CHAPTER IX

PRIMARY EXPLOSIVES, DETONATORS, AND PRIMERS

Primary explosives explode from shock, from friction, and from heat. They are used in primers where it is desired by means of shock or friction to produce fire for the ignition of powder, and they are used in detonators where it is desired to produce shock for the initiation of the explosion of high explosives. They are also used in toy caps, toy torpedoes, and similar devices for the making of noise. Indeed, certain primary explosives were used for this latter purpose long before the history of modern high explosives had yet commenced.

Discovery of Fulminating Compounds

Fulminating gold, silver, and platinum (Latin, *fulmen,* lightning flash, thunderbolt) are formed by precipitating solutions of these metals with ammonia. They are perhaps nitrides or hydrated nitrides, or perhaps they contain hydrogen as well as nitrogen and water of composition, but they contain no carbon and must not be confused with the fulminates which are salts of fulminic acid, HONC. They are dangerously sensitive, and are not suited to practical use.

Fulminating gold is described in the writings of the pseudonymous Basil Valentine,[1] probably written by Johann Thölde (or Thölden) of Hesse and actually published by him during the years 1602–1604. The author called it *Goldkalck,* and prepared it by dissolving gold in an *aqua regia* made by dissolving sal ammoniac in nitric acid, and then precipitating by the addition of potassium carbonate solution. The powder was washed by decantation 8 to 12 times, drained from water, and dried in the air where no sunlight fell on it, "and not by any means over the

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[1] We find the description on page 289 of the second part of the third German edition of the collected writings of Basil Valentine, Hamburg, 1700.

fire, for, as soon as this powder takes up a very little heat or warmth, it kindles forthwith, and does remarkably great damage, when it explodes with such vehemence and might that no man would be able to restrain it." The author also reported that warm distilled vinegar converted the powder into a material which was no longer explosive. The name of *aurum fulminans* was given to the explosive by Beguinus who described its preparation in his *Tyrocinium Chymicum,* printed in 1608.

Fulminating gold precipitates when a solution of pure gold chloride is treated with ammonia water. The method of preparation described by Basil Valentine succeeds because the sal ammoniac used for the preparation of the *aqua regia* supplies the necessary ammonia. If gold is dissolved in an *aqua regia* prepared from nitric acid and common salt, and if the solution is then treated with potassium carbonate, the resulting precipitate has no explosive properties. Fulminating gold loses its explosive properties rapidly if it is allowed to stand in contact with sulfur.

Fulminating gold was early used both for war and for entertainment. The Dutch inventor and chemist, Cornelis Drebbel, being in the service of the British Navy, devoted considerable time to the preparation of fulminating gold and used his material as a detonator in petards and torpedoes in the English expedition against La Rochelle in 1628. Pepys, in his diary for November 11, 1663, reports a conversation with a Dr. Allen concerning *aurum fulminans* "of which a grain . . . put in a silver spoon and fired, will give a blow like a musquett and strike a hole through the silver spoon downward, without the least force upward."

Fulminating silver was prepared in 1788 by Berthollet who precipitated a solution of nitrate of silver by means of lime water, dried the precipitated silver oxide, treated it with strong ammonia water which converted it into a black powder, decanted the liquid, and left the powder to dry in the open air. Fulminating silver is more sensitive to shock and friction than fulminating gold. It explodes when touched; it must not be enclosed in a bottle or transferred from place to place, but must be left in the vessel, or better upon the paper, where it was allowed to dry.

The black material which deposits in a reagent bottle of ammoniacal silver nitrate, and sometimes collects on the rim and around the stopper, contains fulminating silver. Explosions are reported to have been caused by the careless turning of the glass stopper of a bottle containing this reagent. After a test (for aldehyde, for example) has been made with ammoniacal silver nitrate solution, the liquid ought promptly to be washed down the sink, and all insoluble matter left in the vessel ought to be dissolved out with dilute nitric acid.

Fulminating platinum was first prepared by E. Davy, about 1825, by adding ammonia water to a solution of platinum sulfate, boiling the precipitate with a solution of potash, washing, and allowing to dry. It was exploded by heat, but not easily by percussion or friction.

Fourcroy prepared a *fulminating mercury* by digesting red oxide of mercury in ammonia water for 8 or 10 days. The material became white and finally assumed the form of crystalline scales. The dried product exploded loudly from fire, but underwent a spontaneous decomposition when left to itself. At slightly elevated temperatures it gave off ammonia and left a residue of mercury oxide.

In the *Journal de physique* for 1779 the apothecary, Bayen, described a fulminating mercurial preparation of another kind. Thirty parts of precipitated, yellow oxide of mercury, washed and dried, was mixed with 4 or 5 parts of sulfur; the mixture exploded with violence when struck with a heavy hammer or when heated on an iron plate. Other mixtures which react explosively when initiated by percussion have been studied more recently,[2] metallic sodium or potassium in contact with the oxide or the chloride of silver or of mercury or in contact with chloroform or carbon tetrachloride.

The explosion of chloroform in contact with an alkali metal may be demonstrated by means of the apparatus illustrated in Figure 92. About 0.3 gram of sodium or of potassium or of the liquid alloy of the two is introduced into a thin-wall glass tube, or, better yet, is sealed up in a small glass bulb, 6 to 8 mm. in diameter, which has a capillary 15 to 20 mm. in length. The tube or bulb containing the alkali metal is placed in the bottom of a narrow test tube into which 1 or 2 cc. of chloroform has already been introduced, and the apparatus is then

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[2] Staudinger, *Z. Elektrochem.*, **31**, 549 (1925); Davis and McLean, *J. Am. Chem. Soc.*, **60**, 720 (1938).

ready for the experiment. Or, if it is desired to prepare in advance an explosive capsule which can safely be kept as long as desired, then the bulb is held in place at the bottom of the test tube by a collar of glass (a section of glass tubing) sintered to the inner wall of the test tube, and the top of the test tube is drawn down and sealed. When the prepared test tube or capsule is dropped onto a concrete pavement from a height of 6 feet, a loud explosion is produced accompanied by a bright flash which is visible even in the direct sunlight. The chemical reaction is as follows, each one of the three chlorine atoms of the chloroform reacting in a different manner.

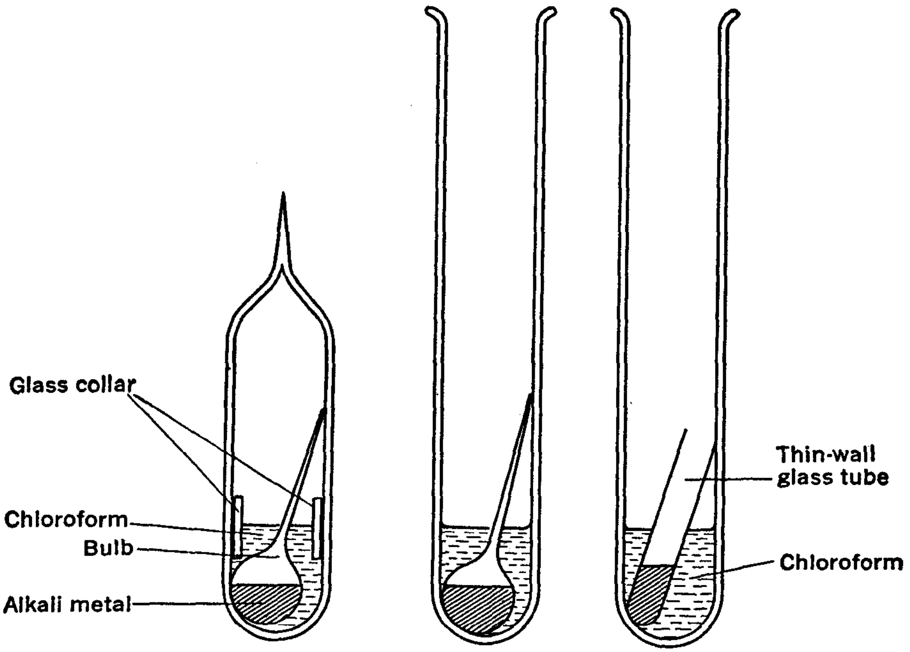
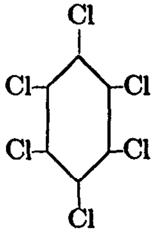


FIGURE 92. Apparatus for Demonstrating the Explosion of Chloroform with an Alkali Metal.

$$6CHCl_3 + 6Na \longrightarrow 6NaCl + 6HCl +$$



Mercury fulminate appears to have been prepared for the first time by Johann Kunckel von Löwenstern (1630–1703), the same chemist who discovered phosphorus and applied the purple of

Cassius practically to the manufacture of ruby glass. In his posthumous *Laboratorium Chymicum* he says: [3]

> Further evidence that mercury is cold is to be seen when you dissolve it in *aqua fortis* (nitric acid), evaporate the solution to dryness, pour highly rectified *spiritum vini* (alcohol) over the residue, and then warm it slightly so that it begins to dissolve. It commences to boil with amazing vigor. If the glass is somewhat stopped up, it bursts into a thousand pieces, and, in consequence, it must by no means be stopped up. I once dissolved silver and mercury together in *aqua fortis* and poured over it an excess of *spiritum vini*, and set the mixture to putrify *in fimum equinum* (horse manure) after having stopped up the glass with mere sealing wax only. When it happened a few days later that the manure became a little warm, it made such a thunder-crack, with the shattering of the glass, that the stable-servant imagined, since I had put it in a box, either that someone had shot at him through the window or that the Devil himself was active in the stable. As soon as I heard this news, I was able easily to see that the blame was mine, that it must have been my glass. Now this was with silver and mercury, 2 *loth* of each. Mercury does the same thing [4] alone, but silver not at all.

The preparation and properties of mercury fulminate were described in much detail by Edward Howard [5] in 1800 in a paper presented to the Royal Society of London. The method of preparation which he found to be most satisfactory was as follows: 100 grains of mercury was dissolved by heating in 1½ drams of nitric acid (specific gravity 1.3), the solution was cooled and added to 2 ounces of alcohol (specific gravity 0.849) in a glass vessel, the mixture was warmed until effervescence commenced, the reaction was allowed to proceed to completion, and the precipitate which formed was collected on a filter, washed with distilled water, and dried at a temperature not exceeding that of the water bath. Howard found that the fulminate was exploded by means of an electric spark or by concentrated sulfuric acid brought into contact with it. When a few grains were placed on a

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[3] Kunckel, "Collegium Physico-Chymicum Experimentale, oder Laboratorium Chymicum," ed. Engelleder, Hamburg, 1716, p. 213. Cf. Davis, *Army Ordnance*, 7, 62 (1926).

[4] Kunckel's meaning in the last sentence is evidently that mercury nitrate reacts with alcohol on warming, and that silver nitrate does not react with alcohol under the same conditions.

[5] *Phil. Trans. Roy. Soc.*, 204 (1800).

cold anvil and struck with a cold hammer, a very stunning disagreeable noise was produced and the faces of the hammer and anvil were indented. A few grains floated in a tinfoil capsule on hot oil exploded at 368°F. (186.7°C.). When a mixture of fine- and coarse-grain black powder was placed on top of a quantity of fulminate and the fulminate was fired, the black powder was blown about but it was not ignited and was recovered unchanged. Howard also attempted by means of alcohol to produce fulminating compounds from gold, platinum, antimony, tin, copper, iron, lead, nickel, bismuth, cobalt, arsenic, and manganese, but silver was the only one of these metals with which he had any success.

Brugnatelli in 1802 worked out a satisfactory method for the preparation of silver fulminate by pouring onto 100 grains of powdered silver nitrate first an ounce of alcohol and then an ounce of nitric acid. After the fulminate had precipitated, the mixture was diluted with water to prevent it from dissolving again and immediately filtered. Silver fulminate explodes more easily from heat and from friction than mercury fulminate and is more spectacular in its behavior. It quickly became an object of amateur interest and public wonderment, one of the standard exhibits of street fakirs and of mountebanks at fairs. Liebig, who was born in 1803, saw a demonstration of silver fulminate in the market place at Darmstadt when he was a boy. He watched the process closely, recognized by its odor the alcohol which was used, went home, and succeeded in preparing the substance for himself. He retained his interest in it, and in 1823 carried out studies on the fulminates in the laboratory of Gay-Lussac at Paris.

Mercury Fulminate

The commercial preparation of mercury fulminate is carried out by a process which is essentially the same as that which Howard originally recommended. Five hundred or 600 grams of mercury is used for each batch, the operation is practically on the laboratory scale, and several batches are run at the same time. Since the reaction produces considerable frothing, capacious glass balloons are used. The fumes, which are poisonous and inflammable, are passed through condensers, and the condensate, which contains alcohol, acetaldehyde, ethyl nitrate, and ethyl nitrite, is utilized by mixing it with the alcohol for the next batch.

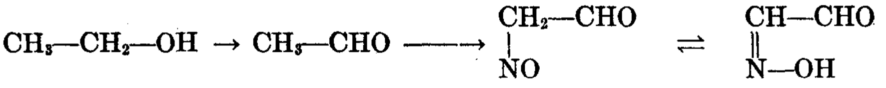
Pure fulminate is white, but the commercial material is often grayish in color. The color is improved if a small amount of cupric chloride is added to the nitric acid solution of mercury before it is poured into the alcohol in the balloon, but the resulting white fulminate is actually less pure than the unbleached material.

Preparation of Mercury Fulminate. Five grams of mercury is added to 35 cc. of nitric acid (specific gravity 1.42) in a 100-cc. Erlenmeyer flask, and the mixture is allowed to stand without shaking until the mercury has gone into solution. The acid liquid is then poured into 50 cc. of 90% alcohol in a 500-cc. beaker in the hood. The temperature of the mixture rises, a vigorous reaction commences, white fumes come off, and crystals of fulminate soon begin to precipitate. Red fumes appear and the precipitation of the fulminate becomes more rapid, then white fumes again as the reaction moderates. After about 20 minutes the reaction is over; water is added, and the crystals are washed with water repeatedly by decantation until the washings are no longer acid to litmus. The product consists of grayish-yellow crystals, and corresponds to a good grade of commercial fulminate. It may be obtained white and entirely pure by dissolving in strong ammonia

FIGURE 93. Fulminate Manufacture. (Courtesy Atlas Powder Company.) At left, flasks in which mercury is dissolved in nitric acid. At right, balloons in which the reaction with alcohol occurs.

water, filtering, and reprecipitating by the addition of 30% acetic acid. The pure fulminate is filtered off, washed several times with cold water, and stored under water, or, if a very small amount is desired for experimental purposes, it is dried in a desiccator.

