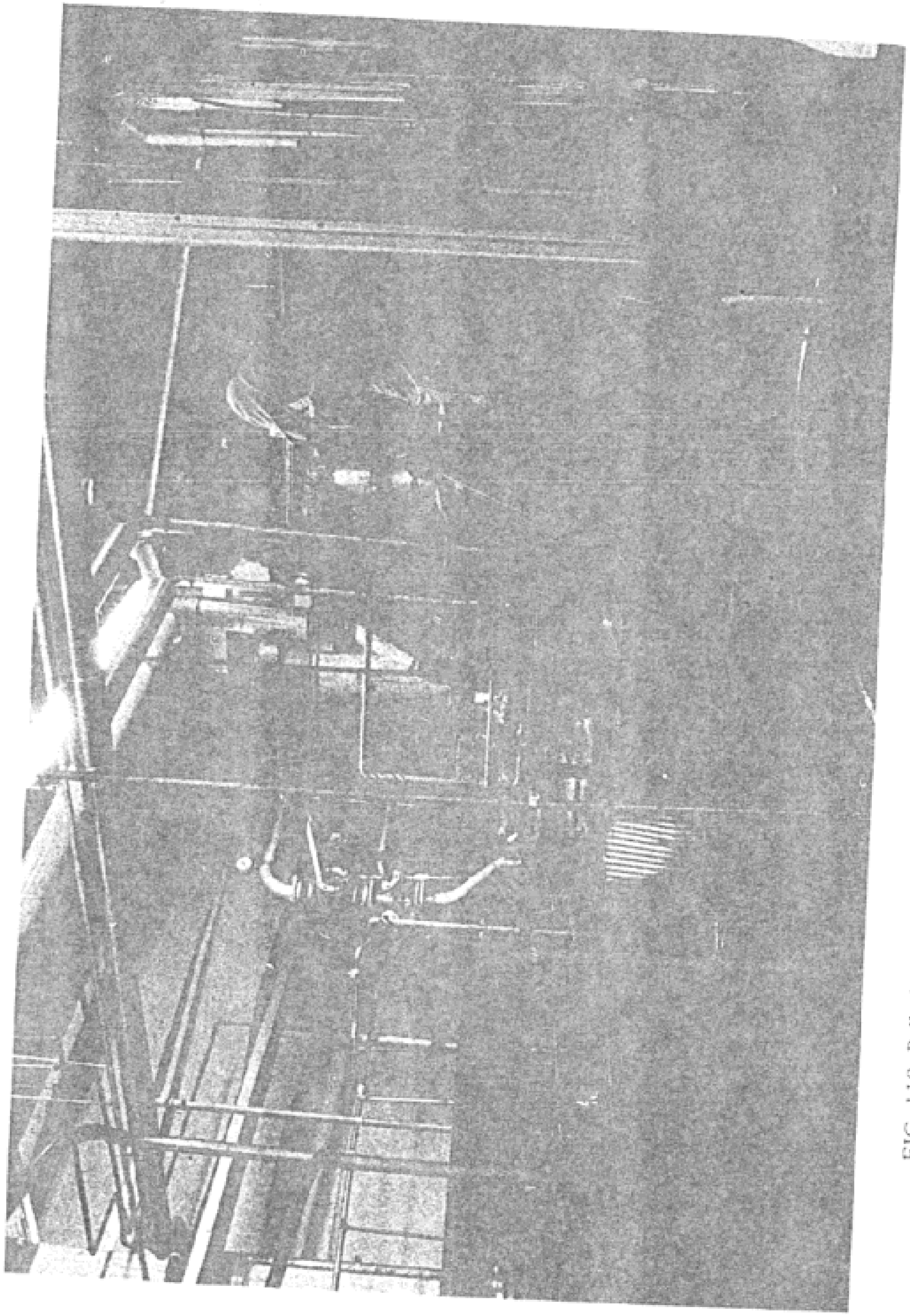


FIG. 119. Pelletizer of a double-base powder, upper part (courtesy Bofors Nobel Chematur).

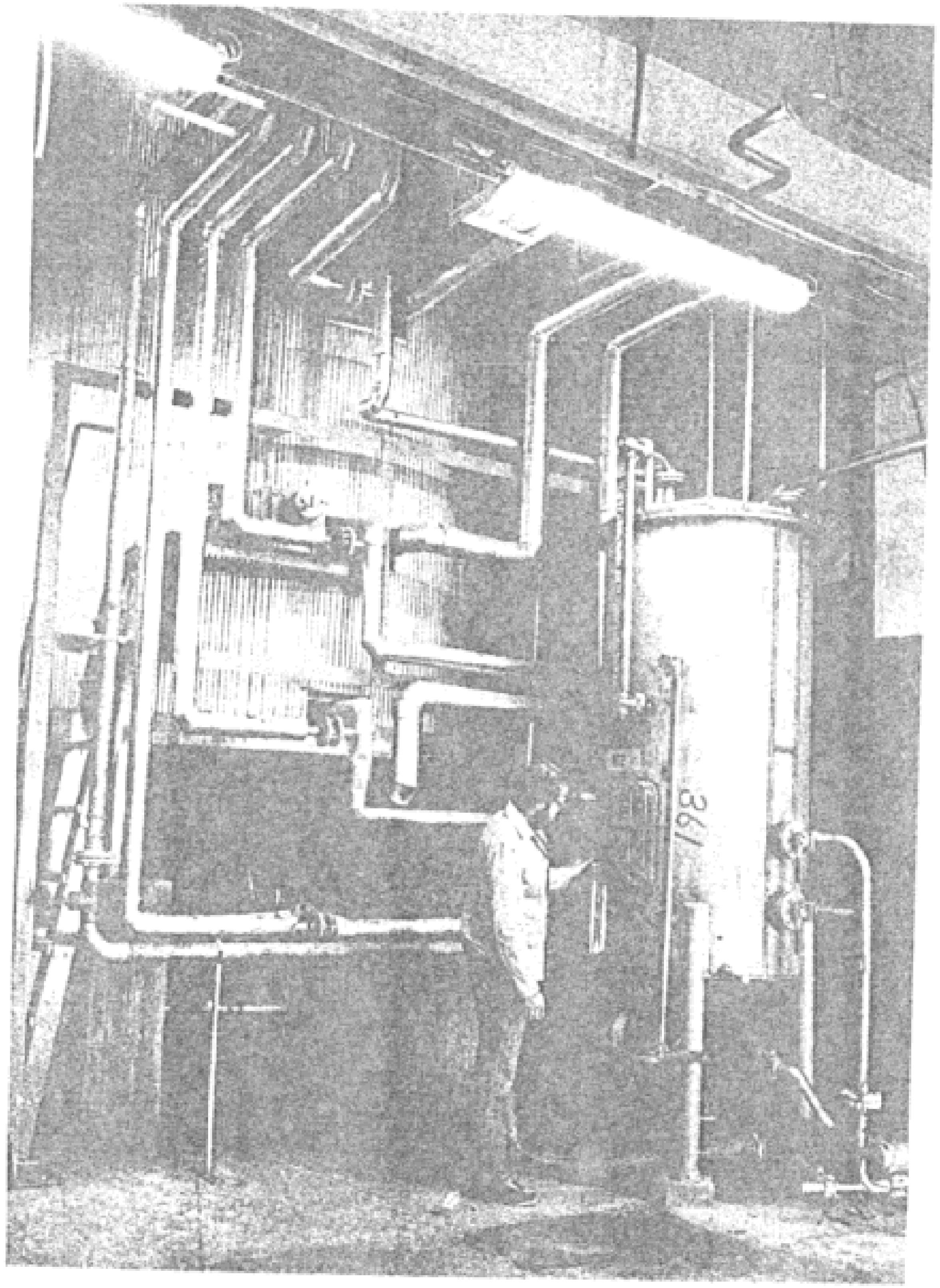


FIG. 120. Pelletizer of a double-base powder lower part (courtesy Bofors Nobel Chematur).

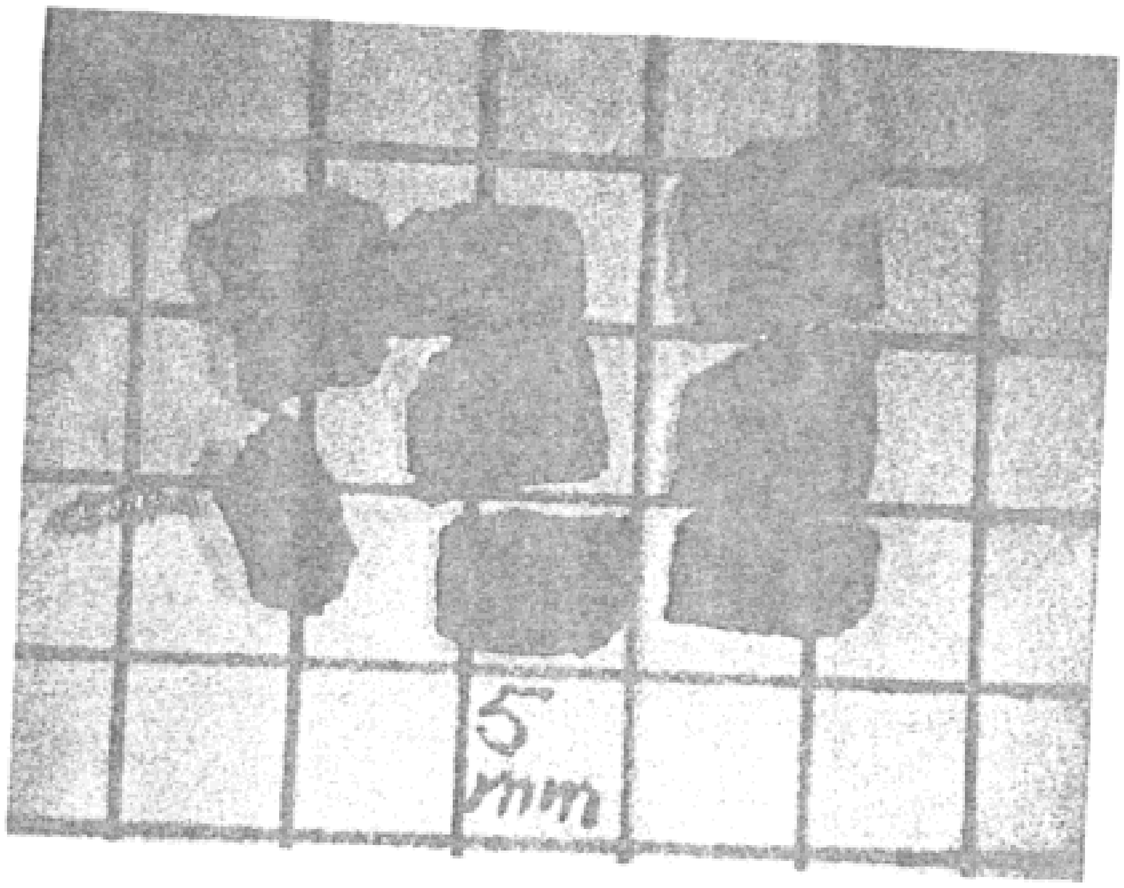


FIG. 121. Granules of a double base powder (courtesy Bofors Nobel Chematur).

cooled by water which reduces the evaporation of nitroglycerine from the cut propellants.

The propellant with a low water content constitutes a risk of explosion if ignited. For that reason the extruders are placed in a separate room. Figure 122 gives a view from inside the room for final extrusion and Fig. 123 – the cutters. The mean production is 50 kg/hr per extruder.

The factory of Bofors has experienced a few explosions caused by ignition in the extruders. The ignition was by a foreign object produced in the extruded material. The remote control operation gives a higher safety level. This new method reduces the manual work and the exposure to nitroglycerine and increases the safety of the manufacture.

Classical Extrusion Method

The modernized classical extrusion method of double base powder by means of a heated hydraulic press Werner and Pfleiderer is shown in Fig. 124.

HIGHER ENERGY SMOKELESS PROPELLANTS (Vol. III, p. 670)

The attempts to increase the energy of smokeless powder by adding a considerable amount of PETN did not pass beyond large-scale experiments. Also the use of polymers containing nitro groups (Chapter XIV) does not seem to have a practical application for propellants.

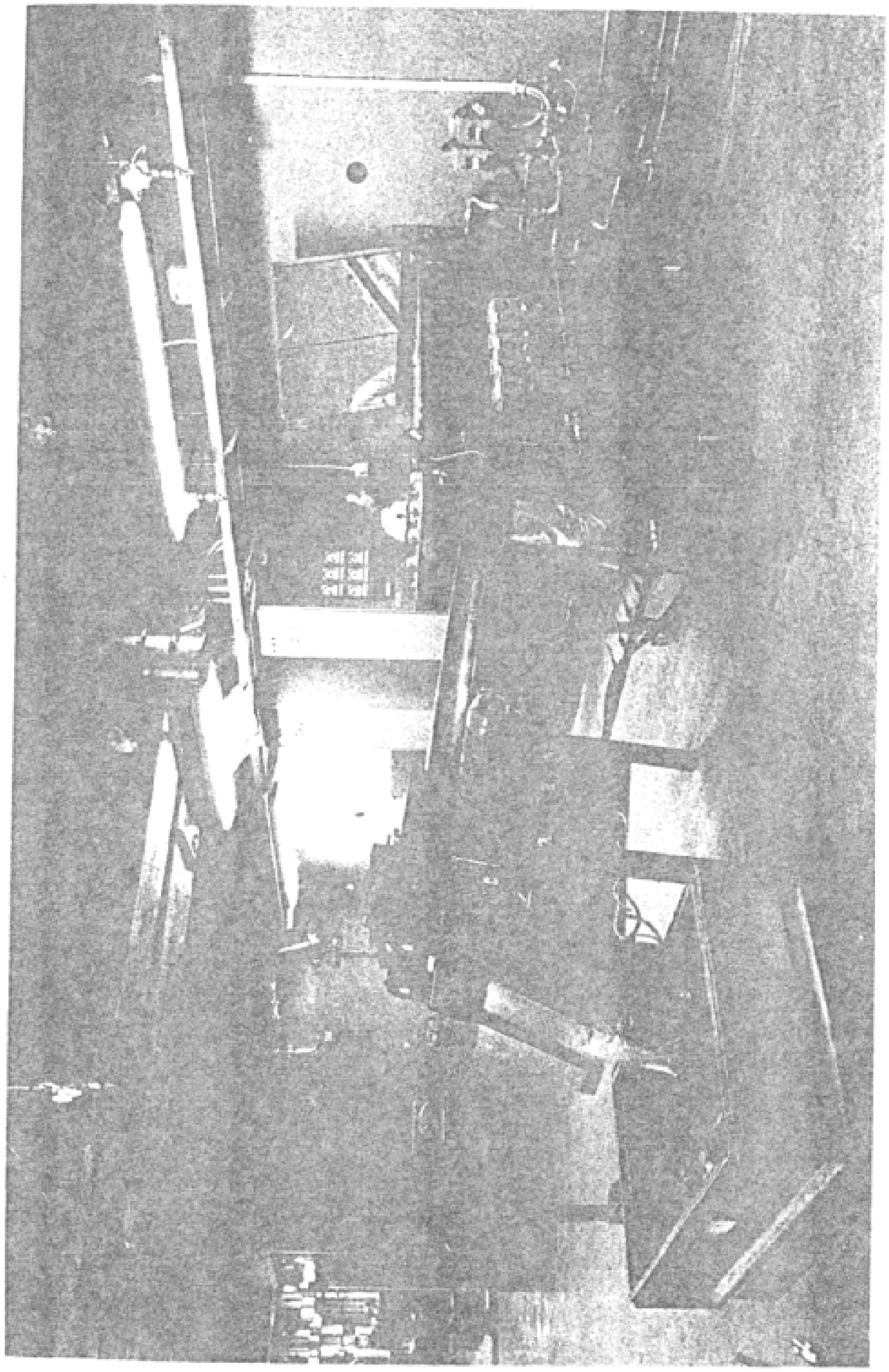


FIG. 122. The room for final extrusion of a double base powder (courtesy Bofors Nobel Chematur).

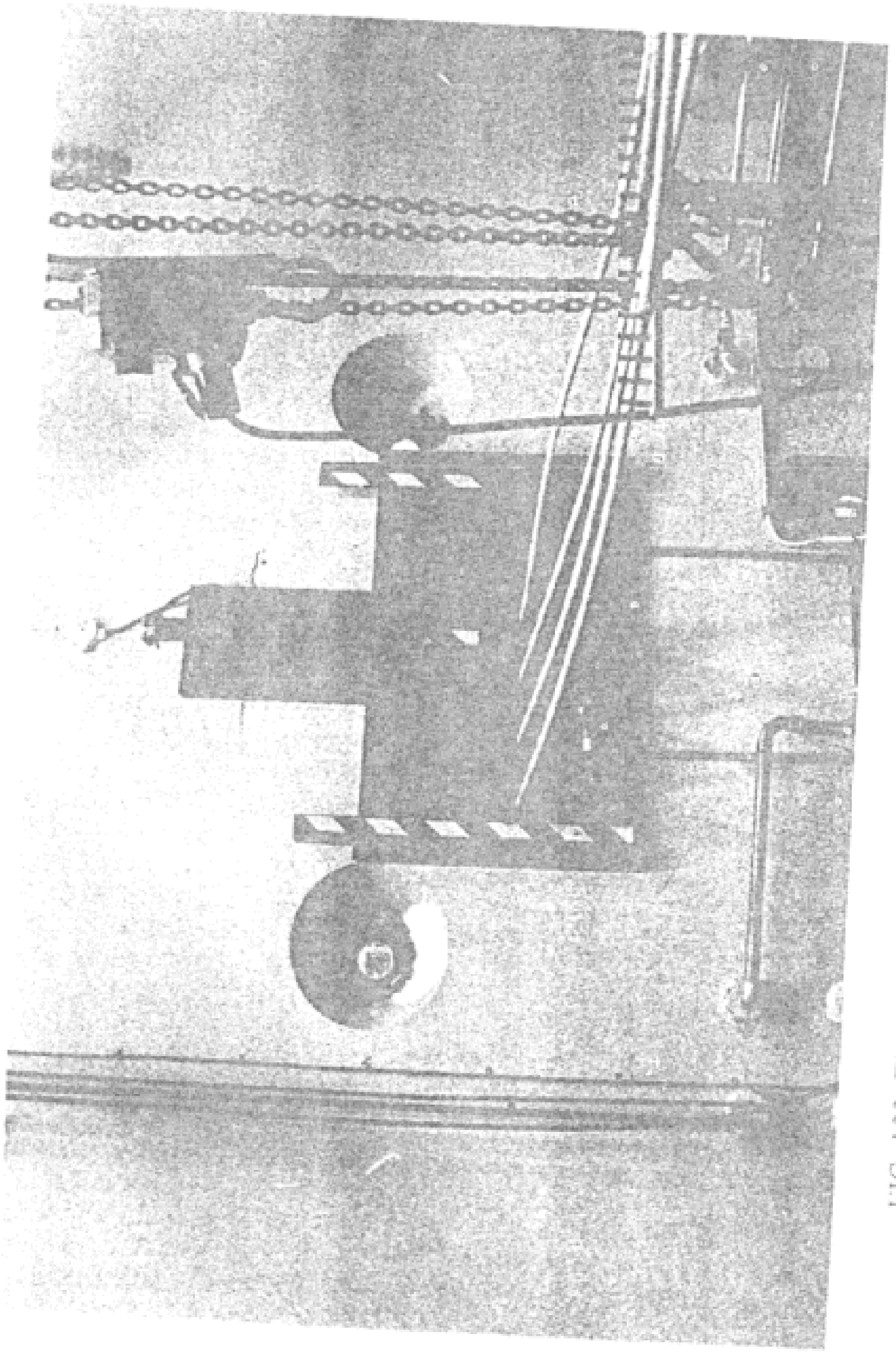


FIG. 123. The cutters of a double base powder (courtesy Bofors Nobel Chematur).

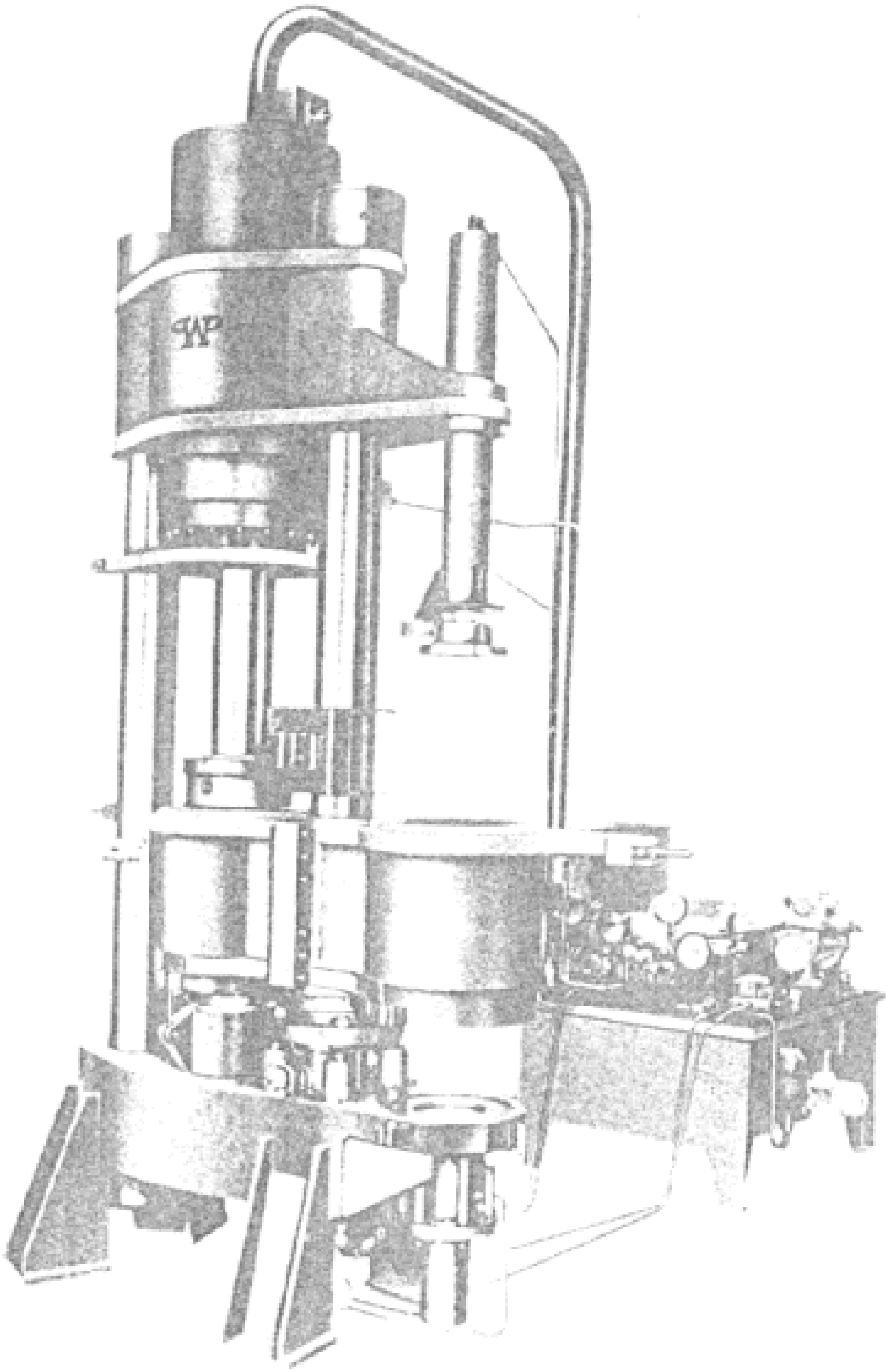


FIG. 124. Modernized classical heated extrusion press for double-base powder (Courtesy Werner & Pfleiderer, D-7000 Stuttgart, FRG).

Nevertheless there are continuing attempts to introduce such compounds as RDX and HMX into smokeless powder. Thus Sumi and Kubota [49] described double base powder containing up to 27% HMX. The propellant was characterised by a low exponent n even at low pressure: $n = 0.3$ at 20 atm.

The addition of RDX or HMX into composite propellants is also known – see Chapter XXIII.

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CHAPTER 23

COMPOSITE PROPELLANTS

(Vol. III, p. 365)

INTRODUCTION

Roth and Capener [1] formulate composite propellants as follows:

'Composite propellants which are used almost entirely in rocket propulsion normally contain a solid phase oxidizer combined with a polymeric fuel binder with a $-CH_2-CH_2-$structure. Practically speaking ammonium perchlorate is the only oxidizer which has achieved high volume production, although ammonium nitrate (AN) has limited special uses such as in gas generators. Other oxidizers which have been studied more or less as curiosities include hydrazinium nitrate, nitronium perchlorate, lithium perchlorate, lithium nitrate, potassium perchlorate and others. Among binders, the most used are: polyurethanes, polybutadiene/acrylonitrile/acrylic acid termopolymers and hydroxy-terminated polybutadienes.'

According to recent information [2], the space shuttle's orbiter *Columbia* was powered by two solid rocket motors with a propellant which consists of:

ca. 70% Ammonium Perchlorate (AP),
16% Al powder,
12% polybutadiene–acrylic acid–acrylonitrile (PBAN) termopolymer (a combustible binder),
2% liquid epoxy resin (a curing agent), and in addition
0.17% iron oxide powder (as a catalyst).

Each rocket motor is loaded with more than one million pounds (*ca.* 454,000 kg) of solid propellants.

The problems of Composite Propellants is a fast developing branch of propellants chemistry and technology. The following are monographs (in addition to those mentioned in Vol. III) dedicated to composite propellants: [3–8, 27]. The Encyclopedia of Kaye [1] and collective volume [6] are particularly important sources of information.

A vast amount of work is being done and continuing progress now merits a special modern monograph. Only the principles of the formulation of composite propellants and their manufacture will be given here. The description will

be based on different polymeric binders mainly with ammonium perchlorate. Some data on the thermal decomposition of ammonium perchlorate will be given here to complete the information in Chapter XVI.

An important feature of ammonium perchlorate propellants is their decomposition at high temperature. Differential thermal analysis of NH_4ClO_4 is given in Fig. 125, according to Sarner [4]. It can be seen that appreciable decomposition occurs at temperatures lower than the main exotherm.