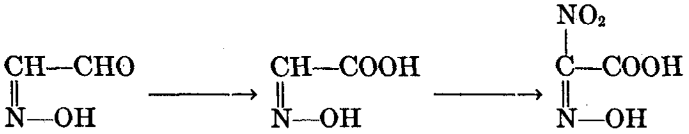
The chemical reactions in the preparation appear to be as follows. (1) The alcohol is oxidized to acetaldehyde, and (2) the nitrous acid which is formed attacks the acetaldehyde to form a nitroso derivative which goes over to the more stable, tautomeric, isonitroso form.



$$CH_3{-}CH_2{-}OH \rightarrow CH_3{-}CHO \longrightarrow \begin{array}{l} CH_2{-}CHO \\ | \\ NO \end{array} \rightleftharpoons \begin{array}{l} CH{-}CHO \\ \| \\ N{-}OH \end{array}$$

Nitrosoacetaldehyde Isonitrosoacetaldehyde

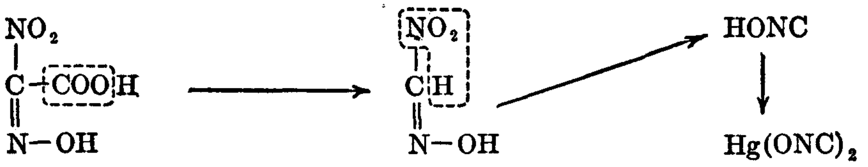
(3) The isonitrosoacetaldehyde is oxidized to isonitrosoacetic acid, and (4) this is nitrated by the nitrogen dioxide which is present to form nitroisonitrosoacetic acid.



$$\begin{array}{l} CH{-}CHO \\ \| \\ N{-}OH \end{array} \longrightarrow \begin{array}{l} CH{-}COOH \\ \| \\ N{-}OH \end{array} \longrightarrow \begin{array}{l} NO_2 \\ | \\ C{-}COOH \\ \| \\ N{-}OH \end{array}$$

Isonitrosoacetic acid Nitroisonitrosoacetic acid

(5) The nitroisonitrosoacetic acid loses carbon dioxide to form formonitrolic acid which (6) decomposes further into nitrous acid and fulminic acid, and (7) the fulminic acid reacts with the mercury nitrate to form the sparingly soluble mercury fulminate which precipitates.



$$\begin{array}{l} NO_2 \\ | \\ C{-}\boxed{COO}H \\ \| \\ N{-}OH \end{array} \longrightarrow \begin{array}{l} \boxed{NO_2} \\ | \\ C\boxed{H} \\ \| \\ N{-}OH \end{array} \longrightarrow \begin{array}{c} HONC \\ \downarrow \\ Hg(ONC)_2 \end{array}$$

Formonitrolic acid Mercury fulminate

Fulminate can be prepared from acetaldehyde instead of from alcohol, and from substances which are convertible into acetaldehyde, such as paraldehyde, metaldehyde, dimethyl- and diethylacetal. Methyl alcohol, formaldehyde, propyl alcohol, butyraldehyde, glycol, and glyoxal do not yield fulminate.[6]

Fulminate can, however, be prepared from a compound which contains only one carbon atom. The sodium salt of nitromethane gives with an aqueous solution of mercuric chloride at 0° a white

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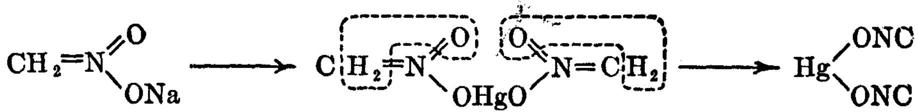
[6] Wöhler and Theodorovits, *Ber.*, **38**, 1345 (1905).

precipitate of the mercuric salt of nitromethane which gradually becomes yellow and which, digested with warm dilute hydrochloric acid, yields mercury fulminate.[7]



Sodium fulminate, soluble in water, has a molecular weight which corresponds[8] to the simple monomolecular formula, NaONC. These facts, taken together with the fact that mercury fulminate warmed with concentrated aqueous hydrochloric acid yields hydroxylamine and formic acid,[9] prove that fulminic acid is the oxime of carbon monoxide.

$$HO{-}N{=}C\Large\substack{\cdot^{\cdot^{\cdot}}\\ \cdot_{\cdot_{\cdot}}} + 2H_2O \longrightarrow HO{-}NH_2 + H{-}COOH$$

Mercury fulminate dissolves readily in an aqueous solution of potassium cyanide to form a complex compound from which it is reprecipitated by the addition of strong acid. It dissolves in pyridine and precipitates again if the solution is poured into water. A sodium thiosulfate solution dissolves mercury fulminate with the formation of mercury tetrathionate and other inert compounds, and this reagent is used both for the destruction of fulminate and for its analysis.[10] The first reaction appears to be as follows.

$$Hg(ONC)_2 + 2Na_2S_2O_3 + H_2O \longrightarrow HgS_4O_6 + 2NaOH + NaCN + NaNCO$$

The cyanide and cyanate are salts of weak acids and are largely hydrolyzed, and the solution, if it is titrated immediately, appears to have developed four molecules of sodium hydroxide for every molecule of mercury in the sample which was taken. If the solution is allowed to stand, the alkalinity gradually decreases because of a secondary reaction whereby sulfate and thiocyanate are formed.

[7] Nef, *Ann.*, **280**, 275 (1894); Jones, *Am. Chem. J.*, **20**, 33 (1898).

[8] Wöhler, *Ber.*, **43**, 754 (1910).

[9] Carstenjen and Ehrenberg, *J. prak. Chem.*, [2] **25**, 232 (1883); Steiner, *Ber.*, **16**, 1484, 2419 (1883); Divers and Kawita, *J. Chem. Soc.*, **45**, 17 (1884).

[10] Brownsdon, *Chem. News*, **89**, 303 (1904); Philip, *Z. ges. Schiess- u. Sprengstoffw.*, **7**, 109, 156, 180, 198, 221 (1912); Taylor and Rinkenbach, "Explosives, Their Materials, Constitution, and Analysis," *U. S. Bureau of Mines Bulletin* 219, Washington, 1923, p. 62.

$$HgS_4O_6 + NaCN + NaNCO + 2NaOH \longrightarrow HgSO_4 + Na_2SO_4 + 2NaNCS + H_2O$$

This reaction is restrained by a large excess of thiosulfate, and even more effectively by potassium iodide. A moderate excess of thiosulfate is commonly used, and an amount of potassium iodide equal to 10 times the weight of the fulminate, and the titration for acidity (methyl orange indicator) is made as rapidly as possible. After that, the same solution is titrated with iodine (starch indicator) to determine the amount of unused thiosulfate and hence, by another method, the amount of actual fulminate in the sample. Speed is not essential in the second titration, for the iodine value does not change greatly with time as does the alkalinity. Blank determinations ought to be made because of the

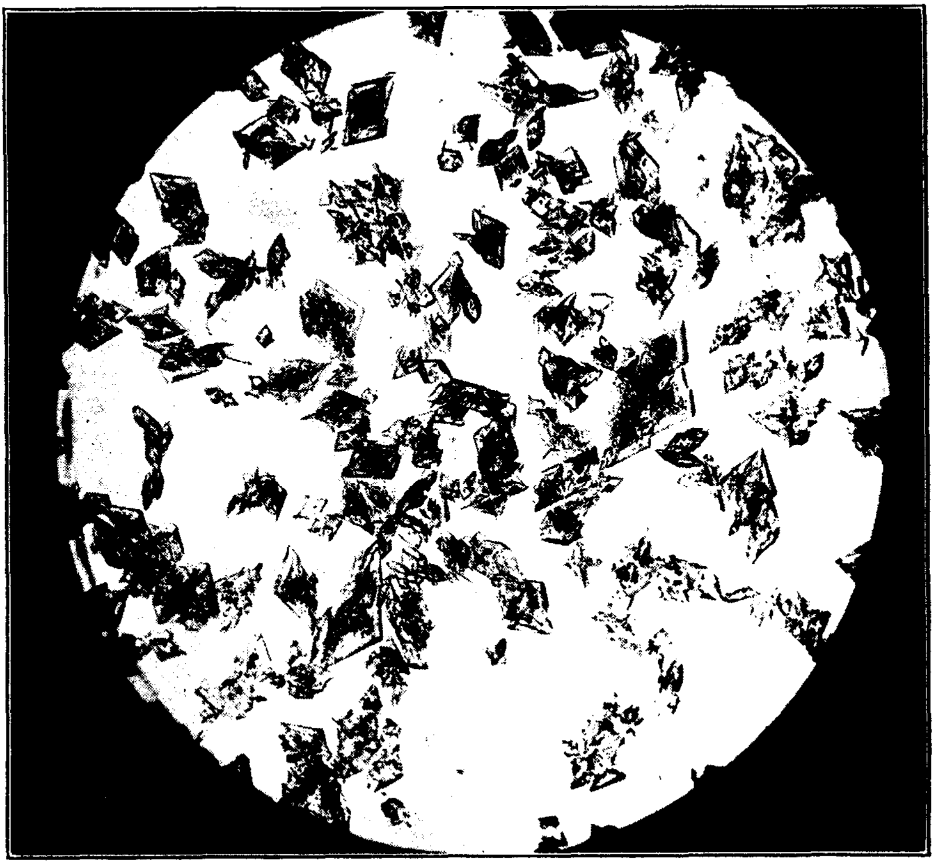


FIGURE 94. Mercury Fulminate Crystals for Use in Primer Composition (30×).

possibility that the iodide may contain iodate, and the apparent analytical results ought to be corrected accordingly.

Mercury fulminate has a specific gravity of 4.45, but a mass of the crystals when merely shaken down has an apparent density (gravimetric density) of about 1.75. In detonators the material is usually compressed to a density of about 2.5, but densities as high as 4.0 have been obtained by vigorous compression. Mercury fulminate crystallizes from water in crystals which contain $\frac{1}{2}H_2O$, from alcohol in crystals which are anhydrous. One liter of water at 12° dissolves 0.71 gram, at 49° 1.74 grams, and at 100° 7.7 grams.

Mercury fulminate is usually stored under water, or, where there is danger of freezing, under a mixture of water and alcohol. When wet it is not exploded by a spark or by ordinary shock, but care must be taken that no part of the individual sample is allowed to dry out, for wet fulminate is exploded by the explosion of dry fulminate. It is not appreciably affected by long storage, either wet or dry, at moderate temperatures. At the temperature of the tropics it slowly deteriorates and loses its ability to explode. At 35°C. (95°F.) it becomes completely inert after about 3 years, at 50°C. (122°F.) after about 10 months. The heavy, dark-colored product of the deterioration of fulminate is insoluble in sodium thiosulfate solution.

When loaded in commercial detonators mercury fulminate is usually compressed under a pressure of about 3000 pounds per square inch, and in that condition has a velocity of detonation of about 4000 meters per second, explodes from a spark, and, in general, has about the same sensitivity to fire and to shock as the loosely compressed material. When compressed under greater and greater pressures, it gradually loses its property of detonating from fire. After being pressed at 25,000–30,000 pounds per square inch, mercury fulminate becomes "dead pressed" and no longer explodes from fire but merely burns. Dead-pressed fulminate however is exploded by loosely pressed fulminate or other initial detonating agent, and then shows a higher velocity of detonation than when compressed at a lower density.

The temperature at which mercury fulminate explodes depends upon the rate at which it is heated and, to some extent, upon the state of subdivision of the sample. Wöhler and Matter[11] experi-

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[11] *Z. ges. Schiess- u. Sprengstoffw.*, **2**, 181, 203, 244, 265 (1907).

mented with small particles of various primary explosives, heated in copper capsules in a bath of Wood's metal. If a sample did not explode within 20 seconds, the temperature of the bath was raised 10° and a new sample was tried. The temperatures at which explosions occurred were as follows.

Mercury fulminate	190°
Sodium fulminate	150°
Nitrogen sulfide	190°
Benzenediazonium nitrate	90°
Chloratotrimercuraldehyde	130°
Silver azide	290°
Basic mercury nitromethane	160°

In a later series of experiments Wöhler and Martin[12] studied a large number of fulminates and azides. The materials were in the form of microcrystalline powders, and all were compressed under the same pressure into pellets weighing 0.02 gram. The temperatures at which explosions occurred within 5 seconds were as follows.

Mercury fulminate	215°
Silver fulminate	170°
Copper fulminate	205°
Cadmium fulminate	215°
Sodium fulminate	215°
Potassium fulminate	225°
Thallium fulminate	120°
Cobalt azide	148°
Barium azide	152°
Calcium azide	158°
Strontium azide	169°
Cuprous azide	174°
Nickel azide	200°
Manganese azide	203°
Lithium azide	245°
Mercurous azide	281°
Zinc azide	289°
Cadmium azide	291°
Silver azide	297°
Lead azide	327°

Wöhler and Martin[13] in the same year also reported determinations of the smallest amounts of certain fulminates and

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[12] *Z. angew. Chem.*, 30, 33 (1917).

[13] *Z. ges. Schiess- u. Sprengstoffw.*, 12, 1, 18 (1917).

azides necessary to cause the detonation of various high explosives.

Smallest Amount (Grams) Which Will Cause Detonation of:	Tetryl	Picric Acid	Trinitrotoluene	Trinitroanisol	Trinitroxylene
Cadmium azide	0.01	0.02	0.04	0.1	..
Silver azide	0.02	0.035	0.07	0.26	0.25
Lead azide	0.025	0.025	0.09	0.28	..
Cuprous azide	0.025	0.045	0.095	0.375	0.40
Mercurous azide	0.045	0.075	0.145	0.55	0.50
Thallium azide	0.07	0.115	0.335	...	..
Silver fulminate	0.02	0.05	0.095	0.23	0.30
Cadmium fulminate	0.008	0.05	0.11	0.26	0.35
Copper fulminate	0.025	0.08	0.15	0.32	0.43
Mercury fulminate	0.29	0.30	0.36	0.37	0.40
Thallium fulminate	0.30	0.43	...	...	..

From these data it is apparent that mercury fulminate is by no means the most efficient initiating agent among the fulminates and azides. Silver fulminate is about 15 times as efficient as mercury fulminate for exploding tetryl, but only about ⅓ as efficient for exploding trinitroxylene. Mercury fulminate however will tolerate a higher temperature, and is much less sensitive to shock and friction, than silver fulminate. Lead azide, which has about the same initiating power as silver fulminate, has an explosion temperature more than 100° higher than that of mercury fulminate. Many other interesting inferences are possible from the data. Among them we ought especially to note that the order of the several fulminates and azides with respect to their efficiency in detonating one explosive is not always the same as their order with respect to their efficiency in detonating another.

Silver Fulminate

Silver fulminate is so sensitive and so dangerous to handle that it has not been used for practical purposes in blasting or in the military art. It early found use in toys, in tricks, and in such devices for entertainment as those which Christopher Grotz described in 1818 in his book on "The Art of Making Fireworks, Detonating Balls, &c."

> Amusements with Fulminating Silver. . . .
>
> Segars.
>
> Are prepared by opening the smoking end, and inserting a little of the silver; close it carefully up, and it is done.
>
> Spiders.
>
> A piece of cork cut into the shape of the body of a spider, and a bit of thin wire for legs, will represent with tolerable exactness this insect. Put a small quantity of the silver underneath it; and on any female espying it, she will naturally tread on it, to crush it, when it will make a loud report.

Silver fulminate is still used for similar purposes in practical jokes, in toy torpedoes (see Vol. I, p. 106), and in the snaps or pull-crackers which supply the noise for bon-boms, joy-boms, and similar favors.

Silver fulminate is insoluble in nitric acid, and is decomposed by hydrochloric acid. It darkens on exposure to light. One liter of water at 13° dissolves 0.075 gram of the salt, and at 30° 0.18 gram. The double fulminate of silver and potassium, AgONC·KONC, is soluble in 8 parts of boiling water.

Detonators

The discovery of the phenomenon of initiation by Alfred Nobel and the invention of the blasting cap[14] stand at the beginning of the development of modern explosives, perhaps the most important discovery and invention in the history of the art. The phenomenon has supplied a basis for the definition of high explosives, that is to say, of those explosives, whether sensitive or insensitive, which are incapable, without the invention, of being used safely and controllably or perhaps even of being used at all.