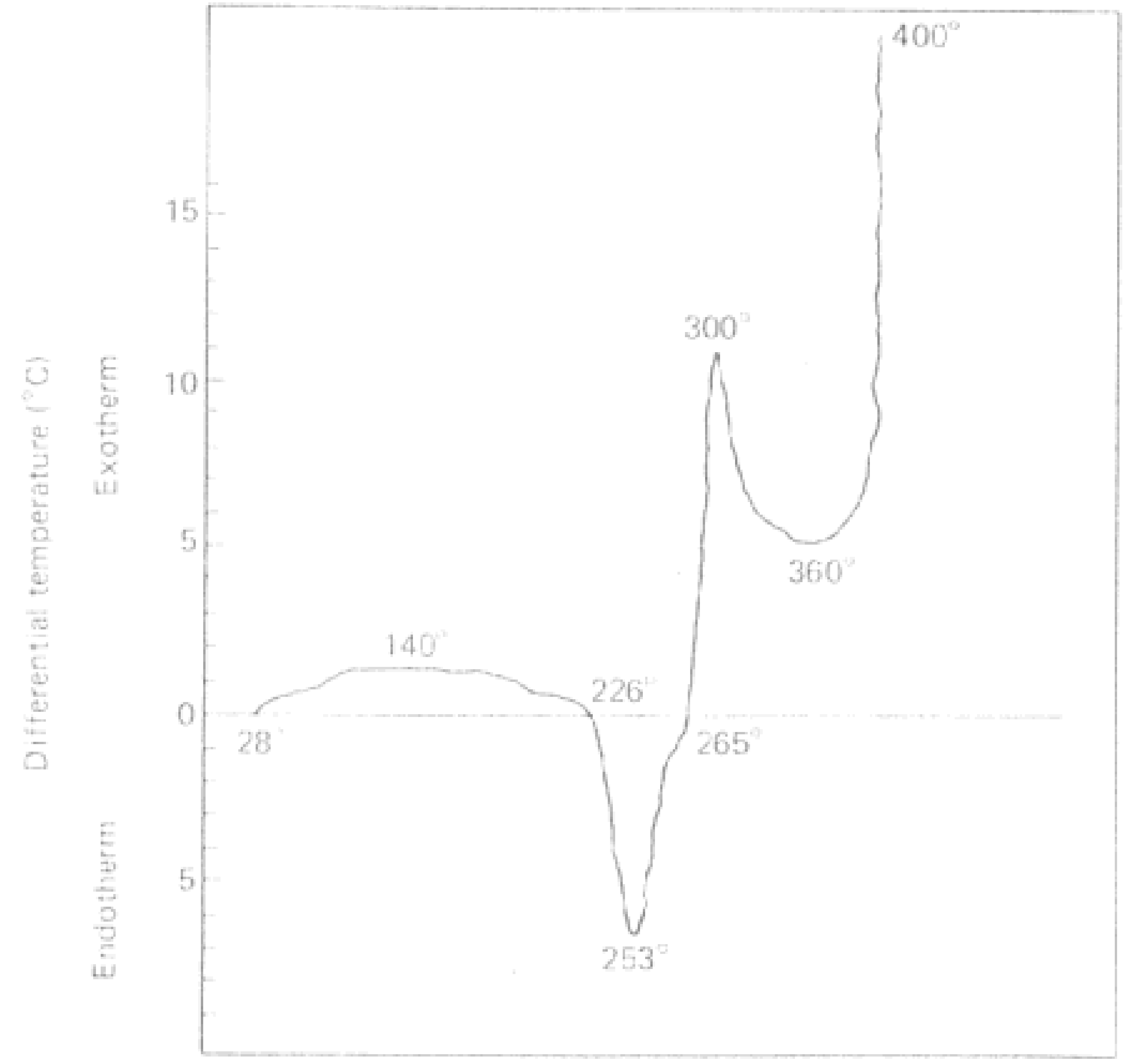


FIG. 125. Differential thermal analysis of NH_4ClO_4 from Propellant Chemistry by Stanley Sarner [4]. Copyright © 1966 by Van Nostrand Reinhold Company. Reprinted by permission of the publisher.

The ammonium perchlorate crystal size is of great importance.

Baldwin and Reed [24] give figures for the rate of burning of ammonium perchlorate composite propellant depending on the size of crystals of the salt as:

Particle size of NH_4ClO_4	Rate of burning cm/sec
75 μ	5.1
35 μ	6.1
15 μ	7.6
5 μ	9.2

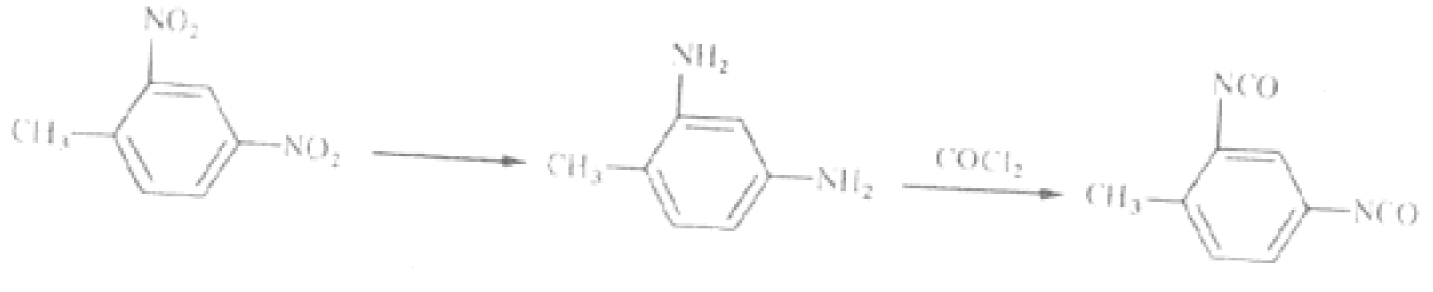
POLYURETHANE BINDERS

As is known, urethanes are formed by reacting isocyanates with hydroxyl carrying compounds:

$$\mathrm{RNCO + R'\,OH \longrightarrow R\,NHCOOR'.} \qquad (1)$$

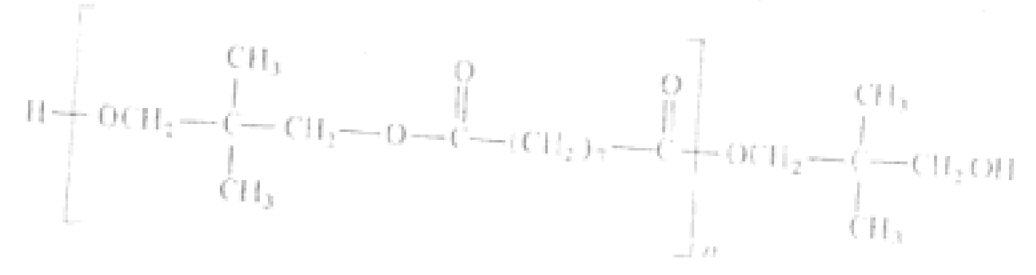
With di- or polyfunctional isocyanates and dihydroxylic compounds a rubbery polymer is obtained and with tri-hydroxylic alcohols cross-linked polymers are formed.

The most common polyurethane binders are from 2,4-toluene diisocyanate (TDI) obtained from 2,4-dinitrotoluene by the sequence of reactions (2):



(2)

and long chain glycols with primary and secondary alcoholic groups. According to Oberth and Bruenner [9] among the glycols are those with: (a) an ester function, e.g. I:



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(b) and ether function as poly (1,2-oxypropylene)diol (PPG) of M = *ca*. 2000.
(c) polybutadiene chain.

Binder (b) and (c) are more advantageous than (a).

Binders (b) are more readily available, show a low viscosity, good rate of cure and good ageing stability. Their disadvantage is ease of absorbing oxygen to form peroxides, but the addition of aromatic amine antioxidants removes this disadvantage. They withstand prolonged storage (several years) at temperatures of 65–82°C without the loss of mechanical properties.

Hydroxyl-terminated polybutadienes (c) are readily subjected to air-oxidation and subsequent hardening.

Polyfunctional alcohols, mainly trifunctional and their esters are used as cross-linking agents.

Table 124 gives typical compositions of unaluminized polyurethane resin propellants, according to [10].

TABLE 124. Polyurethane resin propellants JPL X500

Components	Wt% 70%	80% Oxidizer
NH_4ClO_4		
ground*)	21.0	24.0
unground*)	49.0	56.0
Polypropylene glycol	23.9	15.9
Toluene Diisocyate (TDI)	4.8	3.2
1,2,6-Hexanetriol (HT)	1.2	0.8
Ferric acetyl acetonate	0.1	0.1

* A bimodal oxidizer system is used, consisting of 30% ground and 70% unground ammonium perchlorate.

The propellant shows good mechanical properties (tensile strength, elongation and initial modulus) at temperatures from −40° to +70°C.

By the addition of aluminium (and berillium) higher energy propellants are formed. Figure 126 gives, according to Oberth and Bruenner [9], the calculated specific impulse of ammonium perchlorate–aluminium–polyurethane (polyether) binder (max. I_s = 247 s).

POLYBUTADIENE BINDERS WITH CARBOXYLIC FUNCTION

The polybutadiene polymers containing carboxyl functional groups appear to be the most important group of binders in composite propellants. The following are co-polymers used in this type of propellant, according to Mastrolia and Klager [11]:

(1) butadiene and acrylic acid (PBAA),
(2) terpolymer of butadiene, acrylic acid and acrylonitrile (PBAN),
(3) the carboxyl terminate polybutadiene (CTPB).

Here is a brief description from the same source [11].

(1) PBAA was the first butadiene polymer to be used in rockets. It was made by free radical emulsion polymerization to an average M = 3000. It was a random mixture of polymers of different molecular weights and functionality

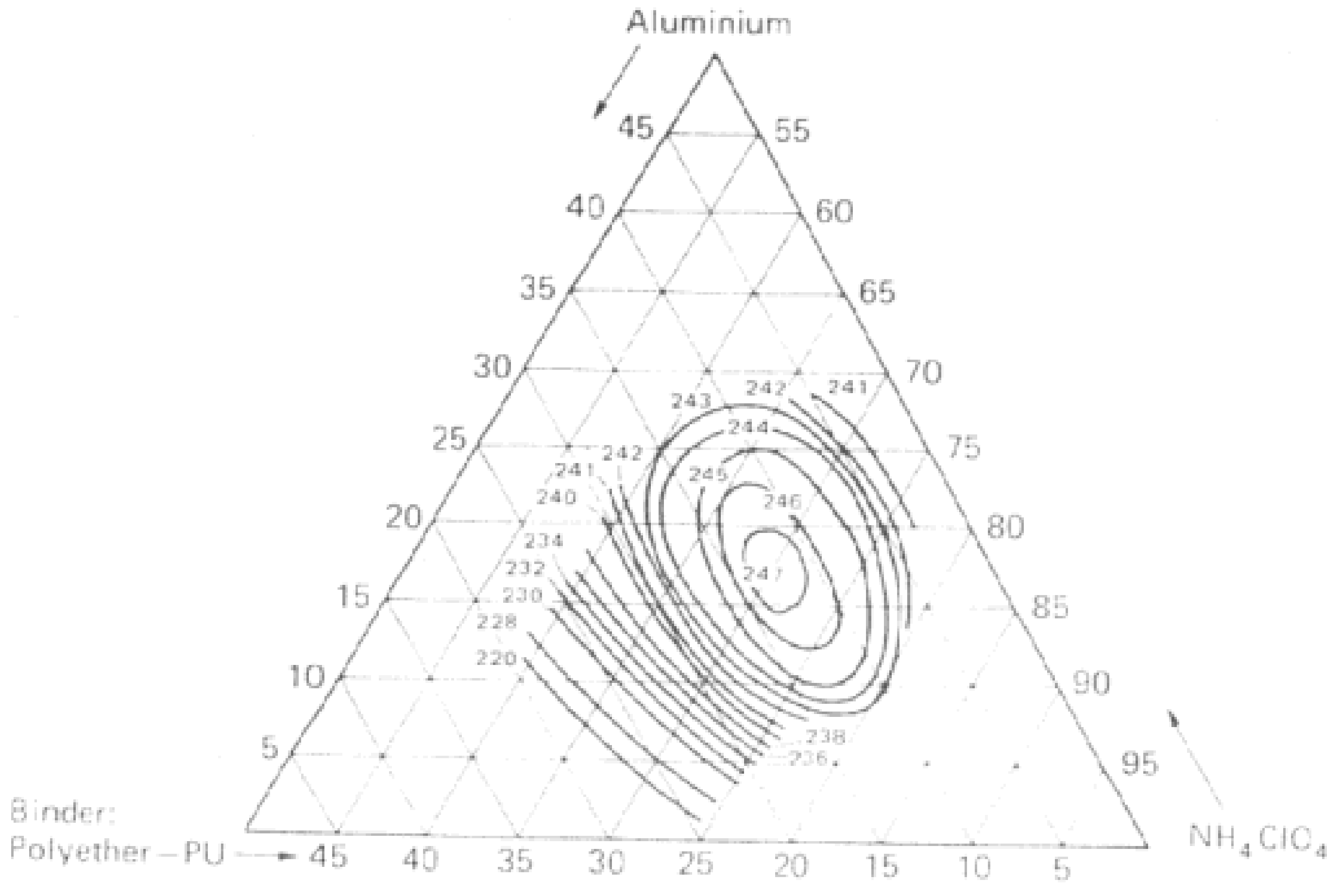


FIG. 126. Calculated Specific Impulse of ammonium perchlorate–aluminium–polyurethane (polyether) binder, according to Oberth and Bruenner [9].

and therefore did not possess proper mechanical properties. The use of such polymers was eventually discontinued.

(2) PBAN was also made by emulsion polymerization. Mechanical properties of polymer were improved through steric action by introducing acrylonitrile. Also acrylonitrile reduced deteriorating action of oxygen on double bonds of the polymer as known to be suppressed in nitrile rubber.

The following are data for the physical properties of PBAN:

Molecular weight	3000–4500
Viscosity at 25°C	300–350 poise
Density	0.93–0.94.

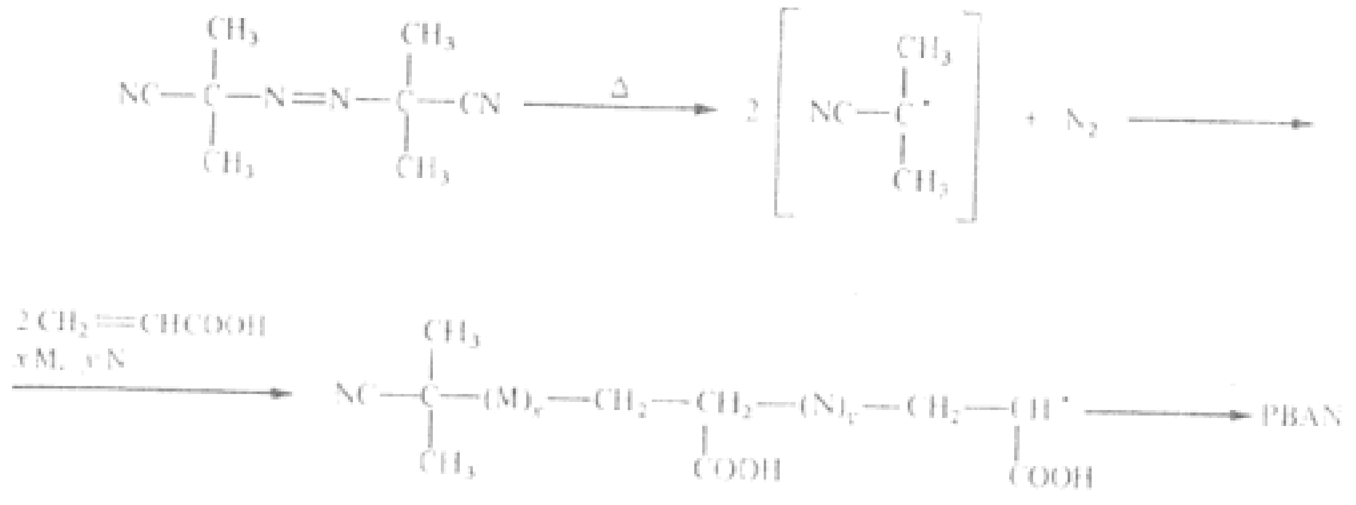
The composition of propellants with PBAN and of increased energy through the addition of Al is kept within the limits in wt. %:

$NHClO_4$	60–84
PBAN	12–16
Al	2–20
Stabilizer	0–1
Curing agents	0.2–1.0

The resistance against the action of oxygen can be seen from the effect of keeping the propellant in oxygen atmosphere at 105°C at 96 hours:

	Hardness	
	internal	surface
Before the action	40	40
After 96 hours	49	47

The PBAN preparation can be presented by scheme (3). The butadiene–acrylic acid–acrylonitrile can be varied over a wide range.



$$NC-\overset{CH_3}{\underset{CH_3}{C}}-N{=}N-\overset{CH_3}{\underset{CH_3}{C}}-CN \xrightarrow{\Delta} 2\left[NC-\overset{CH_3}{\underset{CH_3}{C}}{}^{\bullet}\right] + N_2 \longrightarrow$$

(3)

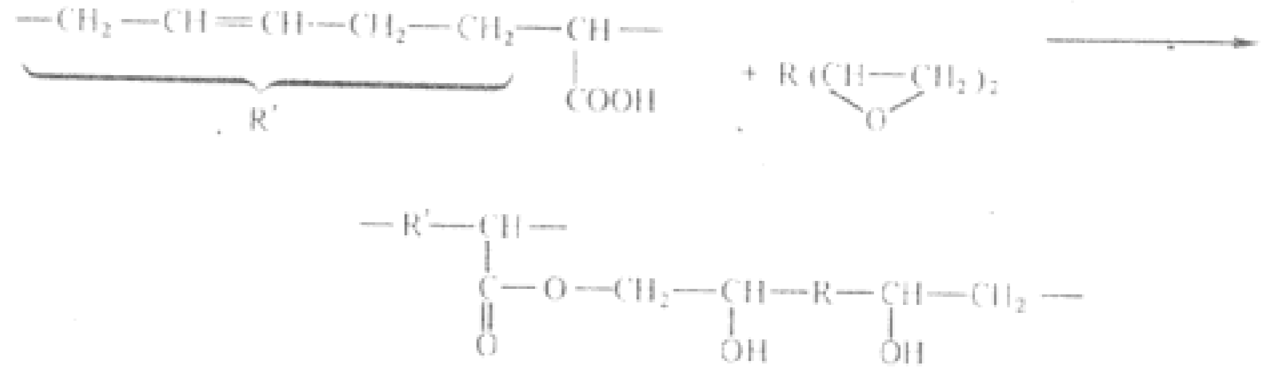
$$\xrightarrow[xM,\ yN]{2\,CH_2{=}CHCOOH} NC-\overset{CH_3}{\underset{CH_3}{C}}-(M)_x-CH_2-\underset{COOH}{CH_2}-(N)_y-CH_2-\underset{COOH}{CH}{}^{\bullet} \longrightarrow PBAN$$

$M = CH_2-CH-CH = CH_2$

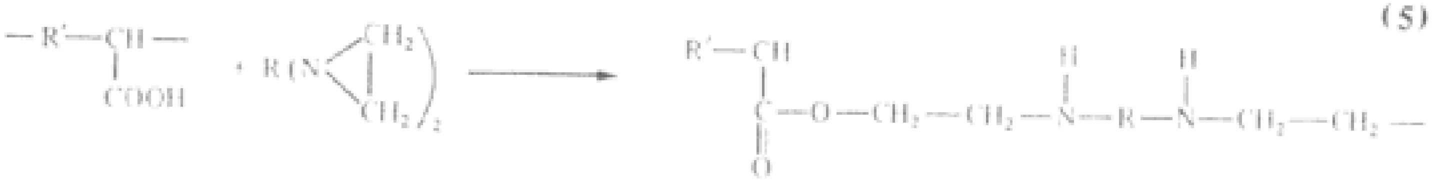
$N = CH_2 = CH-CN$

The acrylic acid and acrylonitrile are fed into the reactor containing the butadiene emulsion and the chain termination is achieved by adding a mercaptan when the molecular weight reaches 2000–4000. After that an antioxidant is added, the polymer purified by washing with water and vacuum drying.

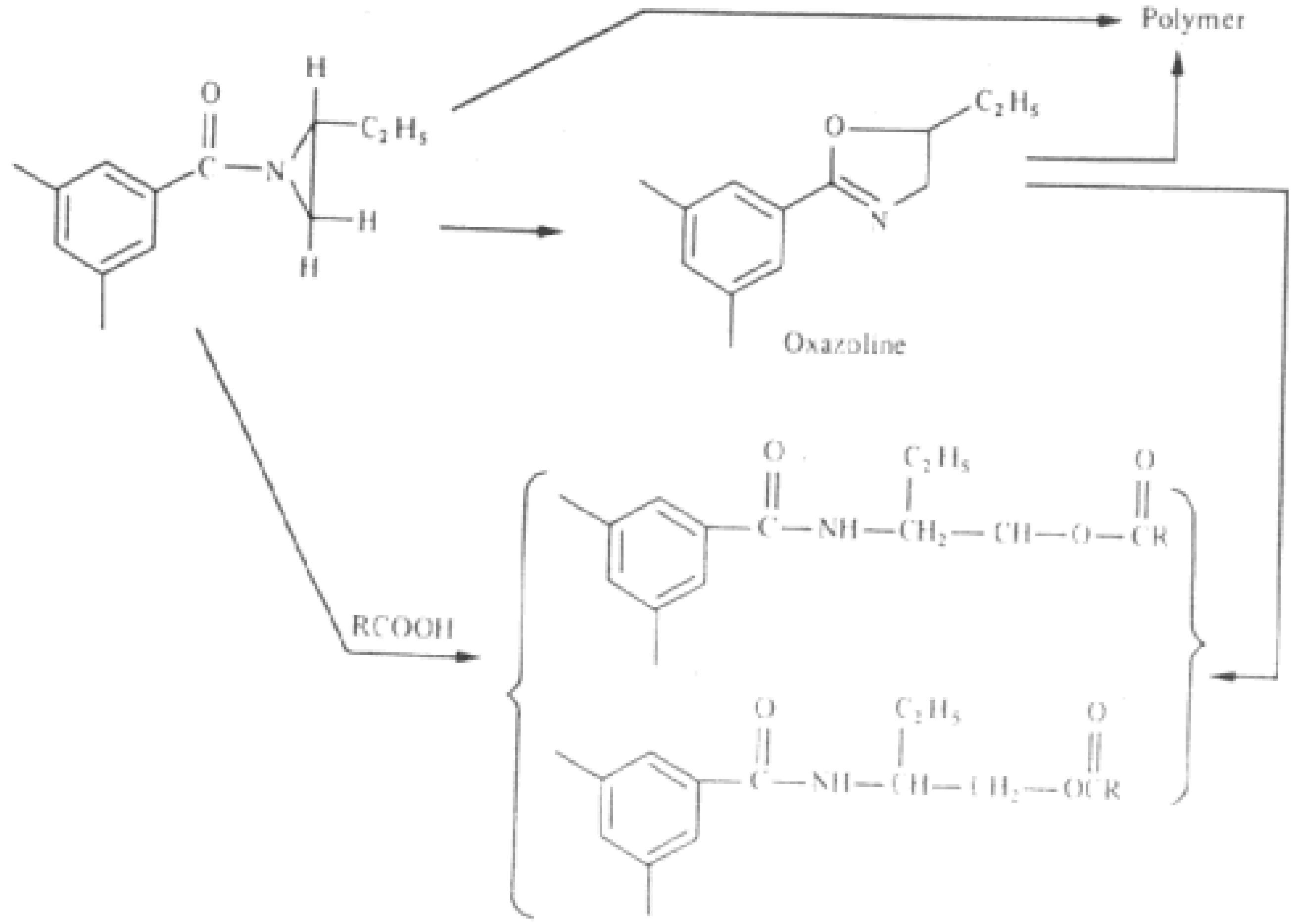
To form a three-dimensional structure the curing reaction is carried out through difunctional epoxides (4) or aziridines (5), *R* is curing agent radical e.g. (6). Carboxylic groups supply *N*-hydrogen atoms. The PBAN polymer has a sufficient number of functional group to produce a firm gel without using separate cross-linking agents



(4)



(5)



(6)

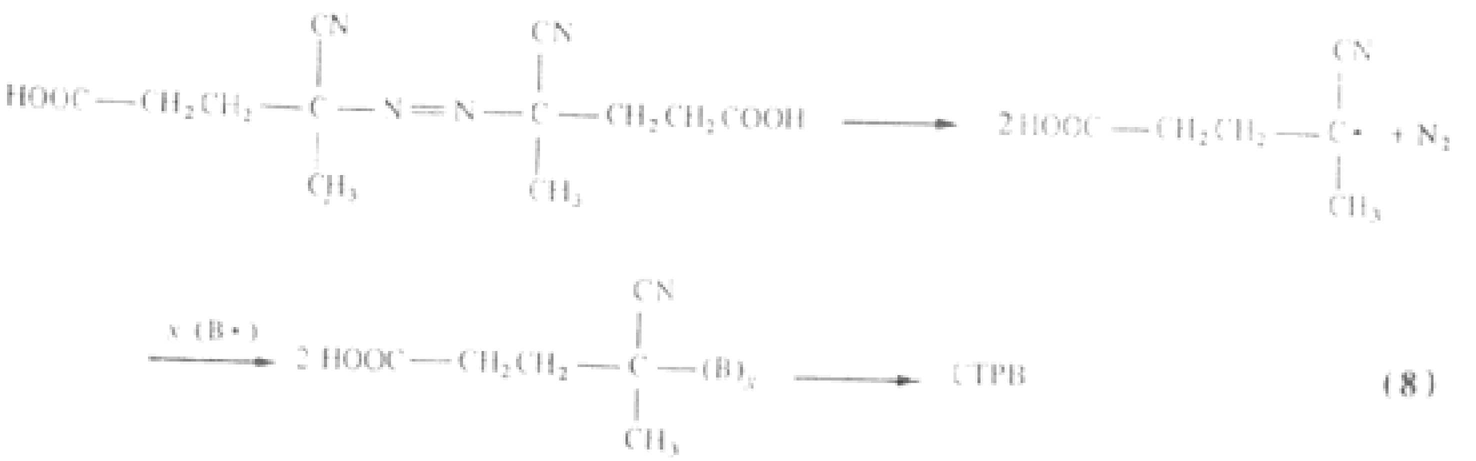
(3) CTPB – Carboxy Terminated Polybutadiene free radical terminated polymers.

Two methods have been given by Mastrolia and Klager [11]. One of the methods is by using the glutaric acid peroxide as the initiator of free radical and butadiene (7):

$$\mathrm{HOOC{-}R{-}\underset{\underset{O}{\|}}{C}{-}O{-}O{-}\underset{\underset{O}{\|}}{C}{-}RCOOH} \longrightarrow 2\cdot\mathrm{RCOO} \xrightarrow{x\,(B\cdot)}$$

$$\cdot(\mathrm{B})_x{-}\mathrm{R}{-}\mathrm{COOH} \longrightarrow \mathrm{CTPB} \qquad (\mathrm{R}{=}\mathrm{C_3H_6}) \qquad (7)$$

Another method used 4,4′-azobis-4-cyanopentanoic acid as the initiator:



$$\mathrm{HOOC{-}CH_2CH_2{-}\overset{CN}{\underset{CH_3}{C}}{-}N{=}N{-}\overset{CN}{\underset{CH_3}{C}}{-}CH_2CH_2COOH} \longrightarrow \mathrm{2HOOC{-}CH_2CH_2{-}\overset{CN}{\underset{CH_3}{C}}\cdot + N_2}$$

$$\xrightarrow{x\,(B\cdot)} \mathrm{2\,HOOC{-}CH_2CH_2{-}\overset{CN}{\underset{CH_3}{C}}{-}(B)_x} \longrightarrow \mathrm{CTPB} \qquad (8)$$

Here is an example of the composition of a CTPB propellant according to [28]:

Ammonium perchlorate	80.0–80.9%
Al powder	5.
CTPB	14
Ferric oxide	0.1–1.0

HYDROXYTERMINATED POLYBUTADIENE BINDER (HTPB)

An example of a composite propellant with hydroxyterminated polybutadiene binder is given here [28]:

Ammonium perchlorate	77.6–76.0%
Al powder	10
HTPB	11.6
Ferric oxide	0.4–2.0

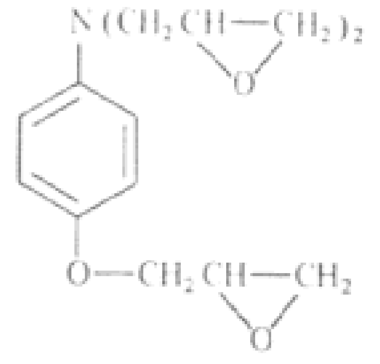
CURING BUTADIENE POLYMERS

Carboxyl terminated polybutadiene polymers require curing in order to form a tridimensional network. Polyfunctional epoxides and aziridines are used for cross-linking.