Nobel's experiments quickly led him to the form of the blasting cap which is now in use, a cylindrical capsule, generally of copper but sometimes of aluminum or zinc, filled for about half of its length with a compressed charge of primary explosive. The charge is fired either by an electric igniter or by a fuse, crimped into place, its end held firmly against the charge in order that the chances of a misfire may be reduced. Its action depends upon the development of an intense pressure or shock. Fulminate of mercury was the only substance known at the time of Nobel's invention which could be prepared and loaded for the purpose with reasonable safety, and caps loaded with straight fulminate were the first to

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[14] Nobel, Brit. Pat. 1345 (1867).

be manufactured. The original fulminate detonators were numbered according to the amount of fulminate which they contained, the same numbers being used throughout the world. The charges of fulminate for the various sizes are shown in the following table,

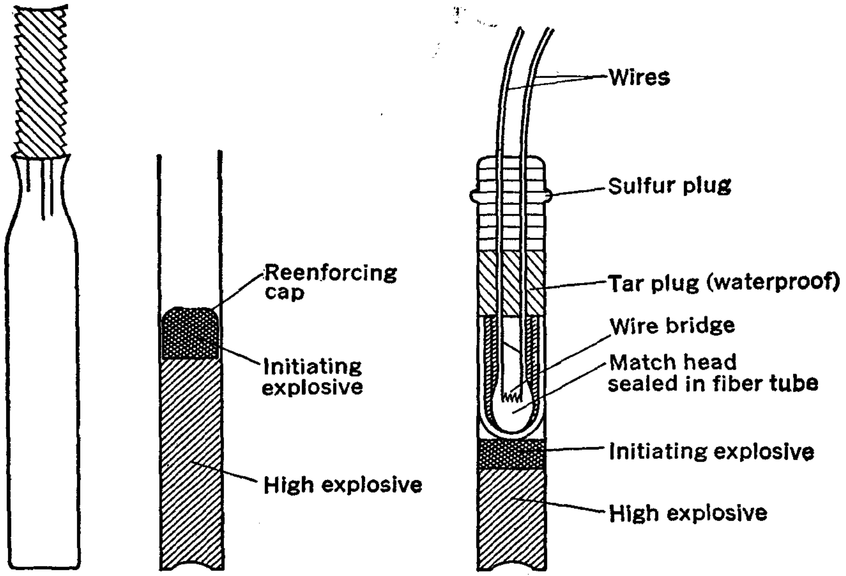

FIGURE 95. Blasting Caps. Detonator crimped to miner's fuse. Compound detonator. Compound electric detonator.

Detonator	Weight of Mercury Fulminate		External Dimensions of Capsule	
	Grams	Grains	Diameter, mm.	Length, mm.
No. 1	0.30	4.6	5.5	16
No. 2	0.40	6.2	5.5	22
No. 3	0.54	8.3	5.5	26
No. 4	0.65	10.0	6	28
No. 5	0.80	12.3	6	30–32
No. 6	1.00	15.4	6	35
No. 7	1.50	23.1	6	40–45
No. 8	2.00	30.9	6–7	50–55

along with the usual (but not universal) dimensions of the cylindrical copper capsules. The same numbers are now applied to commercial blasting caps of the same sizes, whatever the weights and characters of the charges. A No. 6 cap, for example, is a cap of the same size as one which contains 1 gram of straight fulminate. No. 6 caps of different manufacturers may differ in their power

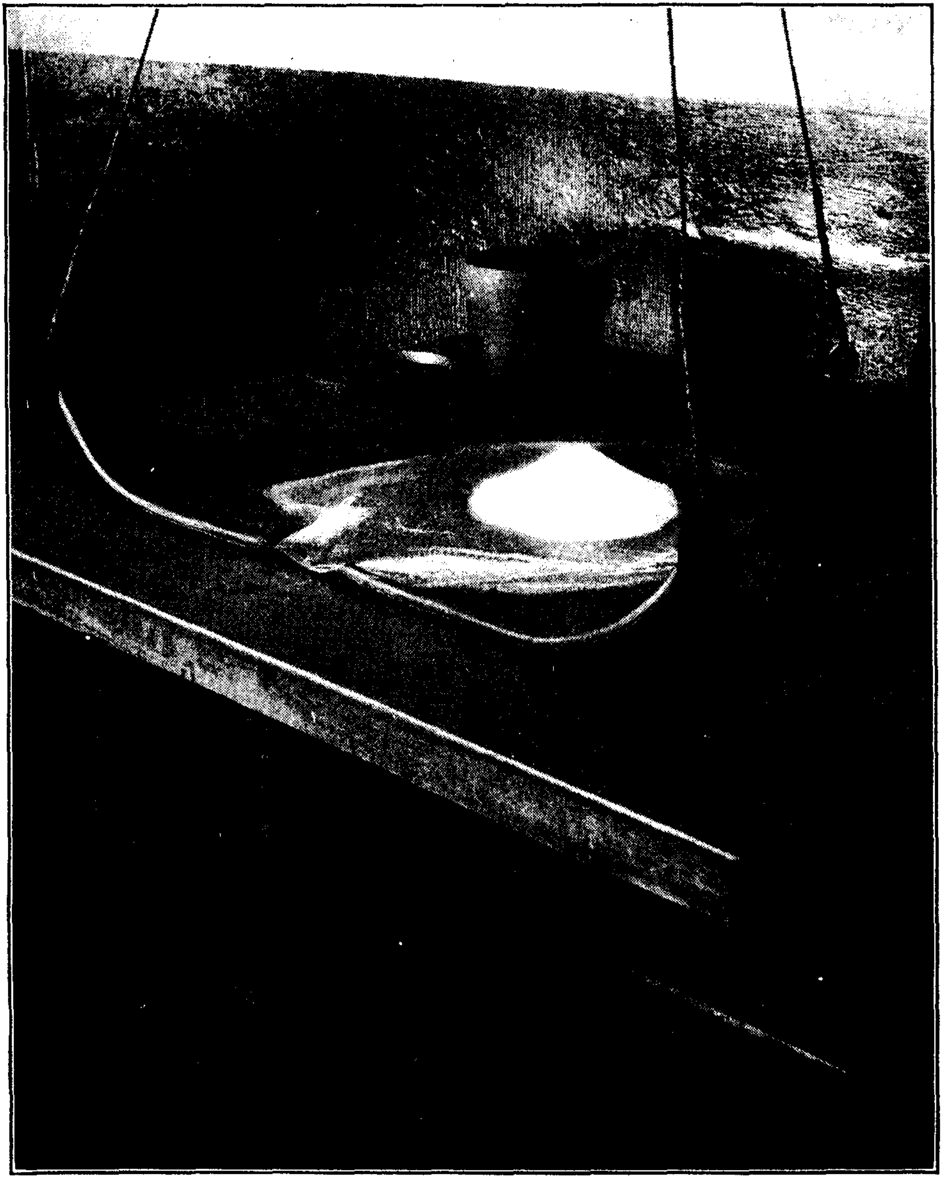

Figure 96. Manufacture of Detonators. (Courtesy Hercules Powder Company.) The safe mixing of the primary explosive charge for blasting caps is accomplished mechanically behind a concrete barricade by lifting slowly and then lowering first one corner of the triangular rubber tray, then the next corner, then the next, and so on. In the background, the rubber bowl or box in which the mixed explosive is carried to the building where it is loaded into caps.

as they differ in their composition. No. 6, 7, and 8 caps are the only ones which are manufactured regularly in the United States, and the No. 6 cap is the one which is most commonly used.

The fulminate in detonators was first modified by mixing it with black powder, then with potassium nitrate, and later with

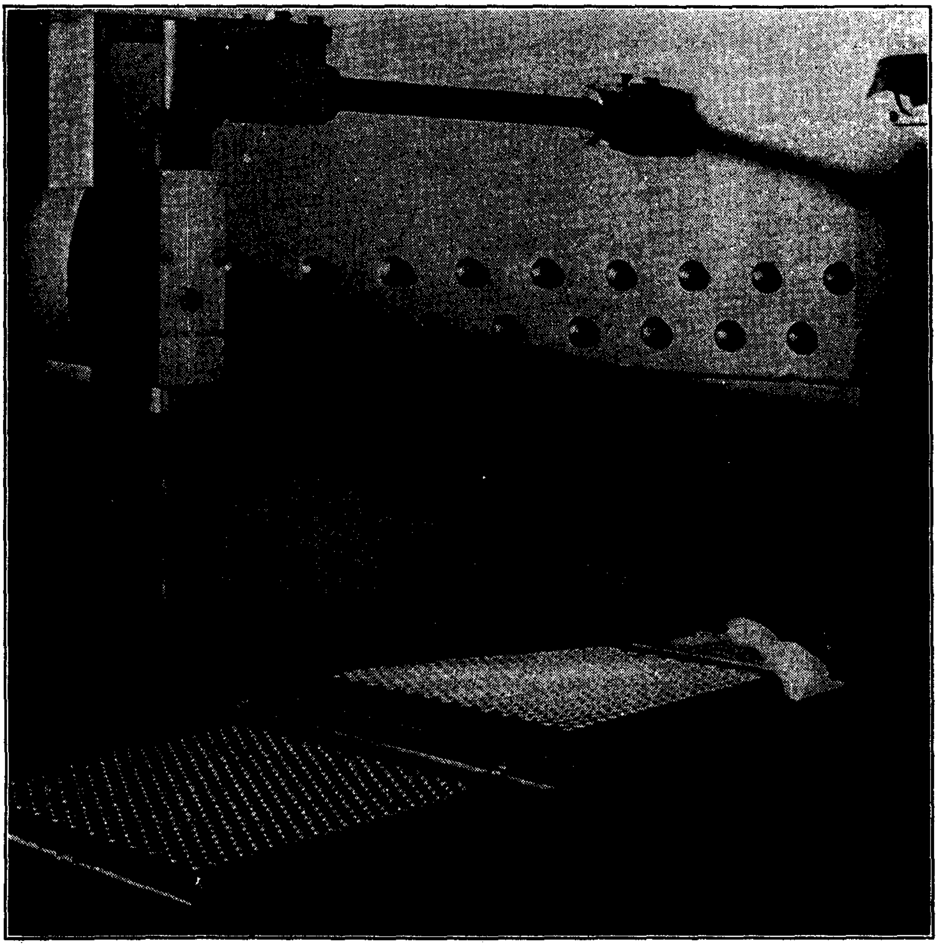

FIGURE 97. Manufacture of Detonators. (Courtesy Hercules Powder Company.) Charging the capsules. Each of the holes in the upper steel plate (*charging plate*) is of the right size to contain exactly enough explosive for the charging of one detonator. The mixed explosive is emptied onto the plate, the rubber-faced arm sweeps the material over the charging plate filling all the holes and throwing the excess into the box at the right. Under the charging plate is the thin *indexing plate* which supplies a bottom to all the holes in the charging plate. The detonator capsules, seen at the left, are placed under the indexing plate and in line with the holes in the charging plate; the indexing plate is then removed, the explosive falls down into the capsules, exactly the right amount into each, and is later pressed into place.

potassium chlorate.[15] The chlorate mixtures soon attained commercial importance in the United States, and by 1910 had largely displaced straight fulminate. Detonators containing them dominated the market until recently, and are now largely, but not yet wholly, displaced by compound detonators in which use is made of the principle of the booster. Mixtures of fulminate and potassium chlorate are distinctly more hygroscopic than straight fulminate, but are cheaper and slightly safer to handle and to load. Weight for weight they make better detonators. Storm and Cope[16] in a series of experiments in the sand test bomb found that 80/20 fulminate-chlorate pulverizes more sand than the same weight of the 90/10 mixture and that this pulverizes more than straight fulminate. The results show that the sand test is an instrument of considerable precision. A difference of 1/40 gram in the size of the charge of fulminate generally caused a difference of more than 1 gram in the weight of sand which was pulverized.

	WEIGHT OF SAND (GRAMS) PULVERIZED FINER THAN 30-MESH BY		
WEIGHT OF CHARGE, GRAMS	Mercury Fulminate	90/10 Fulminate-Chlorate	80/20 Fulminate-Chlorate
2.0000	56.94	58.57	59.68
1.5000	47.71	51.11	52.54
1.0000	38.33	40.13	41.42
0.7500	29.65	32.30	34.28
0.5000	22.45	23.07	23.22
0.4000	17.91	17.90	18.13
0.3500	14.16	15.13	15.94
0.3250	12.20	12.90	13.13
0.3000	10.01	12.71	12.61
0.2500	8.84	9.57	11.94
0.2250	6.93	8.71	10.29
0.2000	5.48	8.33	9.44

Storm and Cope[17] also used the sand test to determine the

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[15] Detonators were manufactured abroad and sold for a time under Nobel's patent, A. V. Newton (from A. Nobel, Paris), Brit. Pat. 16,919 (1887), covering the use, instead of fulminate, of a granulated mixture of lead picrate, potassium picrate, and potassium chlorate, but the invention apparently contributed little to the advance of the explosives art.

[16] C. G. Storm and W. C. Cope, "The Sand Test for Determining the Strength of Detonators," *U. S. Bur. Mines Tech. Paper* **125**, Washington, 1916, p. 43.

[17] *Ibid.*, p. 59.

minimum amounts of fulminate and of the fulminate-chlorate mixtures which were necessary to detonate several high explosives in reenforced detonators. It is necessary to specify that the tests were made with reenforced detonators, for the results would have been quite different if reenforcing caps had not been used. In an ordinary detonator TNA required 0.3125 gram of 80/20 fulminate-chlorate instead of the 0.1700 gram which was sufficient when a reenforced detonator was used.

	MINIMUM INITIATING CHARGE (GRAMS) NECESSARY FOR EXPLOSION OF 0.4 GRAM OF		
PRIMARY EXPLOSIVE	TNT	TNA	Picric Acid
Mercury fulminate	0.26	0.20	0.25
90/10 Fulminate-chlorate	0.25	0.17	0.23
80/20 Fulminate-chlorate	0.24	0.17	0.22

The reenforced detonators which were used in this work were made by introducing the weighed charge of high explosive into the detonator shell and the weighed charge of primary explosive into the small reenforcing cap while the latter was held in a cavity in a brass block which served to prevent the explosive from falling through the hole in the end of the cap. The primary explosive was then pressed down gently by means of a wooden rod, the cap was filled by adding a sufficient quantity of the high explosive from the detonator shell, this was similarly pressed down, and the reenforcing cap was then removed from the brass block and inserted carefully in the detonator shell with its perforated end upward. The detonator was then placed in a press block, a plunger inserted, and the contents subjected to a pressure of 200 atmospheres per square inch maintained for 1 minute. The pressure expanded the reenforcing cap against the detonator shell and fixed it firmly in place.

The minimum initiating charge was determined as follows. The amount of sand pulverized by a detonator loaded, say, with TNT and with fulminate insufficient to explode the TNT was determined. Another experiment with a slightly larger amount of fulminate was tried. If this showed substantially the same amount of sand pulverized, then the charge of fulminate was increased still further, and so on, until a sudden large increase in the amount of sand pulverized showed that the TNT had detonated. After this point had been reached, further increases in the amount of fulminate caused only slight increases in the amount of sand pulverized. The magnitude of the effects, and the definiteness of the results, are shown by the following data of Storm and Cope.[18]

Primary Explosive	Weight of Sand (Grams) Pulverized Finer than 30-Mesh by Reenforced Detonator Containing 0.40 Gram TNT and a Priming Charge (Grams) of					
	0.3000	0.2800	0.2600	0.2500	0.2400	0.2300
Mercury fulminate	34.20	34.70	33.00	13.55	12.60	...
	...	...	31.50	...	...	...
	...	...	30.00	...	...	...
	...	...	32.70	...	...	...
	...	...	32.00	...	...	...
90/10 Fulminate-chlorate	...	...	33.55	34.45	32.95	13.90
	...	...	34.05	34.67	13.20	...
	...	...	34.35	34.07	...	...
	...	...	34.42	35.07	...	...
	...	...	34.70	33.80	...	...
80/20 Fulminate-chlorate	...	...	...	...	34.40	16.80
	...	...	...	...	34.60	...
	...	...	...	...	34.60	...
	...	...	...	...	33.80	...
	...	...	...	...	34.85	...

Fulminate owes its success as an initiating agent primarily to the fact that it explodes easily from fire—and it catches the fire more readily than do lead azide and many another primary explosive—to the fact that it quickly attains its full velocity of detonation within a very short length of material, and probably also to the fact that the heavy mercury atom which it contains enables it to deliver an especially powerful blow. Its maximum velocity of detonation is much lower than that of TNT and similar substances, and its power to initiate the detonation of high explosives is correspondingly less. Wöhler[19] in 1900 patented detonators in which a main charge of TNT or other nitro compound is initiated by a relatively small charge of fulminate.