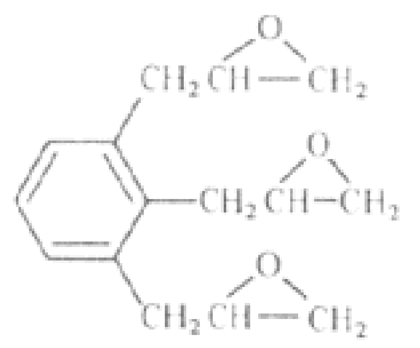
When making propellants with ammonium perchlorate the oxidizing properties of the latter produce side reactions interfering with the action of the curing agent. This involves the formation of a less complete three dimensional structure.

The structure of a few epoxide and aziridine curing agents are given (II–VIII).

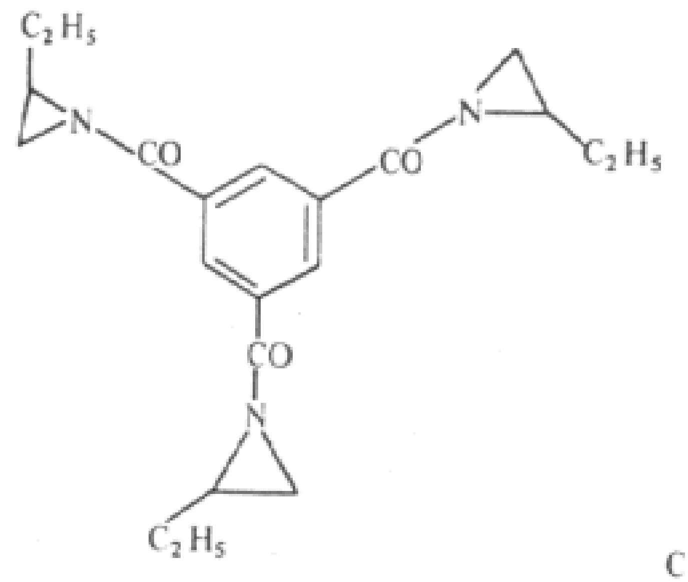
Epoxy compound IV exhibits a minimum of side reactions in the presence of ammonium perchlorate. Epoxy curing agent II shows a high reaction rate but side reactions dominate in the presence of ammonium perchlorate. The compound BITA (V) can be subjected to various transformations shown in scheme (6). They also possess similar properties as V but are less active. Zirconium



ERLA-0510
II

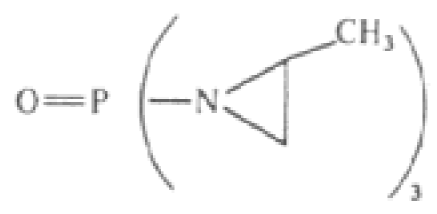


Epon X-801
III



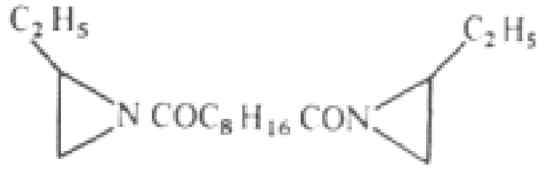
BITA

V



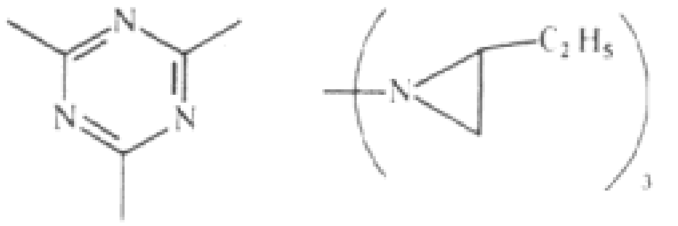
MAPO

VII



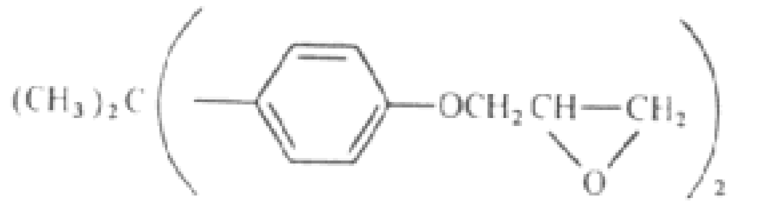
BISA

VI



TEAT

VIII



DER-332

IV

acetylacetonate is an effective polymerization catalyst and can be added in quantity 0.5 wt. %. Propellants made with MAPO (VII) possess good properties but a problem arises with ageing, probably due to the presence of P—N bond. A mixed curing agent made of VII and II gave more satisfactory results.

The fact that a variety of reactions given by different curing agents led to developing mixed curing agents composed of both epoxy- and aziridine compounds. This is still a developing side of problems of composite propellants – a specialized problem – connected with polymer chemistry and technology and outside the scope of the present book.

Figure 127 gives theoretical specific impulse for ammonium perchlorate-Al-polybudiene propellants. The maximum specific impulse was calculated as high as I_s = 266s [11].

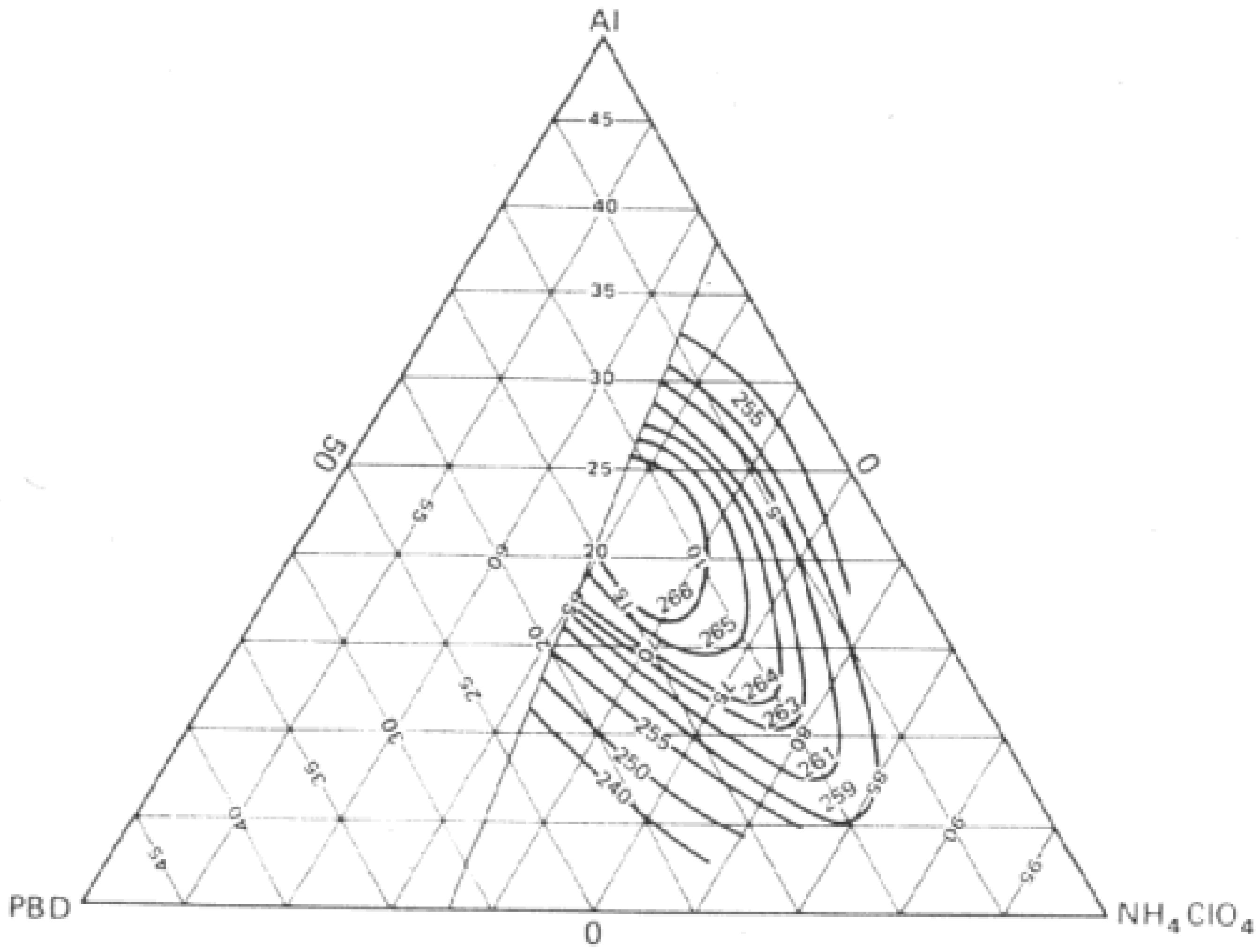


FIG. 127. Calculated specific impulse of ammonium perchlorate–aluminium–polybutadiene (PBAN) according to Mastrolia and Klager [11].

POLY (VINYL CHLORIDE) PLASTISOL PROPELLANT (PVC)

According to the description by Rumbel [12] PVC plastisol propellant consists of ammonium perchlorate, uniformly dispersed and cured PVC plastisol. A number of propellants have been developed by the Atlantic Research Corporation under the name Arcite.

Standard Arcite has the composition in wt. %.

NH_4ClO_4 (equal parts of coarser and finer passing through mesh 62 μ)	75.0
PVC	12.5
Plasticizer (dibutyl sebacate)	12.5
Stabilizer (undisclosed compound) added	0.4

The influence of adding aluminium (or magnesium) to increase the specific impulse I_s up to 242 s is given in Fig. 128. One of the aluminized propellants Arcite 373 D has the composition in wt. %.

NH_4ClO_4	58.9
Al	21.1

PVC	8.6
Plasticizer (2-ethylhexyl adipate)	10.8
Wetting agent (a mixed detergent: glycerol pentaerythritol dioleate, dioetyl sodium sulphosuccinate)	0.25
Stabilizer (undisclosed)	0.35

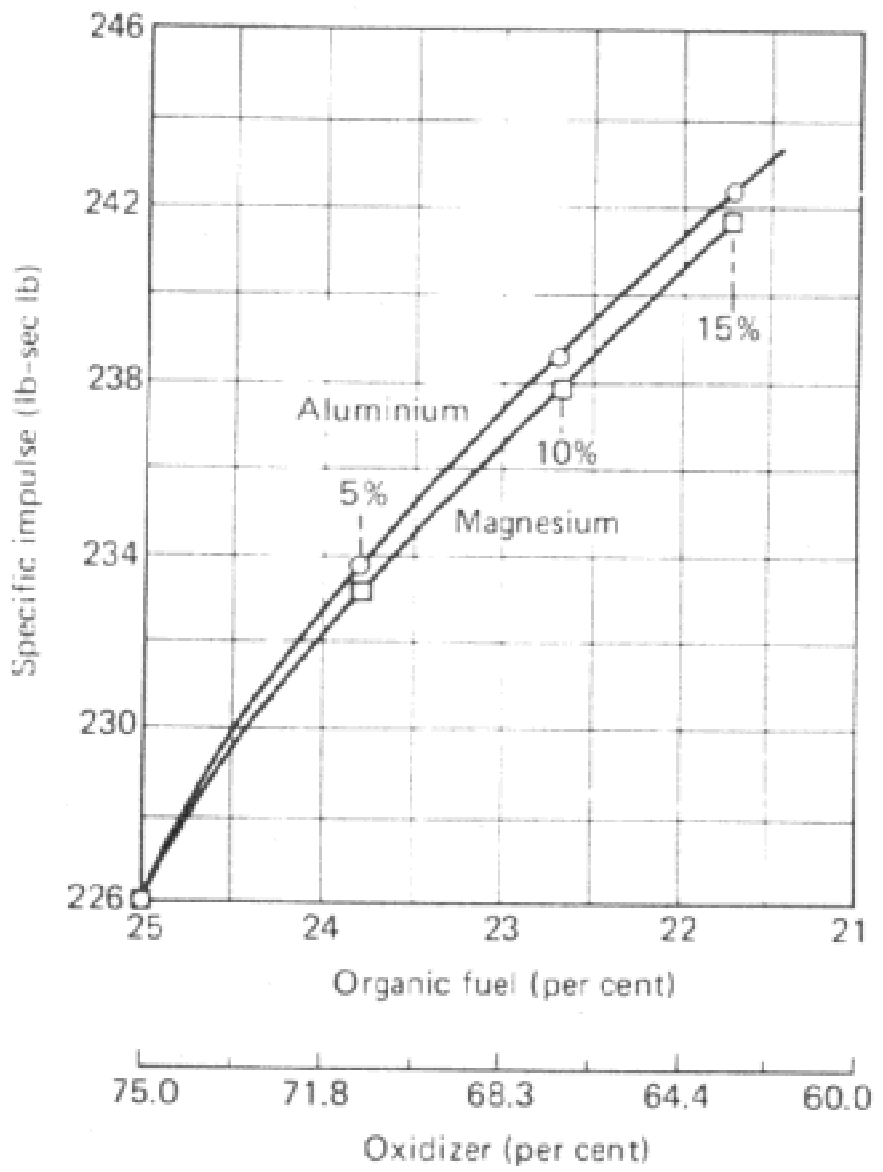


FIG. 128. Increase of specific impulse of PVC Plastisol Propellants by adding Al and Mg according to Rumbel *et al.* in [12].