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[18] *Ibid.*, p. 55.

[19] Brit. Pat. 21,065 (1900). For an account of Wöhler's theory of initiation see *Z. ges. Schiess- u. Sprengstoffw.*, **6**, 253 (1911) and *Z. angew. Chem.*, **24**, 1111, 2089 (1911).

Detonators which thus make use of the principle of the booster are known as compound detonators and are made both with and without reenforcing caps. Some manufacturers insert the reenforcing cap with the perforated end down, others with the perforated end up.[20]

Not long after Curtius[21] had discovered and described hydrazoic (hydronitric) acid and its salts, Will and Lenze[22] experimented with the azides (hydronitrides, hydrazotates) at the military testing station at Spandau, but a fatal accident put an end to their experiments and their results were kept secret by the German war office. Wöhler and Matter[23] later studied several primary explosives in an effort to find a substitute for fulminate, and in 1907, in ignorance of the earlier work of Will and Lenze, published experiments which demonstrated the great effectiveness of the azides. At about the same time, the first attempt to use lead azide practically in the explosives industry was made by F. Hyronimus in France who secured a patent[24] in February, 1907, for the use of lead azide in detonators, to replace either wholly or in part the mercury fulminate which had theretofore been used, and this whether or not the fulminate would ordinarily be used alone or in conjunction with some other explosive substance such as picric acid or trinitrotoluene. In March of the same year Wöhler in Germany patented,[25] as a substitute for fulminate, the heavy metal salts of hydrazoic acid, "such as silver and mercury azides." He pointed out, as the advantages of these substances, that a smaller weight of them is necessary to produce detonation than is necessary of mercury fulminate, as, for example, that a No. 8 blasting cap containing 2 grams of mercury fulminate can be replaced, for use in detonating explosives, by a No. 8 copper capsule containing 1 gram of picric acid on top of which 0.023 gram of silver azide has been com-

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[20] In addition to its other functions, the reenforcing cap tends toward greater safety by preventing actual contact between the primary explosive and the squarely cut end of the miner's fuse to which the detonator is crimped.

[21] *Ber.*, **23**, 3023 (1890); *ibid.*, **24**, 3341 (1891).

[22] Cf. Will, *Z. ges. Schiess- u. Sprengstoffw.*, **9**, 52 (1914).

[23] *Loc. cit.*

[24] French Pat. 384,792 (February 14, 1907), Supplement No. 8872 (process of manufacture), January 13, 1908.

[25] Ger. Pat. 196,824 (March 2, 1907).

pressed. In February of the next year Wöhler was granted a French patent[26] in which lead azide was specifically mentioned, but the use of this substance had already been anticipated by the patent of Hyronimus. Lead azide was soon afterwards manufactured commercially in Germany and in France, and compound detonators containing this material were used fairly generally in Europe at the time of the first World War. A few years later the manufacture of lead azide detonators was commenced in the United States. In this country compound detonators having a base charge of tetryl and primed with 80/20 fulminate-chlorate or with lead azide have been superseded in part by detonators loaded with a more powerful high-explosive charge of nitromannite, PETN, or diazodinitrophenol and primed with lead azide, alone or sensitized to flame by the addition of lead styphnate or tetracene, or with diazodinitrophenol as the primary explosive.

Testing of Detonators

Among the tests which are used for determining the relative efficiency of detonators,[27] the lead block or small Trauzl test, in which the detonators are fired in holes drilled in lead blocks and the resulting expansions of the holes are measured, and the lead or aluminum plate test in which the detonators are stood upright upon the plates and fired, and the character and extent of the effects upon the plates are observed, have already been mentioned.[28] The first of these gives results which are expressible by numbers, and in that sense quantitative, and it is evident that both methods may be applied, for example, to the determination of the minimum amount of primary explosive necessary for the initiation of a high explosive, for both show notably different effects according as the high explosive explodes or not. Another useful test is the determination of the maximum distance through which the detonator is capable of initiating the explosion of some standard material, say, a piece of cordeau loaded with TNT. In the *nail test,*[29] a wire nail is fastened to the side of the detonator, the detonator is fired, and the angle of the bend which the ex-

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[26] French Pat. 387,640 (February 28, 1908).

[27] Clarence Hall and Spencer P. Howell, "Investigations of Detonators and Electric Detonators," *U. S. Bur. Mines Bull.* 59, Washington, 1913.

[28] Vol. I, p. 26.

[29] Hall and Howell, *op. cit.*, p. 25.

plosion imparts to the nail is measured. The sand test, in which the detonator is fired in the center of a mass of carefully screened sand contained in a suitable bomb and the sand which has been pulverized is screened off and weighed, is the most precise and significant of the tests on detonators. It is a real test of brisance, and its usefulness is not limited to the study of detonators but may be extended to the study of high explosives as well. Thus, two explosives may be compared by loading equal amounts in detonator shells, priming with equal amounts of the same initiator, firing in the sand test bomb, and comparing the amounts of sand pulverized.

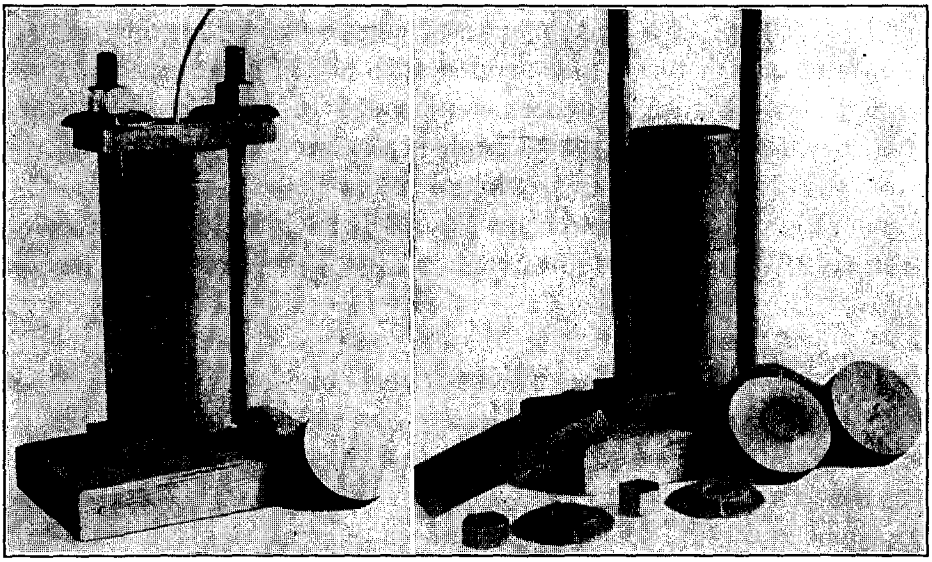

FIGURE 98. U. S. Bureau of Mines Sand Test Bomb No. 1. (Courtesy U. S. Bureau of Mines.) At left, assembled for making the test. At right, disassembled showing the parts. Two covers, one with a single hole for miner's fuse, the other with two holes for the two wires of an electric detonator.

The sand test was devised in 1910 by Walter O. Snelling, explosives chemist of the U. S. Bureau of Mines, who worked out the technique of its operation and designed the standard Bureau of Mines sand test bomb No. 1 which was used in his own investigations and in those of Storm and Cope.[30] Munroe and Taylor[31]

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[30] Snelling, *Proc. Eng. Soc. Western Pennsylvania,* 28, 673 (1912); Storm and Cope, *loc. cit.*

[31] C. E. Munroe and C. A. Taylor, "Methods of Testing Detonators," *U. S. Bur. Mines Repts. of Investigations* 2558, December, 1923.

later recommended a bomb of larger diameter, Bureau of Mines sand test bomb No. 2, as being able to differentiate more exactly between the different grades of detonators in commercial use. The test grew out of an earlier test which Snelling had developed in 1908 for measuring the strength of detonating agents. Starting with the thought that true explosives, when subjected to a sufficiently strong initiating influence, detonate in such manner as to set free more energy than that which had been applied to them by the initiating charge, he tested several materials which failed to be true explosives and, although decomposed by the detonating agent, did not give off energy enough to continue their own decomposition and to propagate a detonation wave. Copper oxalate was the best of the "near explosives" which he tried. He

FIGURE 99. Walter O. Snelling. (Metzger & Son.) Devised the sand test. Has worked extensively with nitrostarch explosives and has patented many improvements in military and in mining explosives. Chemist at the U. S. Bureau of Mines, 1908-1916; Director of Research, Trojan Powder Company, 1917—.

found it possible to measure the initiating effect of mercury fulminate and of other initial detonators by firing them in compositions consisting partly or wholly of copper oxalate, and then by chemical means determining the amount of the oxalate which had been decomposed. The experiments were carried out in a small steel bomb, the detonator was placed in the middle of a mass of oxalate or of oxalate composition, and sand was put in on top to fill the bomb completely. The fact that part of the sand was pulverized by the force of the explosion suggested that the mechanical effect of the initiator might perhaps serve as an approximate measure of the detonating efficiency; the oxalate was omitted, the bomb was filled entirely with sand, and the sand test was devised. Before Snelling left the Bureau of Mines in 1912 he had made about 40 tests on ordinary and electric detonators. Storm and Cope extended the usefulness of the test and applied it not only to the study of detonators but also to the study of the materials out of which detonators are constructed, both initial detonating agents and high explosives.

Lead Azide

Lead azide is a more efficient detonating agent than mercury fulminate. It requires a higher temperature for its spontaneous explosion, and it does not decompose on long continued storage at moderately elevated temperatures. It cannot be dead-pressed by any pressure which occurs in ordinary manufacturing operations. Lead azide pressed into place in a detonator capsule takes the fire less readily, or explodes from spark less readily, than mercury fulminate. For this reason the main initiating charge of lead azide in a blasting cap is generally covered with a layer of lead styphnate, or of styphnate-azide mixture or other *sensitizer*, which explodes more easily, though less violently, from fire, and serves to initiate the explosion of the azide.

Lead azide is not used in primers where it is desired to produce fire or flame from impact. Fulminate mixtures and certain mixtures which contain no fulminate are preferred for this purpose. Lead azide is used where it is desired to produce, either from flame or from impact, an initiatory shock for the detonation of a high explosive—in compound detonators as already described, and in the detonators of artillery fuzes. For the latter purpose, caps containing azide and tetryl (or other booster explosive) are used; the azide is exploded by impact, and the tetryl communicates the explosion to the booster or perhaps to the main charge of the shell.

Lead azide is produced as a white precipitate by mixing a solution of sodium azide with a solution of lead acetate or lead nitrate. It is absolutely essential that the process should be carried out in such manner that the precipitate consists of very small particles. The sensitivity of lead azide to shock and to friction increases rapidly as the size of the particles increases. Crystals 1 mm. in length are liable to explode spontaneously because of the internal stresses within them. The U. S. Ordnance Department specifications require that the lead azide shall contain no needle-shaped crystals more than 0.1 mm. in length. Lead azide is about as sensitive to impact when it is wet as when it is dry. Dextrinated lead azide can apparently be stored safely under water for long periods of time. The belief exists, however, that crystalline "service azide" becomes more sensitive when stored under water because of an increase in the size of the crystals.

The commercial preparation of lead azide is carried out on what is practically a laboratory scale, 300 grams of product constituting an ordinary single batch. There appear to be diverse opinions as to the best method of precipitating lead azide in a finely divided condition. According to one, fairly strong solutions are mixed while a gentle agitation is maintained, and the precipitate is removed promptly, and washed, and dried. According to another, dilute solutions ought to be used, with extremely violent agitation, and a longer time ought to be devoted to the process. The preparation is sometimes carried out by adding one solution to the other in a nickel vessel, which has corrugated sides, and is rotated around an axis which makes a considerable angle with the vertical, thereby causing turbulence in the liquid. The precipitation is sometimes carried out in the presence of dissolved colloidal material, such as gelatin or dextrin, which tends to prevent the formation of large crystals. Sometimes the lead azide is precipitated on starch or wood pulp, either of which will take up about 5 times its own weight of the material, and the impregnated starch is worked up, say, by tumbling in a sweetie barrel with a little dextrine, to form a free-flowing granular mass which can conveniently be loaded into detonators, or the impregnated wood pulp is converted into pasteboard which is cut into discs for loading. A small amount of basic salt in the lead azide makes it somewhat less sensitive to impact and slightly safer to handle, but has no appreciable effect upon its efficacy as an initiator.

The commercial preparation of the azides is carried out either by the interaction of hydrazine with a nitrite or by the interaction of sodamide with nitrous oxide. The first of these methods follows from the original work of Curtius,[32] the second from a reaction discovered by Wisliscenus [33] in 1892 and later developed for plant scale operation by Dennis and Browne.[34] Curtius first prepared hydrazoic acid by the action of aqueous or alcoholic alkali or ammonia on acyl azides prepared by the action of nitrous acid on acyl hydrazides. The hydrazides are formed by

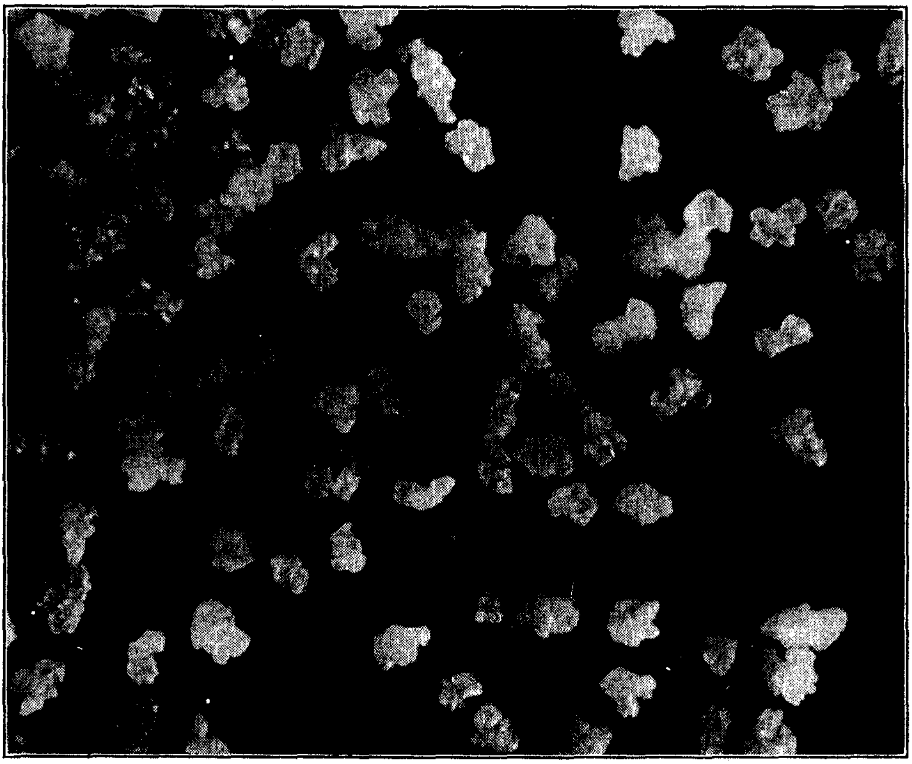

FIGURE 100. Technical Lead Azide, 90-95% pure (75×). For use in detonators. Precipitated in the presence of dextrin, it shows no crystal faces under the microscope.

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[32] *Loc. cit.;* also *J. prak. Chem.*, [2] 50, 275 (1894); *Ber.*, 29, 759 (1896); cf. survey by Darapsky in *Z. ges. Schiess- u. Sprengstoffw.*, 2, 41, 64 (1907).

[33] *Ber.*, 25, 2084 (1892).