A stabilizer is added to retard the decomposition of PVC during curing, which is carried out at 150–175°C. Because of low thermal conductivity, several hours are required to raise the central portion of the propellant grain to curing temperature. The portions of the grain close to the source of heating may show a tendency to decompose and stabilizers are added to inhibit the decomposition. It is advisable that the stabilizer should be able to bind the hydrogen chloride which would decompose the polymer. However propellants with aluminium powder show better thermal conductivity and hence the time of cure can be reduced.

This is of course related to all composite propellants with aluminium.

HIGH ENERGY COMPOSITE PROPELLANTS WITH HMX (OCTOGENE)

Attempts have been made to introduce HMX into composite propellants. According to Sayles [13] propellant 'D' is composed of:

Ammonium perchlorate	19.2 wt. %
Butanetriol trinitrate	25.7
HMX	48.5
Ethyl acrylate-acrylic and co-polymer (EA/AA, 95/5)	4.6
Diepoxydicyclohexyl carboxylate (curing agent)	1.5
Carbon black	0.5

Specific impulse $I_s = 262.4$
RDX can be substituted for HMX.

Some other composite propellants were suggested with nitrogen difluoride groups, for example 1,2,3-tris[1,2-bis(difluoroamino)-ethoxy propane] but high cost of the compound did not seem to encourage its use [1].

ROLE OF INGREDIENTS ON PROPERTIES OF COMPOSITE PROPELLANTS

This problem is discussed in detail by Fluke [14] and here is a brief description of his paper.

Ammonium perchlorate of various fineness is used to give a better 'packing'. Particle size distribution is of great importance to density, rheological properties of the viscous mass, mechanical properties and burning of the propellant. Rheological properties obviously depend on polymer binder which is of course the combustible ingredient in propellants.

Here are some of the outlines given by Fluke on this particular matter:

(1) Formula optimization. In the formulation of new propellants, it may be desirable to optimize certain rheological characteristics.

(2) Formulation characterization. Prior to using a new propellant formulation, the material should be fully characterized and analyzed rheologically. Processability predictions may be extrapolated.

In quality control it is necessary to check rheological properties of propellant samples.

In addition to the above, the following are remarks on some components of composite propellants according to the existing literature.

Plasticizers have a very important effect on physical properties of the cured propellants and on the variation of these properties with temperature. Long chain aliphatic plasticizers improve low temperature flexibility. An increase in plasticizer viscosity obviously leads to an increase in viscosity of the mixed propellants. The burning rate is little changed by changing plasticizers.

Attention should be paid to preventing the formation of cracks and voids during cure [15], which are caused by shrinkage during solidification of the propellant. Specific processing conditions are required for each propellant formulation and rocket size according to Arendale [15].

Wetting agents in propellant compositions facilitate mixing ingredients and reduce the viscosity so that they are cast more readily.

Metals

Aluminium should be used in spheroidal shaped particles [12]. It gives a better pourability of the compositions [16].

A very important observation was recently made by Rumbel [12]. This is the incorporation of fine metal wires into a propellant, which increase the rate of burning as recorded originally in PVC plastisol propellants [12] but seems to be now a general practice in composite propellants. Metal wires are introduced into the composition before cure. When the propellant is burned the wires extend from the unburned propellants into the flame zone. They provide paths for rapid heat transfer and thus burning along the wire is faster than outside the wire. Particularly efficient are silver and copper wire, as described by Rumbel – for PVC plastisol propellants (Table 125).

TABLE 125. Burning rates along 5-mm wires in PVC propellants according to Rumbel *et al.* [12]

Wire	Burning rate along wire cm/s	Ratio of burning rate along the wire standard	Properties of metal melting temperature °C
Silver	6.76	5.3	960
Copper	5.92	4.6	1083
Aluminium	2.96	2.3	660
Magnesium	2.45	1.9	651
Steel	2.04	1.6	*ca.* 1460

Also aluminium staple was suggested [17] together with aluminium powder in composite propellant containing MAPO (VII) curing agent.

Catalysts (Vol. III, pp. 369, 394)

The role of catalysts on burning ammonium perchlorate and other salts, such as ammonium nitrate, potassium perchlorate etc. is widely described in the monograph by Glazkova [18].

Cohen Nir [19] described the catalytic action of Cu_2O and powdered metals – Al, B, Mg – on steady burning of ammonium perchlorate under low pressure:

The catalytic action of iron oxides (mainly ferrous oxide) was described by Bakhman and co-workers [20]. They also reviewed the literature on the catalytic action of Fe, Fe_2O_3, Fe_3O_4, organo-iron compounds, Co_2O_3, NiO, Cu, Cu_2O, CuO, Cu chromite, Cu chlorides, Cr_2O_3, salts of chromic acid, MnO_2, $KMnO_4$, V_2O_5, SiO_2, TiO_2.

Iron oxide catalyst mentioned in the description of the space shuttle's orbiter *Columbia* [2] was probably ferric oxide or a mixture of various iron oxides.

BURNING COMPOSITE PROPELLANTS CONTAINING AMMONIUM PERCHLORATE

It has been shown that perchloric acid is liberated from the solid fuel and reacted further. Gilbert and Jacobs [21] found that the major products of decomposition of perchloric acid are oxygen and chlorine which further react with organic compounds to yield CO, HCl, H_2 and chlorinated short chain hydrocarbons. The mechanism of burning comprises the depolymerization of the organic solid phase to give gaseous fuel fragments which react further [22].

Steinz and Summerfield [23] reviewed existing theories on burning ammonium perchlorate under pressure between one and 100 atm. and built a schematic presentation of the mechanism. In the first stage the dissociation occurs of NH_4ClO_4 into NH_3 and $HClO_4$ (A/PA) and reacted with oxidant/fuel (O/F) zone.

The pressure exponent n around 100 atm for ammonium perchlorate propellants is *ca.* 0.3.

Pepekin, Apin and co-workers [28] attempted to rationalize the rate of burning of composite propellants with ammonium perchlorate as a function of the combustible ingredient. They came to the important conclusion that the rate of burning did not depend on the heat of burning, but on the strength of the chemical bond in the combustible substance. A striking example was given by a system with ferrocene. On the basis of the enthalpy of the bond C–Fe (which is 75.0 kcal/mol) it should be expected that the burning rate would be similar to that of ammonium perchlorate with amines. The latter have the enthalpy of the bond C–N equal to 73 kcal/mol. However experiments show that the rate of burning of mixtures of ammonium perchlorate with ferrocene are nearly three times higher than that of ammonium perchlorate with amines.

The authors found an empirical equation:

$$u = 0.9 - 0.005\,E \text{ cm/s},$$

where

u – the rate of burning of the mixture,
E – the energy of the weakest bond of the combustible material.

The bond C – Fe in ferrocene is very weak and ferrocene readily dissociates according to the equation:

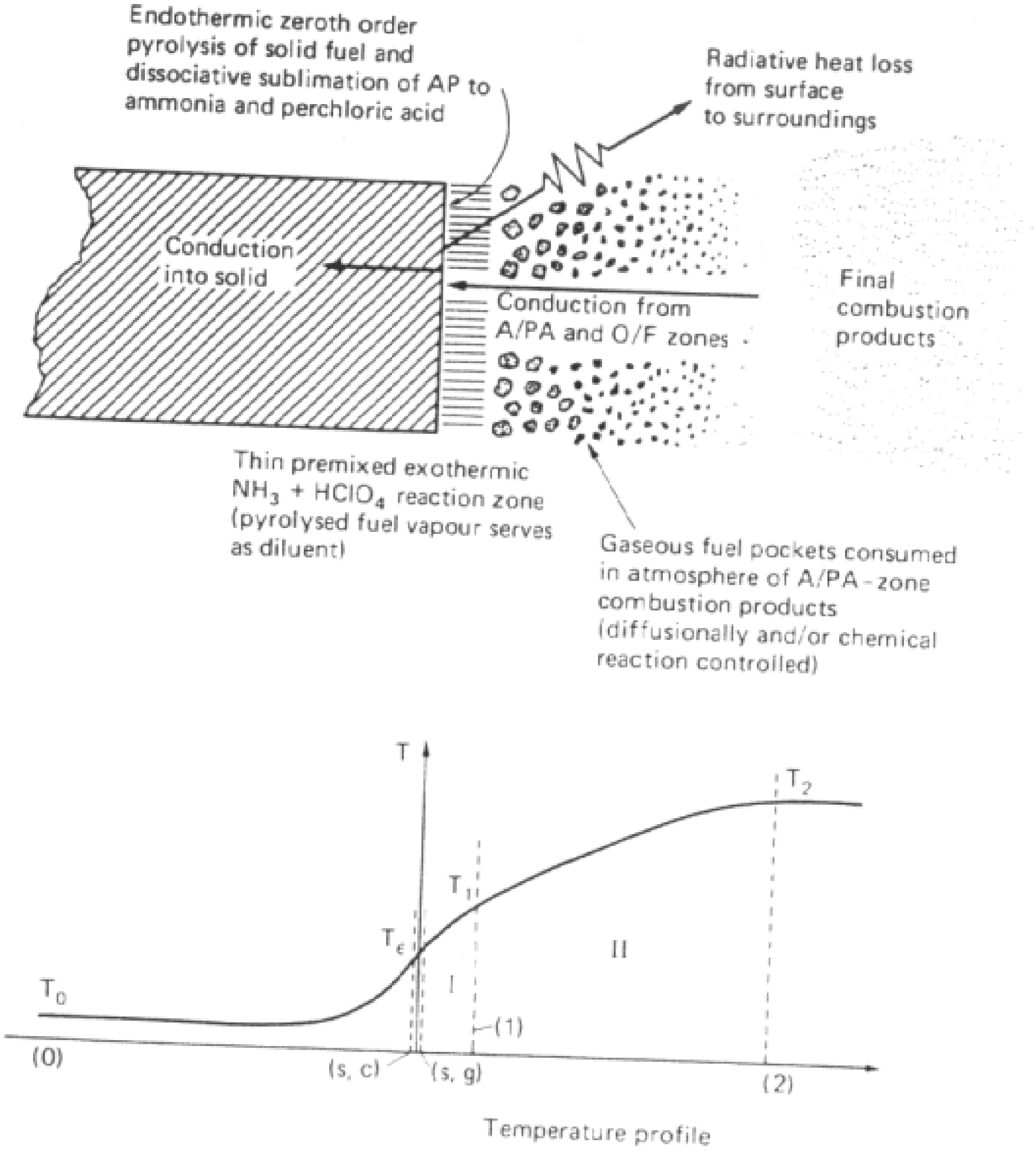


FIG. 129. Diffusion flame model for ammonium perchlorate composite propellants according to Steinz and Summerfield [23]. A/PA and O/F are ammonia perchloric acid and oxidant/fuel respectively.

$$(C_5H_5)_2Fe \longrightarrow Fe + 2\,C_5H_5.$$

Further discussion on burning composite propellants concerns the problems of inner ballistics and is therefore outside the scope of the present book.

MODIFICATIONS OF COMPOSITE PROPELLANTS

Modifications of composite propellants are mainly concerned with modification of the oxidizer. Ammonium nitrate (Vol. III, p. 383) is now less in use owing to such disadvantages as high hygroscopicity, relatively difficult ignitability and polymorphism at different temperatures combined with a change of density (see Chapter XVI).

Potassium perchlorate shows a high exponent $n = ca.\ 0.8$ in equation rate of burning/pressure. It also gives high temperature of burning which can readily produce corrosion of the nozzle.

The other perchlorates, such as hydrazinium, hydroxylaminium and nitronium perchlorates etc. are at present of theoretical interest only. Some of them (e.g. hydrazinium perchlorate) shows poor chemical stability and high sensitivity to mechanical shock.

Also hydrazinium nitrate does not seem to be a promising oxidizer.

MECHANICAL PROPERTIES

The mechanical properties of solid propellants are discussed by Kelly [25]. In the U.S.A. the methods are based on instructions worked out by a Joint–Army–Navy–Air Force (JANAF) Physical Properties Panel and include uniaxial and multiaxial measurements of mechanical strength.

They also include examination of the uniformity of the structure, detection of voids and cracks by X-ray examination.

The problems of testing mechanical properties are outside the chemical problems and are therefore not included in the present book.

MANUFACTURE OF COMPOSITE PROPELLANTS (Vol. III, p. 373)

The principles of the manufacture of composite propellants outlined in Vol. III are still valid. They are also described by Fluke [14] who gave a few schematic presentations for preparing the mixtures.

In principle they consist of:

(a) preparation of oxidizer (grinding, screening, mixing),
(b) binder and fuel preparation (polymerization),
(c) chamber insulation and lining,
(d) mixing of the propellant, casting into the chamber and lining,
(e) extraction of the grain from the chamber.

Mixing should be carried out in a kneading apparatus of the type shown in Figs 102 and 103. It should be done in a well defined sequence [16]. It is advisable to add ammonium perchlorate at the end after aluminium has been added. This is for safety reasons, as finely ground aluminium with ammonium perchlorate can form a dangerous dust when suspended in air.

Curing should not be carried out at a temperature above 80°C. After curing the extraction of the grains from the chamber can easily be done because of the shrinkage of the propellant mass.

Pneumatic mixing of ingredients developed by the Naval Propellant Plant was depicted in Vol. III, p. 390, Fig. 125.

As an illustration of mixing large charges, the following description can be given for preparing propellant for the shuttle's orbiter *'Columbia'*.

The formula is prepared in 7000 lb (*ca.* 3170 kg) batches at a remote complex in Utah operated by Thiokol Corp. The giant mixing bowl is of 2270 l. capacity. Mixing consists of the following steps: aluminium powder, PBAN (polybutadienacrylic acid–acrylonitrile) polymer and ferric oxide powder are mixed. Then the epoxy curing agent is added without mixing so as to delay the start of the curing reaction. The bowl containing this premix is transported by trailer to another building where ammonium perchlorate is added and blended by remote control for explosive properties of ammonium perchlorate and the operation should be considered as dangerous.

The mixing bowl is transferred to another site where the propellant is poured into casting segments. Each booster is built from four such segments assembled in a reusable steel casing. It takes 20 hours to fill one casting segment. The mixture is then cured at 57°C for four days and takes on the consistency of hard rubber.

SHAPES OF THE PROPELLANT GRAINS (Vol. III, p. 366)

A full description of possible shapes of grains and the pressure developed with time of burning has been given in a monograph [3] and is partly reproduced here – Fig. 130.

The most advantageous are shapes (2-cigarette burning), (3) and others (7–10) giving a constant or nearly constant pressure. Tube without inhibiting layers (4) and plain (1) are used when a high initial thrust is needed. Shape (5) and particularly (6) are much appreciated when a high thrust at the later stage of burning is required.

EXPLOSIVE PROPERTIES OF COMPOSITE PROPELLANTS (Vol. III, p. 393)

As mentioned in Vol. III, composite propellant detonate with difficulty because of their non-porous texture and very high density.

When in powdered form they behave as most explosives: sensitive to friction and impact and detonate readily when in low density.

According to information given in the Encyclopedia [1] the standard propellant made of ammonium perchlorate, PBAN and aluminium can detonate when RDX is added. Thus with 4.75, 7.1 and 9.2% the critical diameters were found to be: 28.2, 13.2 and 6.9 cm respectively. No rate of detonation was given.

Bernecker and Price [26] determined the rates of detonation of mixtures of ammonium perchlorate and wax (Table 126).

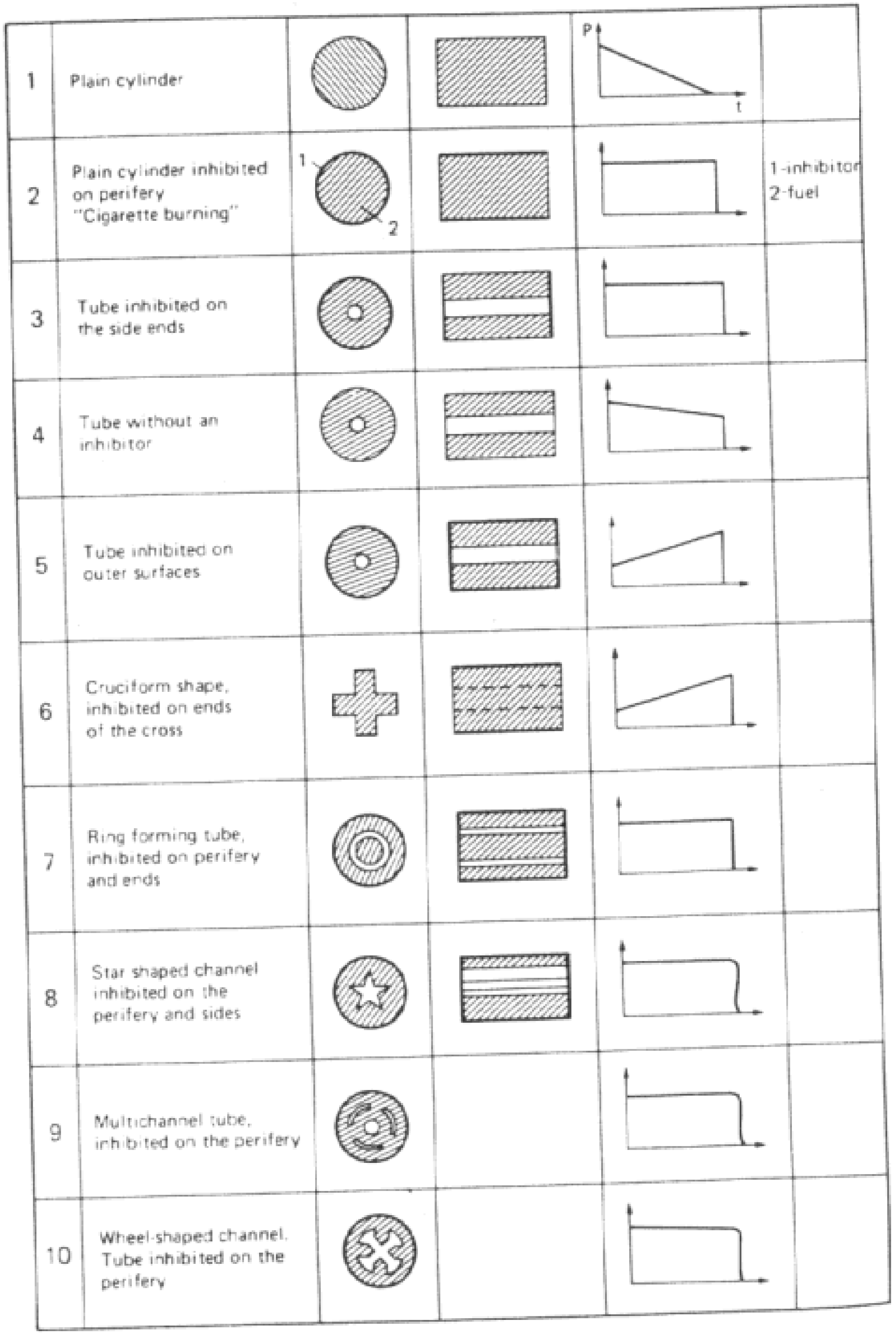


FIG. 130. Shapes of grains and pressure against time of burning according to Krowicki and Syczewski [3].

TABLE 126. Rates of detonation of ammonium perchlorate–wax mixtures [26]

Composition NH_4ClO_4	Wax	Density	Diameter cm	Critical diameter cm	Rate of detonation m/sec
90	10	0.93	7.62	0.65–0.95	4070
		1.20	7.62	0.65–0.95	4540
		1.52	–	*ca.* 5	–
80	20	0.91	7.62	0.65–0.95	4480
		1.10	7.62	0.65–1.27	4790
		1.40		*ca.* 5	–

The above figures can give an approximate idea of the rates of detonation of ammonium perchlorate, PBAN and aluminium.

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CHAPTER 24

PROBLEMS OF SAFETY IN THE MANUFACTURE AND HANDLING OF EXPLOSIVES

The fact that explosive molecules are designed in such a way that they should burn, explode or detonate requires of course that their manufacture, handling and transportation should be carried out with special precautions.

Wide monographs recently appeared on problems of hazards and safety with explosives [14, 15].

MANUFACTURE

Precautions which are necessary in the processes of manufacturing explosives were described in the texts dedicated to their manufacture. However, there are a few principles common to all processes. These are:

Remote control of the functioning of production apparatus which should be provided with the elements connected to the remote control. The following are the most dangerous to manufacture:

(a) black powder,
(b) nitroglycerine and similar *O*-nitro compounds,
(c) initiating explosives and their mixtures.

Remote control ensures that not a single person is present in the proximity of the production apparatus.

There is however a danger when automation is not functioning correctly and has ceased to be reliable. This may lead to a disaster (e.g. an accident in Biazzi nitroglycerine plant in Bhandara, India in 1975) [1]. In this case automation became dangerous. There is always a need for human control in the functioning of automation.

The remote control of temperature is needed in the course of nitration as described in Chapters VI, VIII, XI, XII and in making initiating explosives and their mixing, mixing of commercial explosives (Chapter XX), making smokeless powder (Chapter XXII).

STATIC ELECTRICITY

A great danger exists wherever there is friction and this is through charging with static electricity which on discharging may produce ignition. There are dangerous parts of the manufacture of explosives from that point of view, such as mixing and kneading apparatus, rollers of double and treble-base powder, rotating drums (Vol. III, p. 625), in flowing flammable liquids through the pipes (Vol. III, p. 589) and air with flammable vapours (Vol. III, p. 607), compression of air containing flammable vapours in the course of extrusion of smokeless powder with a volatile solvent (Vol. III, p. 595), friction between the stream of air and the grains of propellants (Vol. III, p. 603), cutting, screening and blending of propellants.

A few monographs have appeared on static electricity and the danger connected with the discharge of it producing explosions of gas mixtures, inflammable dust or even inflammable liquids or solids. These are monographs by Freytag [2] and Haase [3]. Also a book by Gugan should be consulted [4].

The principal method of avoiding the danger of the discharge of the static electricity is to earth all parts of machinery which are subjected to friction.

A general method of avoiding an accumulation of static electricity incorporating substances conducting electricity into the explosive on condition that the manufacturing apparatus is earthed. Relatively high humidity of the atmosphere (wherever it is not harmful to the production [8], ionization of the atmosphere by irradiation with γ- or X-rays are other factors which help in avoiding the accumulation of static electricity [9].

The addition of conducting substances to explosives is a general method of preventing the charging of explosives with static electricity. The conducting substances comprise graphite (a particularly frequent component of smokeless powder Vol. III, p. 625), aluminium powder wherever it can be included in the composition of explosives without creating a new danger (it is known that the addition of aluminium to black powder gives dangerous compositions). Where neither of these substances can be included into the formulation of explosives, some organic conductors, usually CT-complexes (Charge–Transfer complexes) or ionic surface active agents can be added in a small proportion (below 0.5%). Addition of such surface active agents was recently recommended in a patent by Wielgus, Zdrojek and co-workers [10]. Surface active agents were earlier recommended [11] in the textile industry where the problem of static electricity is particularly important (through friction).

The recent facts on new conducting polymers [13] should be used to examine its action against the accumulation of static electricity, provided they are not harmful to the stability of the powder. Particularly interesting seem to be polyacetylene or poly-*p*-phenylene arsenic pentafluoride.

Conductive rubber (with graphite or Al dust) is highly recommended and often compulsory for the soles of workers' shoes, and conductive mats and carpets where certain explosives are handled.

The charging of smokeless powder was described in detail by Uetake and Sato [12]. See also Vol. III, pp. 542–543, 682, 684.

For one exceptional sensitivity of lead styphnate to static electricity and danger of discharge see Vol. III, pp. 217–218.

FOREIGN BODIES IN MIXING MACHINES

Foreign bodies present by accident or carelessness in mixing machines, such as kneaders have frequently been responsible for accidents. The otherwise safe kneaders of Drais, Biazzi, Werner and Pfleiderer can become a source of danger. A few accidents of this type have been described by Biasutti [1].

CONSTRUCTION OF EXPLOSIVE FACTORIES

There is currently a tendency to construct buildings for the manufacture and storage of explosives which could prevent the propagation of a shock wave and thus reduce the area of destruction. Such were heavy underground buildings for some time favoured in Germany (e.g. Vol. II, p. 122, Figs 62, 63).

According to Kaye [5] currently much in use are laced concrete walls (Fig. 131) forming a shock wave barrier, but more modern designs are those of 'suppressive structures'. They are made of new 'suppressive structures' of several layers of louvered and perforated plates of angle iron and 'z' bars. This allows controlled release of blast effects from a detonation within the structure. Subsequently a controlled release of blast effects occurs.

DETECTION OF HIDDEN EXPLOSIVES IN LUGGAGE

The increasing number of acts of terrorism particularly dangerous in airflights have made it necessary to find methods of detecting explosives hidden in luggage. Helf [6] gave a detailed description of the existing method, which consists in irradiating the luggage or suspect package with fast neutrones followed by the measurement of γ-irradiation from the activated explosive if present in the examined package. It is based on the assumption that most explosives contain nitrogen – usually greater than in items present in luggage.

Here is a description of the process as given by Helf: 'when an explosive is irradiated with fast neutrones a ^{14}N nucleus captures the incident fast neutron and ejects two slow neutrons. The resulting nucleus ^{13}N is radioactive and decays with a 10 min half-life to stable ^{13}C. In this last transition a positron β^+ is emitted. Because of its opposite charge, the β^+ is strongly attracted by the nearby electron; in the resulting collision, both the positron and electron are annihilated and in that process the masses of colliding particles are converted into two 0.511 MeV quanta of electromagnetic radiation.