[34] *Z. anorg. allgem. Chem.*, 40, 68 (1904).

the interaction of hydrazine with esters just as the amides are formed by the corresponding interaction of ammonia.

$$R\text{—}COOC_2H_5 + NH_2\text{—}NH_2 \longrightarrow C_2H_5OH + \underset{\text{Acyl hydrazide}}{R\text{—}CO\text{—}NH\text{—}NH_2}$$

$$R\text{—}CO\text{—}NH\text{—}NH_2 + HONO \longrightarrow 2H_2O + \underset{\text{Acyl azide}}{R\text{—}CO\text{—}N_3}$$

$$R\text{—}CO\text{—}N_3 + H_2O \longrightarrow R\text{—}COOH + HN_3$$

$$R\text{—}CO\text{—}N_3 + NH_3 \longrightarrow R\text{—}CO\text{—}NH_2 + \underset{\text{Hydrazoic acid}}{HN_3}$$

By acidifying the hydrolysis mixture with sulfuric acid and by fractionating the product, Curtius procured anhydrous hydrazoic as a colorless liquid which boils at 37°. Hydrazoic acid is intensely poisonous and bad smelling. It is easily exploded by flame, by a brisant explosive, or by contact with metallic mercury. The anhydrous substance is extremely dangerous to handle, but dilute solutions have been distilled without accident.

Angeli[35] obtained a white precipitate of insoluble silver azide by mixing saturated solutions of silver nitrite and hydrazine sulfate and allowing to stand in the cold for a short time. Dennstedt and Göhlich[36] later procured free hydrazoic acid by the interaction of hydrazine sulfate and potassium nitrite in aqueous solution.

$$\underset{\text{Hydrazine sulfate}}{NH_2\text{—}NH_2 \cdot H_2SO_4} + KONO \longrightarrow KHSO_4 + 2H_2O + HN_3$$

The yield from this reaction is greatest if the medium is alkaline, for nitrous acid attacks hydrazoic acid oxidizing it with the liberation of nitrogen. If hydrazine sulfate[37] is used in the mixture, the resulting hydrazoic acid is not available for the preparation of lead azide until it has been distilled out of the solution. (Lead ions added to the solution would cause the precipitation of lead sulfate.) The reaction mixture may be acidified with sulfuric acid, a little ammonium sulfate may be added in order that the

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[35] *Rend. acc. Lincei,* [5] 2, I, 599 (1893).

[36] *Chem.-Ztg.,* 21, 876 (1897).

[37] Hydrazine is produced commercially by treating ammonia in aqueous solution with sodium hypochlorite to form chloramine, $NH_2\text{—}Cl$, and by coupling this with another molecule of ammonia to form hydrazine and hydrochloric acid. Sulfuric acid is added to the liquid, sparingly soluble hydrazine sulfate crystallizes out, and it is in the form of this salt that hydrazine generally occurs in commerce.

ammonia may react with any unchanged nitrous acid which may be present, and the hydrazoic acid may be distilled directly into a solution of a soluble lead salt; but methods involving the distillation of hydrazoic acid present many dangers and have not found favor for commercial production. The alternative is to work with materials which contain no sulfate, and to isolate the azide by precipitation from the solution, and it is by this method that sodium azide (for the preparation of lead azide) is generally manufactured in this country and in England.

Hydrazine[38] reacts in alcohol solution with ethyl nitrite[39] and caustic soda to form sodium azide which is sparingly soluble in alcohol (0.315 gram in 100 grams of alcohol at 16°) and precipitates out.

$$NH_2{-}NH_2 + C_2H_5ONO + NaOH \longrightarrow NaN_3 + C_2H_5OH + 2H_2O$$

The sodium azide is filtered off, washed with alcohol, and dried. It is soluble in water to the extent of 42 grams in 100 grams of water at 18°. It is not explosive, and requires no particular precaution in its handling.

Azide has been manufactured in France and in Germany by the sodamide process. Metallic sodium is heated at about 300° while dry ammonia gas is bubbled through the molten material.

$$2Na + 2NH_3 \longrightarrow 2NaNH_2 + H_2$$

The sodamide which is formed remains liquid (m.p. 210°) and does not prevent contact between the remaining sodium and the ammonia gas. The progress of the reaction is followed by passing the effluent gas through water which absorbs the ammonia and allows the hydrogen to pass; if there is unabsorbed gas which forms an explosive mixture with air, the reaction is not yet complete. For the second step, the sodamide is introduced into a nickel or nickel-lined, trough-shaped autoclave along the bottom

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[38] Hydrazine hydrate is actually used. It is an expensive reagent procured by distilling hydrazine sulfate with caustic soda in a silver retort. It is poisonous, corrosive, strongly basic, and attacks glass, cork, and rubber. Pure hydrazine hydrate is a white crystalline solid which melts at 40° and boils at 118°, but the usual commercial material is an 85% solution of the hydrate in water.

[39] It is necessary to use ethyl nitrite or other alcohol-soluble nitrous ester, instead of sodium nitrite, in order that advantage may be taken of a solvent from which the sodium azide will precipitate out.

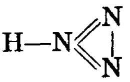
of which there extends a horizontal shaft equipped with teeth. The air in the apparatus is displaced with ammonia gas, the autoclave is heated to about 230°, and nitrous oxide is passed in while the horizontal stirrer is rotated. The nitrous oxide reacts with one equivalent of sodamide to form sodium azide and water. The water reacts with a second equivalent of sodamide to form sodium hydroxide and ammonia.

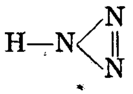
$$NaNH_2 + N_2O \longrightarrow NaN_3 + H_2O$$

$$NaNH_2 + H_2O \longrightarrow NaOH + NH_3$$

The reaction is complete when no more ammonia is evolved. The product, which consists of an equimolecular mixture of sodium hydroxide and sodium azide, may be taken up in water and neutralized carefully with nitric acid, and the resulting solution may be used directly for the preparation of lead azide, or the product may be fractionally crystallized from water for the production of sodium azide. The same material may be procured by washing the product with warm alcohol which dissolves away the sodium hydroxide.

The different methods by which hydrazoic acid and the azides may be prepared indicate that the acid may properly be represented by any one or by all of the following structural formulas.





$$H-N=N\equiv N$$

Hydrazoic acid is a weak acid; its ionization constant at 25°, 1.9×10^{-5}, is about the same as that of acetic acid at 25°, 1.86×10^{-5}. It dissolves zinc, iron, magesium, and aluminum, forming azides with the evolution of hydrogen and the production of a certain amount of ammonia. It attacks copper, silver, and mercury, forming azides without evolving hydrogen, and is reduced in part to ammonia and sometimes to hydrazine and free nitrogen. Its reaction with copper, for example, is closely analogous to the reaction of nitric acid with that metal.

$$Cu + 3HN_3 \longrightarrow Cu(N_3)_2 + N_2 + NH_3$$

$$3Cu + 8HNO_3 \longrightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$$

So also, like nitric acid, it oxidizes hydrogen sulfide with the liberation of sulfur.

$$H_2S + HN_3 \longrightarrow S + N_2 + NH_3$$

$$3H_2S + 2HNO_3 \longrightarrow 3S + 2NO + 4H_2O$$

Mixed with hydrochloric acid it forms a liquid, comparable to *aqua regia,* which is capable of dissolving platinum.

$$Pt + 2HN_3 + 4HCl \longrightarrow PtCl_4 + 2N_2 + 2NH_3$$

$$3Pt + 4HNO_3 + 12HCl \longrightarrow 3PtCl_4 + 4NO + 8H_2O$$

Hydrazoic acid and permanganate mutually reduce each other with the evolution of a mixture of nitrogen and oxygen. The acid and its salts give with ferric chloride solution a deep red coloration, similar to that produced by thiocyanates, but the color is discharged by hydrochloric acid.

The solubilities of the azides in general are similar to those of the chlorides. Thus, silver azide is soluble in ammonia water and insoluble in nitric acid. Lead azide, like lead chloride, is sparingly soluble in cold water, but hot water dissolves enough of it so that it crystallizes out when the solution is cooled. One hundred grams of water at 18° dissolve 0.03 gram, at 80° 0.09 gram.

The true density of lead azide is 4.8, but the loose powder has an apparent density of about 1.2.

Lead azide is dissolved by an aqueous solution of ammonium acetate, but it is not destroyed by it. The solution contains azide ions and lead ions, the latter quantitatively precipitable as lead chromate, $PbCrO_4$, by the addition of potassium dichromate solution. Lead azide in aqueous suspension is oxidized by ceric sulfate with the quantitative production of nitrogen gas which may be collected in an azotometer and used for the determination of the azide radical.

$$Pb(N_3)_2 + 2Ce(SO_4)_2 \longrightarrow PbSO_4 + 3N_2 + Ce_2(SO_4)_3$$

Nitrous acid oxidizes hydrazoic acid with the evolution of nitrogen. A dilute solution of nitric or acetic acid, in which a little sodium nitrite has been dissolved, dissolves and destroys lead azide. Such a solution may conveniently be used for washing floors, benches, etc., on which lead azide may have been spilled.

Silver Azide

Silver azide is a more efficient initiator than mercury fulminate, and about as efficient as lead azide. It melts at 251° and decomposes rapidly above its melting point into silver and nitrogen. Its temperature of spontaneous explosion varies somewhat according to the method of heating, but is considerably higher than that of mercury fulminate and slightly lower than that of lead azide. Taylor and Rinkenbach[40] reported 273°. Its sensitivity to shock, like that of lead azide, depends upon its state of subdivision.

FIGURE 101. William H. Rinkenbach. Has published many studies on the physical, chemical, and explosive properties of pure high-explosive substances and primary explosives. Research Chemist, U. S. Bureau of Mines, 1919-1927; Assistant Chief Chemist, Picatinny Arsenal, 1927-1929; Chief Chemist, 1929—.

Taylor and Rinkenbach prepared a "colloidal" silver azide which required a 777-mm. drop of a 500-gram weight to cause detonation. Mercury fulminate required a drop of 127 mm. According to the same investigators 0.05 gram of silver azide was necessary to cause the detonation of 0.4 gram of trinitrotoluene in a No. 6 detonator capsule, whether the charge was confined by a reenforcing cap or not, as compared with 0.24 gram of mercury ful-

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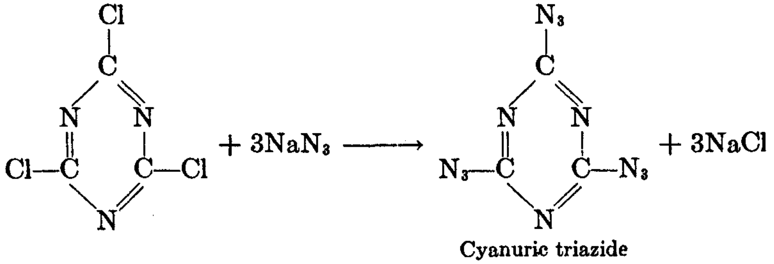
[40] *Army Ordnance,* **5,** 824 (1925).

minate when the charge was confined by a reenforcing cap and 0.37 gram when it was not confined. They also measured the sand-crushing power of silver azide when loaded into No. 6 detonator capsules and compressed under a pressure of 1000 pounds per square inch, and compared it with that of mercury fulminate, with the results which are tabulated below. It thus appears that the sand-crushing power of silver azide is not as much greater than the sand-crushing power of mercury fulminate as the difference in their initiatory powers would suggest. Storm and Cope[41] in their studies on the sand test found that the powers of fulminate and of fulminate-chlorate mixtures to crush sand were about proportional to the initiatory powers of these materials, but the present evidence indicates that the law is not a general one.

	WEIGHT OF SAND CRUSHED (GRAMS) BY	
WEIGHT OF CHARGE, GRAMS	Silver Azide	Mercury Fulminate
0.05	1.4	0.00
0.10	3.3	0.00
0.20	6.8	4.2
0.30	10.4	8.9
0.50	18.9	16.0
0.75	30.0	26.1
1.00	41.1	37.2

Cyanuric Triazide

Cyanuric triazide,[42] patented as a detonating explosive by Erwin Ott in 1921, is prepared by adding powdered cyanuric chloride, slowly with cooling and agitation, to a water solution of slightly more than the equivalent quantity of sodium azide.



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[41] *Loc. cit.*

[42] Ott, *Ber.*, **54**, 179 (1921); Ott, U. S. Pat. 1,390,378 (1921); Taylor and Rinkenbach, *U. S. Bur. Mines Repts. of Investigation* 2513, August, 1923; Kast and Haid, *Z. angew. Chem.*, **38**, 43 (1925).

The best results are secured if pure and finely powdered cyanuric chloride is used, yielding small crystals of pure cyanuric triazide in the first instance, in such manner that no recrystallization, which might convert them into large and more sensitive crystals, is necessary. Cyanuric chloride, m.p. 146°, b.p. 190°, is prepared by passing a stream of chlorine into a solution of hydrocyanic acid in ether or chloroform or into liquid anhydrous hydrocyanic acid exposed to sunlight. It is also formed by distilling cyanuric acid with phosphorus pentachloride and by the polymerization of cyanogen chloride, Cl—CN, after keeping in a sealed tube.

Cyanuric triazide is insoluble in water, slightly soluble in cold alcohol, and readily soluble in acetone, benzene, chloroform, ether, and hot alcohol. It melts at 94°, and decomposes when heated above 100°. It may decompose completely without detonation if it is heated slowly, but it detonates immediately from flame or from sudden heating. The melted material dissolves TNT and other aromatic nitro compounds. Small crystals of cyanuric triazide are more sensitive than small crystals of mercury fulminate, and have exploded while being pressed into a detonator capsule. Large crystals from fusion or from recrystallization have detonated when broken by the pressure of a rubber policeman.[43]

Cyanuric triazide is not irritating to the skin, and has no poisonous effects on rats and guinea pigs in fairly large doses.[43]

Taylor and Rinkenbach have reported sand test data which show that cyanuric triazide is much more brisant than mercury fulminate.[43]

WEIGHT OF EXPLOSIVE, GRAMS	WEIGHT OF SAND CRUSHED (GRAMS) BY	
	Cyanuric Triazide	Mercury Fulminate
0.050	2.6	...
0.100	4.8	...
0.200	12.2	3.8
0.400	33.2	12.2
0.600	54.4	20.1
0.800	68.9	28.2
1.000	78.6	36.8

In conformity with these results are the findings of Kast and Haid who reported that cyanuric triazide has a higher velocity of detonation than mercury fulminate. They made their measure-

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[43] Taylor and Rinkenbach, *loc. cit.*, footnote 42.

ments on several primary explosives loaded into detonator capsules 7.7 mm. in internal diameter and compressed to the densities which they usually have in commercial detonators.[44]

Explosive	Density	Velocity of Detonation, Meters per Second
Cyanuric triazide	1.15	5545
Lead azide	3.8	4500
Mercury fulminate	3.3	4490
Mixture: $Hg(ONC)_2$ 85%, $KClO_3$ 15%	3.1	4550
Lead styphnate	2.6	4900

Taylor and Rinkenbach found that cyanuric triazide is a more efficient initiator of detonation than mercury fulminate. This result cannot properly be inferred from its higher velocity of detonation, for there is no direct correlation between that quality and initiating efficiency. Lead azide is also a much more efficient initiator than mercury fulminate but has about the same velocity of detonation as that substance. The following results[43] were secured by loading 0.4 gram of the high explosive into detonator capsules, pressing down, adding an accurately weighed amount of the initiator, covering with a short reenforcing cap, and pressing with a pressure of 200 atmospheres per square inch. The size of the initiating charge was reduced until it was found that a further reduction resulted in a failure of the high explosive to detonate.