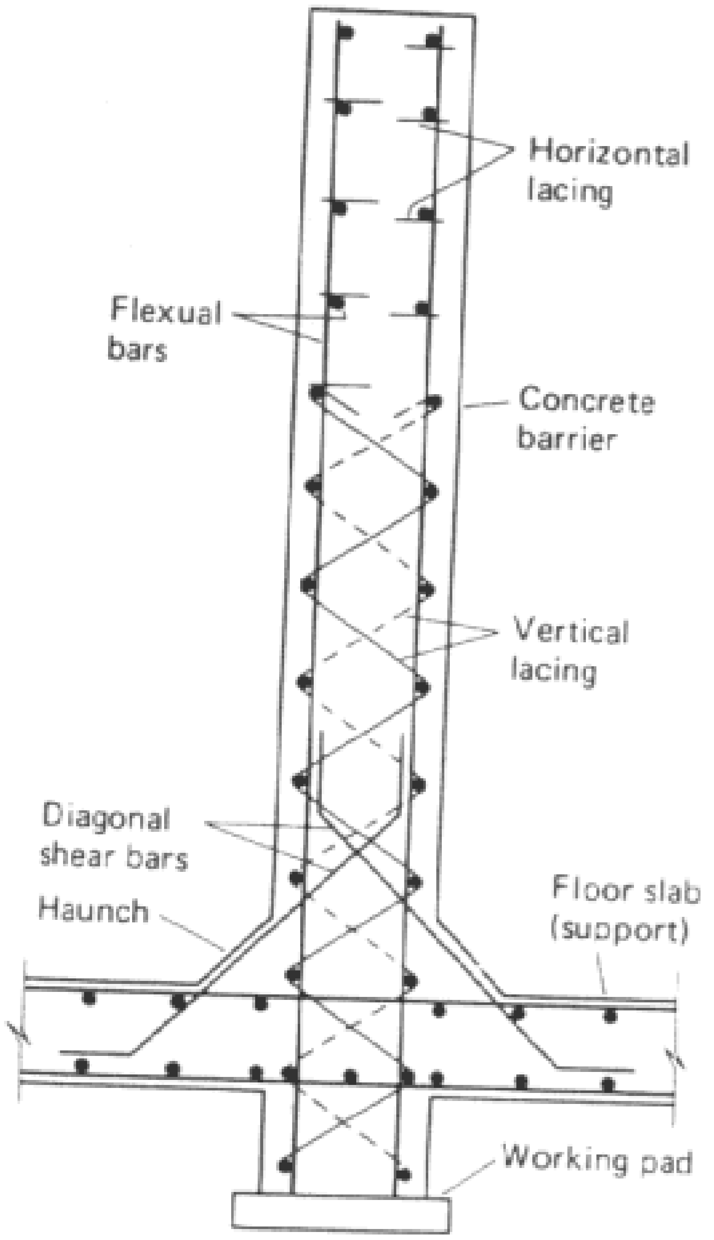

FIG. 131. Typical laced concrete wall according to Kaye [5].

These γ-rays are what are detected to indicate the possible presence of an explosive'.

Figure 132 gives a scheme of the functioning of the apparatus worked out by North American Rockwell Corp. (Los Angeles) 'A conveyer belt transports the luggage first past a neutron generator and then past a detector. The radiation detected is amplified, analysed and compared with a preset threshold. If the detected radiation surpasses the threshold, a visual alarm is activated'.

Both generator and detector should be heavily shielded by concrete and lead, to protect the environment from the harmful radiation.

The drawback of this system is in the fact that harmless substances containing nitrogen, such as wool and synthetic fibres can give a signal similar to that of explosives.

Picatinny Arsenal [6] developed a method of activating both nitrogen and oxygen considering that explosives contain a characteristic ratio N/O and thus lower the proportion of false alarms.

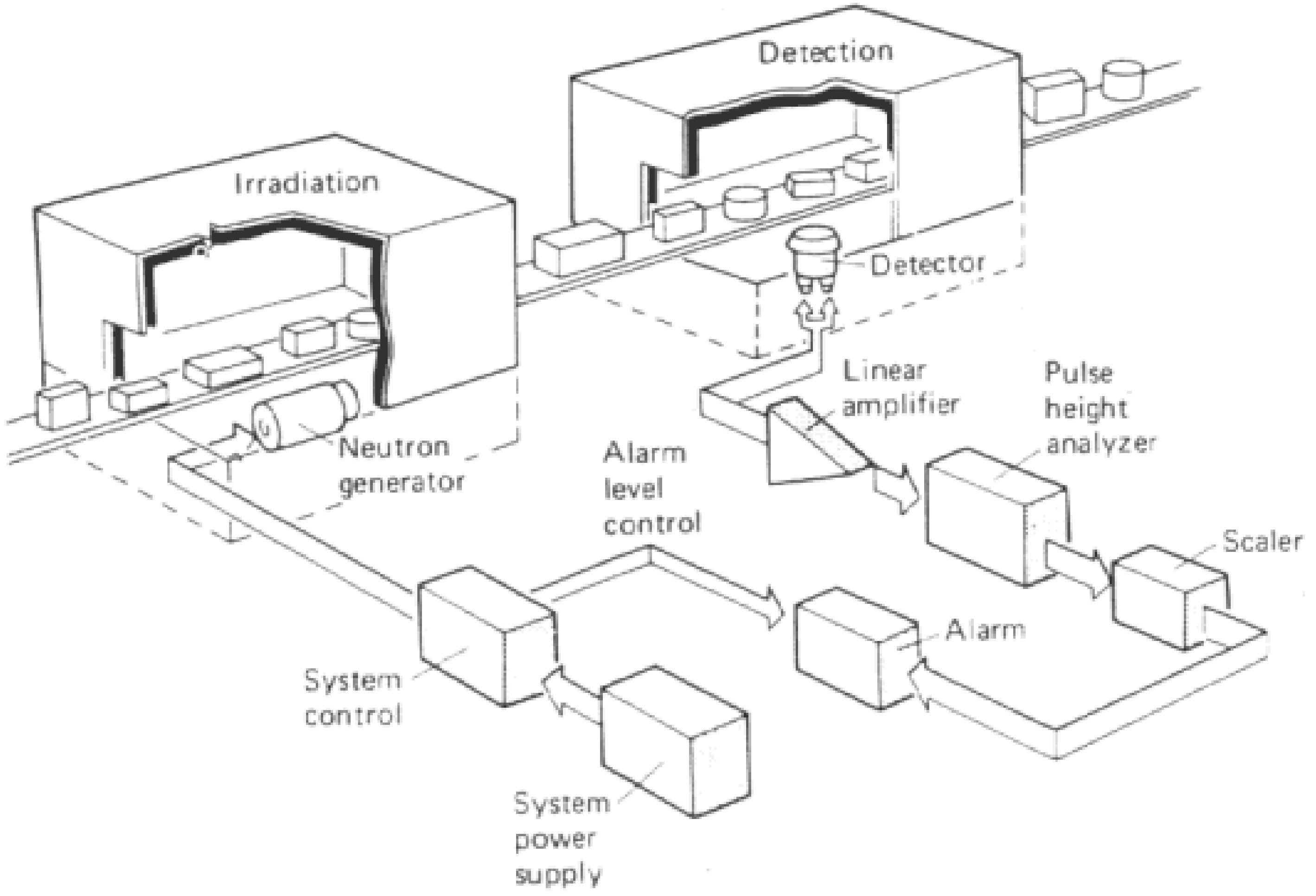

FIG. 132. Fast neutron activation system for the inspection of airline luggage for the presence of hidden explosives, according to Helf [6].

TAGGING OF COMMERCIAL EXPLOSIVES

It is now required in the United States that commercial explosives should be 'tagged' in such a way that the detection and post-detonation identification of explosives should be possible. Materials added to explosives for these purposes are called taggants.

The information on taggants was given by Boyars [7]. They are tiny coded particles added to explosives during their manufacture that 'can survive detonation in sufficient quantity to be recovered and decoded and, through distribution records, allow the explosives to be traced back to the last legal possessor. They are incorporated in quantities of 0.05% or less by the explosives manufacturers'.

They are made of a laminated melaminealkyd core encapsulated in polyethylene wax. The core is colour coded by the inclusion of pigments. One of the layers contains iron particles to make the taggant magnet-sensitive and one or both exterior layers contain fluorescent compounds which respond to ultraviolet radiation.

Obviously they should not increase the sensitivity to impact, friction and chemical (thermal) stability.

Two types of taggants are in use:

Type A (unencapsulated) and C (encapsulated).

Type B made of melamineacrylic resin is hard and has sensitized explosives, it seems not to be in use.

GENERAL DESCRIPTION OF SAFETY

A general description of safety in the manufacture, handling and storage of 'Reactive Chemicals' and mainly of explosives is described in a Japanese book [14]. It contains chapters on:

1. Fire and explosion hazards from reactive chemicals
2. Estimation of energy hazards
3. Computational prediction of explosion, deflagration and exothermic decomposition
4. Standard tests for reactive chemicals
5. Screening tests
6. Comprehensive evaluation
7. Activities of safety organization in various countries
8. Emergency response system for hazardous material
9. Earthquake countermeasures.

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CHAPTER 25

TOXICITY OF EXPLOSIVES

The toxicity of explosives was described in Vols I–III and more information has appeared recently as a result of the progress of toxicology and hygiene. Thus the former information needs some additions. An excellent review of the toxic properties of more important explosives was recently given by Rosenblatt [1]. Some information from this and other sources will be given below.

AROMATIC NITRO COMPOUNDS

m-Dinitrobenzene

The toxicity of this compound is of a great importance because of its intensity and also because of the importance of the substance as an intermediate in organic industry. The toxicity of *m*-DNB was described in Vol. I, pp. 240–242 and also in this volume: Chapter VI, refs [8, 82, 83]. Many fatal accidents have been attributed to poisoning by TNT were caused in fact by the impurities of TNT produced by the presence of small proportions of *m*-DNB. Rosenblatt [1] reported that 24,000 cases of poisoning with TNT were recorded during World War I and out of this 580 were fatal. During World War II the number of fatalities was only 22.

This should be attributed not only to better hygiene (as pointed out by Rosenblatt) but also to the higher purity of TNT, because of a higher purity of toluene used for the nitration.

As already pointed out (Vol. I, p. 240) dinitrobenzene affects haemoglobin and damages the liver.

2,4-Dinitrotoluene

This compound – an intermediate in the formation of TNT, can also be an impurity of TNT. The symptoms of poisoning are similar to poisoning with other nitro compounds the chief clinical findings are [1]: pallor, cyanosis and anaemia in which the blood cells are of normal size and contain normal amounts of haemoglobin. Patients recover from DNT poisoning after being treated in a DNT free atmosphere.

The lethal dose in rats (LD_{50}) was found to be 568–650 mg/kg. Dogs showed high sensitivity: doses 20–25 mg/kg/day were toxic in subchronic test which lasted 90 days, and in some cases were lethal. It was also found that 2,4-DNT is carcinogenic in mammalian animals.

2,4,6-Trinitrotoluene

TNT exposures can occur by inhalation of the dust, through ingestion and via skin absorption [1]. The action of TNT produces changes in blood: the red blood cells count and haemoglobin content decreases on longer exposure because the activity of the bone marrow is lowered. Another type of symptoms are due to atrophy of the liver. No carcinogenic effect has been recorded in men or animals.

The maximum permissible inhalation level in U.S.S.R. is 1.0 mg/m^3 and in the U.S.A. Army 0.5 mg/m^3.

The lethal dose by oral administration (LD_{50}) in rats is 820–1010 mg/kg.

Among metabolites in humans the following were identified: 4-amino- and 6-aminodinitrotoluene, tetranitroazoxytoluene, 2-hydroxylamino-4,6-dinitrotoluene, 2,4-diamino-6-nitro- and 2,6-diamino-4-nitrotoluene, 2,4,6-trinitrobenzoic acid. A former finding that TNT is toxic to fish has been confirmed.

'Red water' from the treatment of TNT with sodium sulphite is more toxic than TNT, this is mainly due to the presence of dinitrotoluene derivatives.

ALIPHATIC NITRO COMPOUNDS

2-Nitropropane

2-Nitropropane is being used extensively in the U.S.A. as a solvent. It was recently reported that prolonged exposure of rats to the action of 2-nitropropane can produce cancer [2].

Tetranitromethane

Experiments with animals show that inhalation of tetranitromethane can produce respiratory tract irritation and severe pneumonia but no methaemoglobinaemia [1].

NITRATE ESTERS

Methyl Nitrate [1]

The action is similar to nitroglycerine, but much weaker. Oral LD_{50} in rats was 344 mg/kg. Inhalation of 117 mg by humans induce headache.

Nitroglycerine [1]

It is known in medicine as a vasodilator and there is an extensive literature on its biochemical and clinical aspects. The most common dose is *ca*. 0.01 mg/kg. Chronic human exposure to NG produces a methemoglobinaemia and the development of tolerance to the drug. Withdrawal from frequent exposure to NG may cause severe headaches. The LD_{50} in rats is 822–884 mg/kg by oral administration. It is toxic to fish, e.g. LD_{50} 1.38 mg/l.

Nitrocellulose

Owing to the insolubility of nitrocellulose, no toxic effect has been found to experimental animals including fish.

NITRAMINES

Nitroguanidine

It is of very low toxicity. LD_{50} in rats was found to be 4640 mg/kg. [1].

Cyclonite (RDX, Hexogene)

More information has been collected on the toxicity of Cyclonite. Experiments with animals confirmed earlier findings on convulsions caused by Cyclonite. Important observations with humans were: the same effects were caused by inhaling the dust of Cyclonite and one fatal accident was recorded [3]. Rosenblatt [1] described acute intoxication of soldiers either chewing a plastic explosive C–4 containing 91% RDX or using it for cooking and inhaling the fumes. RDX intoxication involves gastrointestinal, central nervous system and renal effects. No liver involvement has been recorded and the cerebrospinal fluid was normal.

Acute toxicity in rats (LD_{50}) was determined: by oral administration 200 mg/kg and by intravenous and intraperitoneal administration: 18 mg/kg and 10 mg/kg respectively. Chronic toxicity by oral administration to rats gave variable results: in one series of experiments 10 mg/kg daily in rats for two years showed no toxic symptoms except a retarded weight in females. No carcinogenic effect was found.

In fish LD_{50} was found to be *ca*. 3.6 mg/l.

Octogene (HMX)

Very low solubility of HMX (as compared with RDX) makes experiments on toxicity of the compounds less conclusive than with RDX. So far it appears that HMX is less toxic than RDX [1].

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