	Minimum Initiating Charge (Grams) of	
High Explosive	Cyanuric Triazide	Mercury Fulminate
Trinitrotoluene	0.10	0.26
Picric acid	0.05	0.21
Tetryl	0.04	0.24
Tetranitroaniline	0.09	0.20
Ammonium picrate	0.15	0.85

Cyanuric triazide is slightly more hygroscopic and distinctly more sensitive in the drop test than fulminate of mercury.[44] It is slightly volatile, and must be dried at as low a temperature as possible, preferably in vacuum.[44] Detonators in which it is used

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[44] Kast and Haid, *loc. cit.*, footnote 42.

Temperature of Explosion

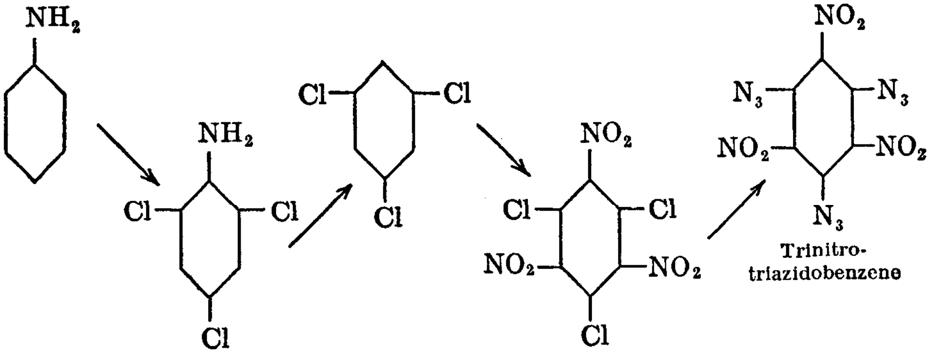
	When temperature is raised 20° per minute in		In Iron Tube	
Explosive	Glass Tube	Iron Tube	Temp., °C.	Elapsed time, seconds
Cyanuric triazide	206°	205°	200	40, 2
	208°	207°	205	0,
Lead azide	338°	337°	335	12, 9
			340	5, 7
			345	7, 6
			350	4, 5
			355	0
			360	0
Mercury fulminate	175°	166°	145	480, 331
			150	275, 255
			155	135, 165
			160	64, 85
			170	40, 35
			180	15, 13
			190	10, 8
			195	8, 7
			200	7, 8
			205	5, 5
			210	1, 3
			215	0
Mixture:	168°	169°	145	370, 365
$Hg(ONC)_2$ 85%	171°	170°	150	210, 215
$KClO_3$ 15%			155	155, 145
			160	125, 74
			170	45, 50
			180	23, 22
			190	8, 8
			195	7, 7
			200	7, 8
			205	7, 6
			210	4, 3
			215	0
Lead styphnate	276°	275°	250	90, 85
	277°	276°	265	65, 45
		275°	270	0

must be manufactured in such a way that they are effectively sealed.

Kast and Haid have determined the temperatures at which cyanuric triazide and certain other initiators explode spontaneously, both by raising the temperature of the samples at a constant rate and by keeping the samples at constant temperatures and noting the times which elapsed before they exploded. When no measurable time elapsed, the temperature was "the temperature of instantaneous explosion." Their data are especially interesting because they show the rate of deterioration of the materials at various temperatures.[44]

Trinitrotriazidobenzene

1,3,5-Trinitro-2,4,6-triazidobenzene[45] is prepared from aniline by the reactions indicated below.



Aniline is chlorinated to form trichloroaniline. The amino group is eliminated from this substance by means of the diazo reaction, and the resulting *sym*-trichlorobenzene is nitrated. The nitration, as described by Turek, is carried out by dissolving the material in warm 32% oleum, adding strong nitric acid, and heating at 140–150° until no more trinitrotrichlorobenzene, m.p. 187°, precipitates out. The chlorine atoms of this substance are then replaced by azido groups. This is accomplished by adding an acetone solution of the trinitrotrichlorobenzene, or better, the powdered substance alone, to an actively stirred solution of sodium azide in moist alcohol. The precipitated trinitrotriazidobenzene is filtered off, washed with alcohol and with water, and, after drying, is sufficiently pure for technical purposes. It may be

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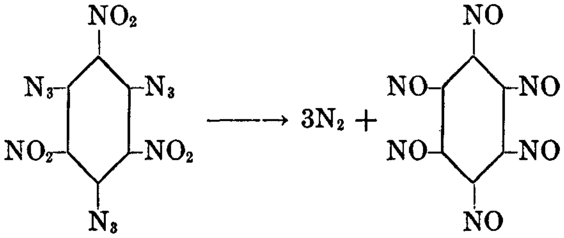
[45] Turek, *Chimie et industrie,* **26,** 781 (1931); Ger. Pat. 498,050; Brit. Pat. 298,981. Muraour, *Mém. artillerie franç.,* **18,** 895 (1939).

purified further by dissolving in chloroform and allowing to cool, greenish-yellow crystals, m.p. 131° with decomposition. It is decomposed slowly by boiling in chloroform solution.

Trinitrotriazidobenzene is readily soluble in acetone, moderately soluble in chloroform, sparingly in alcohol, and insoluble in water. It is not hygroscopic, is stable toward moisture, and does not attack iron, steel, copper, or brass in the presence of moisture. It is not appreciably volatile at 35–50°. It darkens in color superficially on exposure to the light. It decomposes on melting with the evolution of nitrogen and the formation of hexanitrosobenzene.



The same reaction occurs at lower temperatures: 0.665% of a given portion of the material decomposes in 3 years at 20°, 2.43% in 1 year at 35°, 0.65% in 10 days at 50°, and 100% during 14 hours heating at 100°. The decomposition is not self-catalyzed. The product, hexanitrosobenzene, m.p. 159°, is stable, not hygroscopic, not a primary explosive, and is comparable to tetryl in its explosive properties.

Trinitrotriazidobenzene, if ignited in the open, burns freely with a greenish flame; enclosed in a tube and ignited, it detonates with great brisance. It is less sensitive to shock and to friction than mercury fulminate. It gives a drop test of 30 cm., but it may be made as sensitive as fulminate by mixing with ground glass. The specific gravity of the crystalline material is 1.8054. Under a pressure of 3000 kilograms per square centimeter it yields blocks having a density of 1.7509, under 5000 kilograms per square centimeter 1.7526. One gram of TNT compressed in a No. 8 detonator shell under a pressure of 500 kilograms per square centimeter, with trinitrotriazidobenzene compressed on top of it under 300 kilograms per square centimeter, required 0.02 gram of the latter substance for complete detonation. Tetryl under similar conditions required only 0.01 gram. Trinitrotriazidobenzene may be dead-pressed and in that condition burns or puffs when it is ignited. It is a practical primary explosive and is prepared for loading in the granular form by mixing the moist material with nitrocellulose, adding a small amount of amyl acetate, kneading, rubbing through a sieve, and allowing to dry.

In the Trauzl test, trinitrotriazidobenzene gives 90% as much net expansion as PETN; tetryl gives 70%, TNT 60%, mercury fulminate 23%, and lead azide 16%. Used as a high explosive in compound detonators and initiated with lead azide, trinitrotriazidobenzene is about as strong as PETN and is stronger than tetryl.

Nitrogen Sulfide

Nitrogen sulfide was first prepared by Soubeiran in 1837 by the action of ammonia on sulfur dichloride dissolved in benzene.

$$6SCl_2 + 16NH_3 \longrightarrow N_4S_4 + 2S + 12NH_4Cl$$

It is conveniently prepared by dissolving 1 volume of sulfur chloride in 8 or 10 volumes of carbon disulfide, cooling, and passing in dry ammonia gas until the dark brown powdery precipitate which forms at first has dissolved and an orange-yellow solution results which contains light-colored flocks of ammonium chloride. These are filtered off and rinsed with carbon disulfide, the solution is evaporated to dryness, and the residue is extracted with boiling carbon disulfide for the removal of sulfur. The undissolved material is crude nitrogen sulfide. The hot extract on cooling deposits a further quantity in the form of minute golden-yellow crystals. The combined crude product is recrystallized from carbon disulfide.

The same product is also produced by the action of ammonia on disulfur dichloride in carbon disulfide, benzene, or ether solution.

$$6S_2Cl_2 + 16NH_3 \longrightarrow N_4S_4 + 8S + 12NH_4Cl$$

Nitrogen sulfide has a density of 2.22 at 15°. It is insoluble in water, slightly soluble in alcohol and ether, somewhat more soluble in carbon disulfide and benzene. It reacts slowly with water at ordinary temperature with the formation of pentathionic acid, sulfur dioxide, free sulfur, and ammonia.[46] It melts with sublimation at 178°, and explodes at a higher temperature which, however, is variable according to the rate at which the substance is heated. Berthelot found that it deflagrates at 207° or higher, and remarked that this temperature is about the same as the temperature of combustion of sulfur in the open air. Berthelot and Vieille[47] studied the thermochemical properties of nitrogen sulfide. Their data, recalculated to conform to our present notions of atomic and molecular weight, show that the substance is strongly endothermic and has a heat of formation of -138.8 Calories per mol. It detonates with vigor under a hammer blow, but is less sensitive to shock and less violent in its effects than mercury fulminate. Although its rate of acceleration is considerably less than that of mercury fulminate, it has been recommended as a filling for fuses, primers, and detonator caps, both alone and in mixtures with oxidizing agents such as lead peroxide, lead nitrate, and potassium chlorate.[48]

Nitrogen selenide was first prepared by Espenschied[49] by the action of ammonia gas on selenium chloride. His product was an orange-red, amorphous powder which exploded violently when heated and was dangerous to handle. Verneuil[50] studied the substance further and supplied a sample of it to Berthelot and Vieille[51] for thermochemical experiments. It detonates when brought into contact with a drop of concentrated sulfuric acid or when warmed to about 230°. It also detonates from friction, from a very gentle blow of iron on iron, and from a slightly stronger blow of wood on iron. It has a heat of formation of -169.2 Calories per mol, and, with nitrogen sulfide, illustrates the principle, as Berthelot pointed out, that in analogous series (such as that of the halides and that of the oxides, sulfides, and selenides) "the explosive character of the endothermic compounds becomes more and more pronounced as the molecular weight becomes larger."

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[46] Van Valkenburgh and Bailor, *J. Am. Chem. Soc.*, 47, 2134 (1925).

[47] Berthelot, "Sur la force des matières explosives," 2 vols., third edition, Paris, 1883, Vol. 1, p. 387.

[48] Claessen, Brit. Pat. 6057 (1913); Carl, U. S. Pat. 2,127,106 (1938).

[49] *Ann.*, **113**, 101 (1860).

[50] *Bull. soc. chim.*, [2] **38**, 548 (1882).

[51] Berthelot, *op. cit.*, p. 389.

Lead Styphnate (Lead trinitroresorcinate)

Lead styphnate is commonly prepared by adding a solution of magnesium styphnate[52] at 70° to a well-stirred solution of lead acetate at 70°. A voluminous precipitate of the basic salt separates. The mixture is stirred for 10 or 15 minutes; then dilute nitric acid is added with stirring to convert the basic to the normal salt, and the stirring is continued while the temperature drops to about 30°. The product, which consists of reddish-brown, short, rhombic crystals, is filtered off, washed with water, sieved through silk, and dried.

FIGURE 102. Lead Styphnate Crystals (90×).

Lead styphnate is a poor initiator, but it is easily ignited by fire or by a static discharge. It is used as an ingredient of the priming layer which causes lead azide to explode from a flash.

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[52] Prepared by adding magnesium oxide to a suspension of styphnic acid in water until a clear solution results and only a very small portion of the styphnic acid remains undissolved.

A 0.05-gram sample of lead styphnate in a test tube in a bath of Wood's metal heated at a rate of 20° per minute explodes at 267–268°.

Wallbaum[53] determined the minimum charges of several primary explosives necessary for initiating the explosion of PETN. In the first series of tests, the PETN (0.4 gram) was tamped down or pressed loosely into copper capsules 6.2 mm. in inside diameter, and weighed amounts of the priming charges were pressed down loosely on top. The weights of the priming charges were decreased until one failure occurred in 10 tests with the same weight of charge. In later series, the PETN was compressed at 2000 kilograms per square centimeter. When the priming charges were pressed loosely on the compressed PETN, considerably larger amounts were generally necessary. One gram of lead styphnate, however, was not able to initiate the explosion of the compressed PETN. When the priming charges were pressed, on top of the already compressed PETN, with pressures of 500, 1000, and 1500 kilograms per square centimeter, then it was found that the tetracene and the fulminate were dead-pressed but that the amounts of lead azide and silver azide which were needed were practically the same as in the first series when both the PETN and the priming charge were merely pressed loosely. Wallbaum reports the results which are tabulated below.

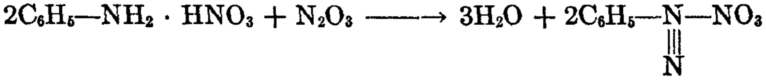
Pressure on PETN, kg. per sq. cm.	0	2000	2000	2000	2000
Pressure on initiator, kg. per sq. cm.	0	0	500	1000	1500
PRIMARY EXPLOSIVE	MINIMUM INITIATING CHARGE, GRAMS				
Tetracene	0.16	0.250	dead-pressed		
Mercury fulminate (gray)	0.30	0.330	" "		
Mercury fulminate (white)	0.30	0.340	" "		
Lead styphnate	0.55	No detonation with 1 g.			
Lead azide (technical)	0.04	0.170	0.05	0.05	0.04
Lead azide (pure)	0.015	0.100	0.01	0.01	0.01
Silver azide	0.005	0.110	0.005	0.005	0.005

Diazonium Salts

Every student of organic chemistry has worked with diazonium salts in solution. The substances are commonly not isolated in the solid state, for the dry materials are easily exploded by shock and by friction, and numerous laboratory accidents have resulted from their unintended crystallization and drying.

[53] *Z. ges. Schiess- u. Sprengstoffw.*, **34**, 126, 161, 197 (1939).

The first volume of the *Mémorial des Poudres et Salpêtres* contains a report by Berthelot and Vieille [54] on the properties of benzenediazonium nitrate (diazobenzene nitrate). They prepared the material by passing nitrous gas into a cooled aqueous solution of aniline nitrate, diluting with an equal volume of alcohol, and precipitating in the form of white, voluminous flocks by the addition of an excess of ether.

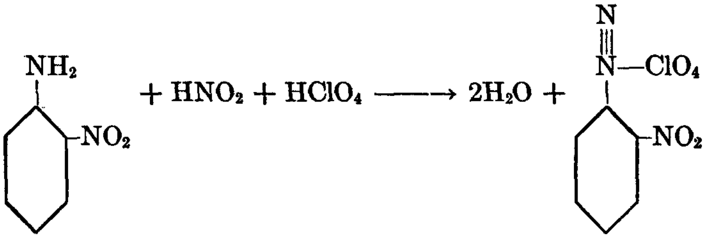


$$2C_6H_5\text{—}NH_2 \cdot HNO_3 + N_2O_3 \longrightarrow 3H_2O + 2C_6H_5\text{—}\underset{\underset{\displaystyle N}{|||}}{N}\text{—}NO_3$$

The product was washed with ether, pressed between pieces of filter paper, and dried in a vacuum desiccator. In dry air and in the dark it could be kept in good condition for many months. In the daylight it rapidly turned pink, and on longer keeping, especially in a moist atmosphere, it turned brown, took on an odor of phenol, and finally became black and swelled up with bubbles of gas.

Benzenediazonium nitrate detonates easily from the blow of a hammer or from any rubbing which is at all energetic. It explodes violently when heated to 90°. Its density at 15° is 1.37, but under strong compression gently applied it assumes an apparent density of 1.0. Its heat of formation is −47.4 Calories per mol, heat of explosion 114.8 Calories per mol.

m-Nitrobenzenediazonium perchlorate was patented by Herz [55] in 1911, and is reported to have been used in compound detonators with a high-explosive charge of nitromannite or other brisant nitric ester. It explodes spontaneously when heated to about 154°. It is sensitive to shock and to blow. Although it is very sparingly soluble in water and is stabilized to some extent by the nitro group on the nucleus, it is distinctly hygroscopic and is not exempt from the instability which appears to be characteristic of diazonium salts.



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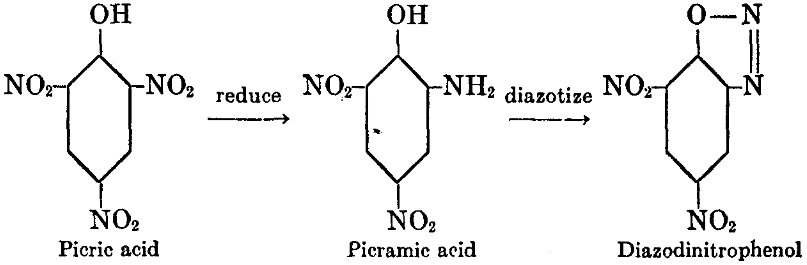
[54] *Mém. poudres,* **1,** 99 (1882–1883). Berthelot, *op. cit.,* Vol. 2, p. 35.

[55] Ger. Pat. 258,679 (1911).

Preparation of m-Nitrobenzenediazonium Perchlorate. Half a gram of *m*-nitroaniline is suspended in 5 cc. of water in a wide test tube, and 0.5 cc. of concentrated hydrochloric acid and 2.2 cc. of 20% perchloric acid solution are added. After the nitraniline has dissolved, 15 cc. of water is added and the solution is cooled by immersing the test tube in a beaker filled with a slurry of cracked ice. One-quarter of a gram of sodium nitrite dissolved in 1 or 2 cc. of water is added in 3 or 4 portions, the mixture being shaken after each addition or stirred with a stirring rod the end of which is covered with a short piece of rubber tubing. After standing in the cold for 5 minutes, the material is transferred to a filter, and the feltlike mass of pale yellow needles is washed with cold water, with alcohol, and with ether. The product is dried in several small portions on pieces of filter paper.

Diazodinitrophenol (DDNP, Dinol)

4,6-Dinitrobenzene-2-diazo-1-oxide, or diazodinitrophenol as it is more commonly called, occupies a place of some importance in the history of chemistry, for its discovery by Griess[56] led him to undertake his classic researches on the diazonium compounds and the diazo reaction. He prepared it by passing nitrous gas into an alcoholic solution of picramic acid, but it is more conveniently prepared by carrying out the diazotization in aqueous solution with sodium nitrite and hydrochloric acid.



Picramic acid, red needles, m. p. 169°, may be prepared by evaporating ammonium picrate in alcohol solution with ammonium sulfide.

Preparation of Diazodinitrophenol. Ten grams of picramic acid is suspended in 120 cc. of 5% hydrochloric acid in a beaker which stands in a basin of ice water, and the mixture is stirred rapidly with a mechanical stirrer. Sodium nitrite (3.6 grams) dissolved in 10 cc. of water is added all at once, and the stirring is continued for 20 minutes. The product is collected on a filter and washed thoroughly with ice

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[56] *Ann.,* **106,** 123 (1858), **113,** 205 (1860).

water. The dark brown granular material may be used as such, or it may be dissolved in hot acetone and precipitated by the addition of a large volume of ice water to the rapidly agitated liquid, a treatment which converts it into a brilliant yellow amorphous powder.

L. V. Clark,[57] who has made an extensive study of the physical and explosive properties of diazodinitrophenol, reports that it has a true density at 25°/4° of 1.63. Its apparent density after being placed in a tube and tapped is only 0.27, but, when compressed in a detonator capsule at a pressure of 3400 pounds per square inch (239 kilograms per square centimeter), it has an apparent density of 0.86. It is not dead-pressed by a pressure of 130,000 pounds per square inch (9139 kilograms per square centimeter). It is soluble in nitrobenzene, acetone, aniline, pyridine, acetic acid, strong hydrochloric acid, and nitroglycerin at ordinary temperatures. Its solubility at 50° in 100 grams of solvent is: in ethyl acetate 2.45 grams, in methyl alcohol 1.25 grams, in ethyl

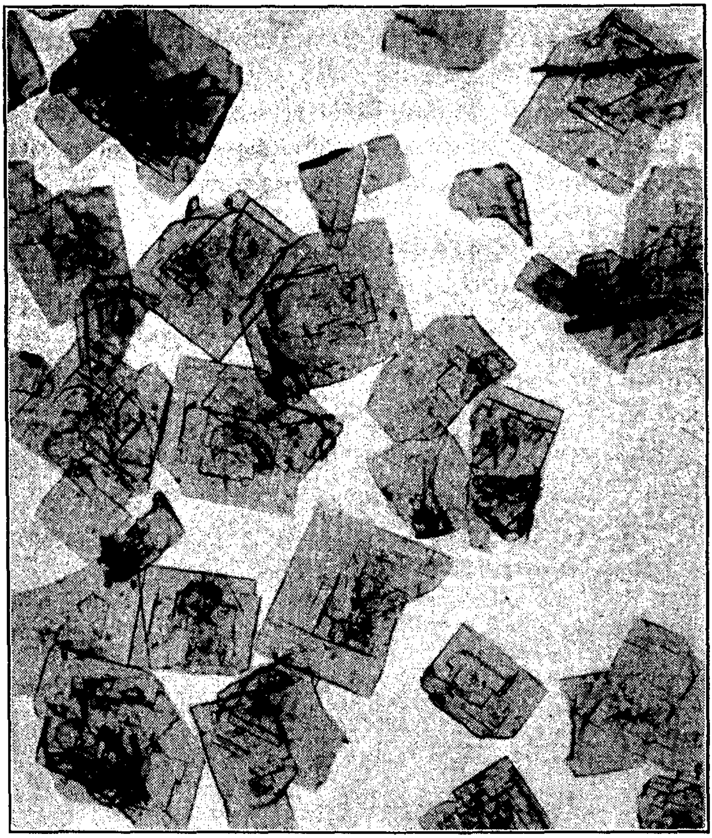

FIGURE 103. Diazodinitrophenol Crystals (90×).

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[57] *Ind. Eng. Chem.*, **25**, 663 (1933).

alcohol 2.43 grams, in benzene 0.23 gram, and in chloroform 0.11 gram.

Diazodinitrophenol is less sensitive to impact than mercury fulminate and lead azide. Its sensitivity to friction is about the same as that of lead azide, much less than that of mercury fulminate. It detonates when struck a sharp blow, but, if it is ignited when it is unconfined, it burns with a quick flash, like nitrocellulose, even in quantities of several grams. This burning produces little or no local shock, and will not initiate the explosion of a high explosive. Commercial detonators containing a high-explosive charge of nitromannite and a primary explosive charge of diazodinitrophenol explode if they are crimped to a piece of miner's fuse and the fuse is lighted, but a spark falling into the open end has been reported to cause only the flashing of the diazodinitrophenol. Likewise, if an open cap of this sort falls into a fire, the diazodinitrophenol may flash, the nitromannite may later melt and run out and burn with a flash, and the detonator may be destroyed without exploding. While it is not safe to expect that this will always happen, it is an advantage of diazodinitrophenol that it sometimes occurs.

Diazodinitrophenol is darkened rapidly by exposure to sunlight. It does not react with water at ordinary temperatures, but is desensitized by it. It is not exploded under water by a No. 8 blasting cap.

Clark reports experiments with diazodinitrophenol, mercury fulminate, and lead azide in which various weights of the explosives were introduced into No. 8 detonator capsules, pressed under reenforcing caps at 3400 pounds per square inch, and fired in the No. 2 sand test bomb. His results, tabulated below, show that diazodinitrophenol is much more powerful than mercury fulminate and lead azide. Other experiments by Clark showed

WEIGHT (GRAMS) OF CHARGE	WEIGHT (GRAMS) OF SAND PULVERIZED FINER THAN 30-MESH BY		
	Diazodinitrophenol	Mercury Fulminate	Lead Azide
0.10	9.1	3.1	3.5
0.20	19.3	6.5	7.2
0.40	36.2	17.0	14.2
0.60	54.3	27.5	21.5
0.80	72.1	38.0	28.7
1.00	90.6	48.4	36.0

that diazodinitrophenol in the sand test has about the same strength as tetryl and hexanitrodiphenylamine.

Clark found that the initiatory power of diazodinitrophenol is about twice that of mercury fulminate and slightly less than that of lead azide. His experiments were made with 0.5-gram charges of the high explosives in No. 8 detonator capsules, with reenforcing caps, and with charges compressed under a pressure of 3400 pounds per square inch. He reported the results which are tabulated below.

	MINIMUM INITIATING CHARGE (GRAMS) OF		
HIGH EXPLOSIVE	Mercury Fulminate	Diazodinitrophenol	Lead Azide
Picric acid	0.225	0.115	0.12
Trinitrotoluene	0.240	0.163	0.16
Tetryl	0.165	0.075	0.03
Trinitroresorcinol	0.225	0.110	0.075
Trinitrobenzaldehyde	0.165	0.075	0.05
Tetranitroaniline	0.175	0.085	0.05
Hexanitrodiphenylamine	0.165	0.075	0.05

One gram of diazodinitrophenol in a No. 8 detonator capsule, compressed under a reenforcing cap at a pressure of 3400 pounds per square inch, and fired in a small Trauzl block, caused an expansion of 25 cc. Mercury fulminate under the same conditions caused an expansion of 8.1 cc., and lead azide one of 7.2 cc.

Clark determined the ignition temperature of diazodinitrophenol by dropping 0.02-gram portions of the material onto a heated bath of molten metal and noting the times which elapsed between the contacts with the hot metal and the explosions: 1 second at 200°, 2.5 seconds at 190°, 5 seconds at 185°, and 10.0 seconds at 180°. At 177° the material decomposed without an explosion.

Tetracene

1-Guanyl-4-nitrosoaminoguanyltetrazene, called tetracene for short, was first prepared by Hoffmann and Roth.[58] Hoffmann and his co-workers [59] studied its chemical reactions and determined

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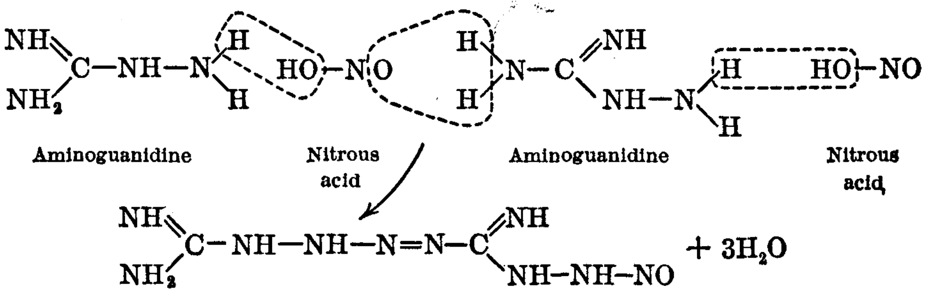
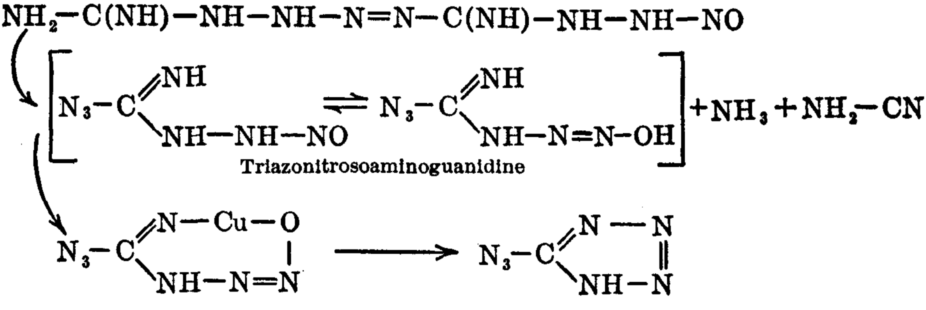
[58] *Ber.*, **43**, 682 (1910).

[59] Hoffmann, Hock, and Roth, *ibid.*, **43**, 1087 (1910); Hoffmann and Hock, *ibid.*, **43**, 1866 (1910), **44**, 2946 (1911); Hoffmann, Hock, and Kirmreuther, *Ann.*, **380**, 131 (1911).

its structure. It is formed by the action of nitrous acid on aminoguanidine, or, more exactly, by the interaction of an aminoguanidine salt with sodium nitrite in the absence of free mineral acid.



Tetracene is a colorless or pale yellow, fluffy material which is practically insoluble in water, alcohol, ether, benzene, and carbon tetrachloride. It has an apparent density of only 0.45, but yields a pellet of density 1.05 when it is compressed under a pressure of 3000 pounds per square inch. Tetracene forms explosive salts, among which the perchlorate is especially interesting. It is soluble in strong hydrochloric acid; ether precipitates the hydrochloride from the solution, and this on treatment with sodium acetate or with ammonia gives tetracene again. With an excess of silver nitrate it yields the double salt, $C_2H_7N_{10}OAg \cdot AgNO_3 \cdot 3H_2O$. Tetracene is only slightly hygroscopic. It is stable at ordinary temperatures both wet and dry, but is decomposed by boiling water with the evolution of $2N_2$ per molecule. On hydrolysis with caustic soda it yields ammonia, cyanamide, and triazonitrosoaminoguanidine which can be isolated in the form of a bright blue precipitate of the explosive copper salt by the addition of copper acetate to the alkaline solution. The copper salt on treatment with acid yields tetrazolyl azide (5-azidotetrazole).[60]



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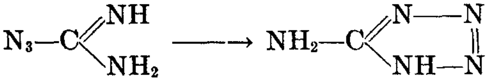
[60] Cf. survey article by G. B. L. Smith, "The Chemistry of Aminoguanidine and Related Substances," *Chem. Rev.*, **25**, 214 (1939).

In the presence of mineral acids, sodium nitrite reacts in a different manner with aminoguanidine, and guanyl azide is formed.

$$\mathrm{NH_2{-}C(NH){-}NH{-}NH_2 + HONO \longrightarrow N_3{-}C}\begin{array}{l}\diagup\mathrm{NH}\\ \diagdown\mathrm{NH_2}\end{array} + \mathrm{2H_2O}$$

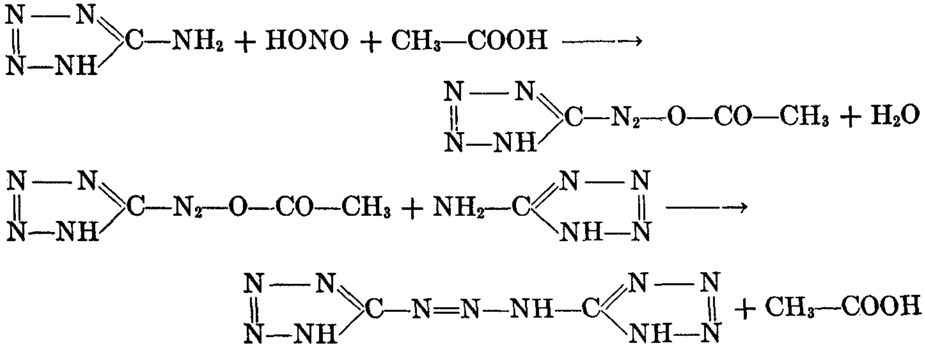
Guanyl azide

This substance forms salts with acids, and was first isolated in the form of its nitrate. The nitrate is not detonated by shock but undergoes a rapid decomposition with the production of light when it is heated. The picrate and the perchlorate explode violently from heat and from shock. Guanyl azide is not decomposed by boiling water. On hydrolysis with strong alkali, it yields the alkali metal salt of hydrazoic acid. It is hydrolyzed by ammoniacal silver nitrate in the cold with the formation of silver azide which remains in solution and of silver cyanamide which appears as a yellow precipitate. By treatment with acids or weak bases it is converted into 5-aminotetrazole.



5-Aminotetrazole

When the reaction between aminoguanidine and sodium nitrite occurs in the presence of an excess of acetic acid, still another product is formed, namely, 1,3-ditetrazolyltriazine, the genesis of which is easily understood from a consideration of the reactions already mentioned. 5-Aminotetrazole is evidently formed first; the amino group of one molecule of this substance is diazotized by the action of the nitrous acid, and the resulting diazonium salt in the acetic acid solution couples with a second molecule of the aminotetrazole.



1,3-Ditetrazolyltriazine

Preparation of Tetracene. Thirty-four grams of aminoguanidine bicarbonate, 2500 cc. of water, and 15.7 grams of glacial acetic acid are brought together in a 3-liter flask, and the mixture is warmed on the steam bath with occasional shaking until everything has gone into solution. The solution is filtered if need be, and cooled to 30° at the tap. Twenty-seven and sixth-tenths grams of solid sodium nitrite is added. The flask is swirled to make it dissolve, and is set aside at room temperature. After 3 or 4 hours, the flask is shaken to start precipitation of the product. It is allowed to stand for about 20 hours longer (22 to 24 hours altogether). The precipitate of tetracene is washed several times by decantation, transferred to a filter, and washed thoroughly with water. The product is dried at room temperature and is stored in a bottle which is closed by means of a cork or rubber stopper.

Tetracene explodes readily from flame without appreciable noise but with the production of much black smoke. Rinkenbach and Burton,[61] who have made an extended study of the explosive properties of tetracene, report that it explodes in 5 seconds at 160° (mercury fulminate 190°). They found that it is slightly more sensitive to impact than mercury fulminate; an 8-inch drop of an 8-ounce weight was needed to explode it, a drop of 9–10 inches to explode fulminate.

The brisance of tetracene, if it is used alone and is fired by a fuse, is greatest when the explosive is not compressed at all. Thus, 0.4 gram of tetracene, if uncompressed, crushed 13.1 grams of sand in the sand test; if compressed under a pressure of 250 pounds per square inch, 9.2 grams; if under 500 pounds per square inch, 7.5 grams; and, if under 3000 pounds per square inch, 2.0 grams. The data show the behavior of tetracene as it approaches the condition of being dead-pressed.

In another series of experiments, Rinkenbach and Burton used charges of 0.4 gram of tetracene, compressed under a pressure of 3000 pounds per square inch and initiated with varying amounts of fulminate (loaded under the same pressure), and found that the tetracene developed its maximum brisance (21.1 grams of sand crushed) when initiated with 0.4 gram of fulminate. A compound primer of 0.15 gram of tetryl initiated with 0.25 gram of mercury fulminate caused 0.4 gram of tetracene to crush 22.6 grams, or substantially the same amount, of sand. It appears

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[61] *Army Ordnance,* **12,** 120 (1931). See also Stettbacher, *Nitrocellulose,* **8,** 141 (1936); Grottanelli, *Chimica e industria,* **18,** 232 (1936).

then that tetracene is more brisant—and presumably explodes with a greater velocity of detonation—when initiated by fulminate or tetryl than when self-initiated by fire.

Tetracene is easily dead-pressed, its self-acceleration is low, and it is not suitable for use alone as an initiating explosive. It is as efficient as fulminate only if it is externally initiated. It is used in detonators either initiated by another primary explosive and functioning as an intermediate booster or mixed with another primary explosive to increase the sensitivity of the latter to flame or heat. A recent patent[62] recommends the use of a mixture of tetracene and lead azide in explosive rivets. Tetracene is used in primer caps where as little as 2% in the composition results in an improved uniformity of percussion sensitivity.

FIGURE 104. Tetracene Crystals (150×).

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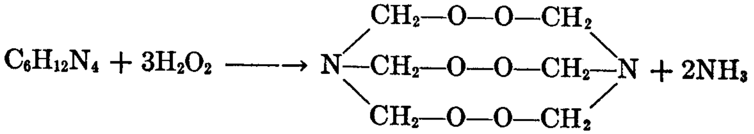
[62] Brit. Pat. 528,299 (1940) to Dynamit-Aktien Gesellschaft vorm. Alfred Nobel & Co.

Hexamethylenetriperoxidediamine (HMTD)

Hexamethylenetriperoxidediamine is the only organic peroxide which has been considered seriously as an explosive. Its explosive properties commend it, but it is too reactive chemically and too unstable to be of practical use. It is most conveniently prepared by treating hexamethylenetetramine with hydrogen peroxide in the presence of citric acid which promotes the reaction by combining with the ammonia which is liberated.



Hexamethylenetriperoxidediamine

Preparation of Hexamethylenetriperoxidediamine. Fourteen grams of hexamethylenetetramine is dissolved in 45 grams of 30% hydrogen peroxide solution which is stirred mechanically in a beaker standing in a freezing mixture of cracked ice with water and a little salt. To the solution 21 grams of powdered citric acid is added slowly in small portions at a time while the stirring is continued and the temperature of the mixture is kept at 0° or below. After all the citric acid has dissolved, the mixture is stirred for 3 hours longer while its temperature is kept at 0°. The cooling is then discontinued, the mixture is allowed to stand for 2 hours at room temperature, and the white crystalline product is filtered off, washed thoroughly with water, and rinsed with alcohol in order that it may dry out more quickly at ordinary temperatures.

Hexamethylenetriperoxidediamine is almost insoluble in water and in the common organic solvents at room temperature. It detonates when struck a sharp blow, but, when ignited, burns with a flash like nitrocellulose. Taylor and Rinkenbach[63] found its true density (20°/20°) to be 1.57, its apparent density after being placed in a tube and tapped 0.66, and its density after being compressed in a detonator capsule under a pressure of 2500 pounds per square inch only 0.91. They found that it required a 3-cm. drop of a 2-kilogram weight to make it explode, but that fulminate required a drop of only 0.25 cm. In the sand test it pulverized 2½ to 3 times as much sand as mercury fulminate, and slightly more sand than lead azide. It is not dead-pressed by a pressure of 11,000 pounds per square inch. It is considerably

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[63] *Army Ordnance,* 5, 463 (1924).

more effective than mercury fulminate as an initiator of detonation. Taylor and Rinkenbach, working with 0.4-gram portions of the high explosives and with varying weights of the primary explosives, compressed in detonator capsules under a pressure of 1000 pounds per square inch, found the minimum charges necessary to produce detonation to be as indicated in the following table.

	MINIMUM INITIATING CHARGE (GRAMS) OF		
		Hexamethylenetriperoxidediamine	
HIGH EXPLOSIVE	Fulminate with Reenforcing Cap	With Reenforcing Cap	Without Reenforcing Cap
Trinitrotoluene	0.26	0.08	0.10
Picric acid	0.21	0.05	0.06
Tetryl	0.24	0.05	0.06
Ammonium picrate	0.8–0.9	0.30	0.30
Tetranitroaniline	0.20	0.05	0.05
Guanidine picrate	0.30	0.13	0.15
Trinitroresorcinol	0.20	0.08	0.10
Hexanitrodiphenylamine	...	0.05	0.05
Trinitrobenzaldehyde	...	0.08	0.10

Taylor and Rinkenbach found that 0.05-gram portions of hexamethylenetriperoxidediamine, pressed in No. 8 detonator capsules under a pressure of 1000 pounds per square inch and fired by means of a black-powder fuse crimped in the usual way, caused the detonation of ordinary 40% nitroglycerin dynamite and of a gelatin dynamite which had become insensitive after storage of more than a year. The velocity of detonation of HMTD, loaded at a density of 0.88 in a column 0.22 inch in diameter, was found by the U. S. Bureau of Mines Explosives Testing Laboratory to be 4511 meters per second.

A small quantity of HMTD decomposed without exploding when dropped onto molten metal at 190°, but a small quantity detonated instantly when dropped onto molten metal at 200°. A 0.05-gram sample ignited in 3 seconds at 149°. At temperatures which are only moderately elevated the explosive shows signs of volatilizing and decomposing. Taylor and Rinkenbach report the results of experiments in which samples on watch glasses were heated in electric ovens at various temperatures, and weighed and examined from time to time, as shown below. The sample which had been heated at 60° showed no evidence of decomposition. The sample which had been heated at 75° was unchanged in color but had a faint odor of methylamine and appeared slightly moist. At 100° the substance gave off an amine odor. The residue which remained after 24 hours of heating at 100° consisted of a colorless liquid and needle crystals which were soluble in water.

% Weight Lost at	60°	75°	100°
In 2 hrs.	0.10	0.25	3.25
In 8 hrs.	0.35	0.60	29.60
In 24 hrs.	0.50	1.30	67.95
In 48 hrs.	0.50	2.25	....

When hexamethylenetriperoxidediamine is boiled with water, it disappears fairly rapidly, oxygen is given off, and the colorless solution is found to contain ammonia, formaldehyde, ethylene glycol, formic acid, and hexamethylenetetramine.

Friction Primers

Friction primers (friction tubes, friction igniters) are devices for the production of fire by the friction of the thrust, either push or pull, of a roughened rod or wire through a pellet of primer composition. They are used for firing artillery in circumstances where the propelling charge is loaded separately and is not enclosed in a brass case supplied with a percussion primer. They are sometimes crimped to an end of Bickford fuse for the purpose of lighting it. They are sometimes used for lighting flares, etc., which are thrown overboard from airplanes. For this use, the pull element of the primer is attached to the airplane by a length of twine or wire which the weight of the falling flare first pulls and then breaks off entirely.

The following table shows three compositions which have been widely used in friction primers for artillery. All the materials are in the powdered condition except in the first mixture where half of the potassium chlorate is powdered and half of it is granu-

Potassium chlorate	2	56.2	44.6
Antimony sulfide	1	24.6	44.6
Sulfur	..	9.0	3.6
Meal powder	..	...	3.6
Ground glass	..	10.2	3.6

lar. The first mixture is probably the best. The sulfur which is contained in the second and third mixtures makes them more sensitive, but also makes them prone to turn sour after they have been wet-mixed, and these mixtures ought to be made up with a small amount of anti-acid (calcium carbonate, trimethylamine, etc., not mentioned in the table). All the mixtures are wet-mixed with 5% gum arabic solution, loaded wet, and dried out *in situ* to form pellets which do not crumble easily.

In a typical friction primer for an airplane flare, ignition is secured by pulling a loop of braided wire coated with red phosphorus and shellac through a pellet, made from potassium chlorate (14 parts) and charcoal (1.6 parts), hardened with dextrin (0.3 part).

Percussion Primers

Percussion primers produce fire or flame from the impact of the trigger or firing pin of a pistol, rifle, or cannon, or of the inertia-operated device in a fuze which functions when the projectile starts on its flight (the so-called concussion element, the primer of which is called a concussion primer) or of that which functions when the projectile strikes its target (the percussion element). A typical primer composition consists of a mixture of mercury fulminate (a primary explosive which produces the first explosion with heat and flame), antimony sulfide (a combustible material which maintains the flame for a longer time), and potassium chlorate (an oxidizing agent which supplies oxygen for the combustion). Sometimes no single primary explosive substance is present; the mixture itself is the primary explosive. Sometimes the compositions contain explosives such as TNT, tetryl, or PETN, which make them hotter, or ground glass which makes them more sensitive to percussion. Hot particles of solid (glass or heavy metal oxide) thrown out by a primer will set fire to black powder over a considerable distance, but they will fall onto smokeless powder without igniting it. The primers which produce the hottest gas are best suited for use with smokeless powder.

Primer compositions are usually mixed by hand on a glass-top table by a workman wearing rubber gloves and working alone in a small building remote from others. They are sometimes mixed dry, but in this country more commonly wet, with water or with water containing gum arabic or gum tragacanth, with alcohol alone or with an alcohol solution of shellac. The caps are loaded in much the same manner that blasting caps are loaded, the mixture is pressed down by machine and perhaps covered with a disc of tinfoil, the anvil is inserted and pressed into place (unless the primer is to be used in a cartridge or fuze of which the anvil is already an integral part), and the caps are finally dried in a dry-house and stored in small magazines until needed for loading.

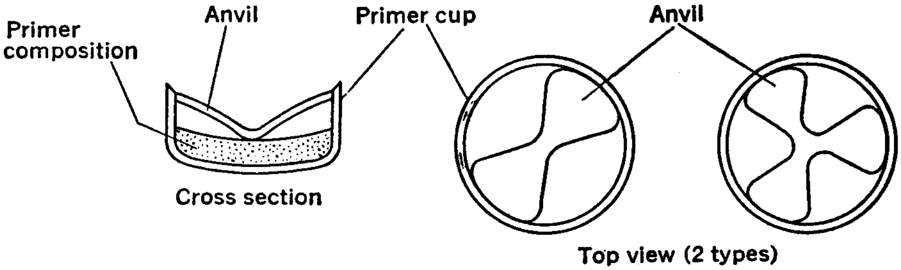

FIGURE 105. Primer Cap for Small Arms Cartridge.

For many years the standard mixture in France for all caps which were to be fired by the blow of a hammer was made from 2 parts of mercury fulminate, 1 of antimony sulfide, and 1 of saltpeter. This was mixed and loaded dry, and was considered to be safer to handle than similar mixtures containing potassium chlorate. Where a more sensitive primer was needed, the standard French composition for all concussion and percussion primers of fuzes was made from 5 parts of mercury fulminate and 9 parts each of antimony sulfide and potassium chlorate.

All the compositions listed in the following table (gum or shellac binder not included) have been used, in small arms primers or in fuze primers, by one or another of the great powers, and they illustrate the wide variations in the proportions of the ingredients which are possible or desirable according to the design of the device in which the primer is used.

Mercury fulminate	10.0	28.0	48.8	4	5	2	11.0	32	16.5	7	19.0
Potassium chlorate	37.0	35.5	24.4	2	9	3	52.5	45	50.0	21	33.0
Antimony sulfide	40.0	28.0	26.2	3	3	3	36.5	23	33.5	17	43.0
Sulfur	...	...	...	..	..	..	...	..	...	..	2.5
Meal powder	...	...	...	..	..	..	...	..	...	..	2.5
Ground glass	13.0	8.5	...	5	..	..	...	..	...	5	...
Ground coke	...	...	...	..	1	..	...	..	...	..	...
Tetryl	...	...	...	..	2	..	...	..	...	..	...

A non-fulminate primer composition is probably somewhat safer to mix than one which contains fulminate. It contains no single substance which is a primary explosive, only the primary explosive mixture of the chlorate with the appropriate combustible material, or, more exactly, the explosive which exists at the point of contact between particles of the two substances. For a non-fulminate primer to perform properly, it is necessary that the composition should be mixed thoroughly and very uniformly in order that dissimilar particles may be found in contact with each other beneath the point of the anvil and may be crushed together by the blow of the trigger. It is not absolutely essential that fulminate compositions should be mixed with the same uniformity. Even if no fulminate happens to lie beneath the point of the anvil, the trigger blow sufficiently crushes the sensitive material in the neighborhood to make it explode. For mechanical reasons, the ingredients of primer composition ought not to be pulverized too finely.[64]

Several non-fulminate primer compositions are listed below.

Potassium chlorate	50	50.54	67	60	53
Antimony sulfide	20	26.31	..	30	17
Lead thiocyanate	..	...	..	..	25
Lead peroxide	25	...	..	..	..
Cuprous thiocyanate	..	...	15	3	..
TNT	5	...	..	..	5
Sulfur	..	8.76	16	7	..
Charcoal	..	...	2	..	..
Ground glass	..	12.39	..	..	..
Shellac	..	2.00	..	..	..

Sulfur ought not to be used in any primer composition, whether fulminate or non-fulminate, which contains chlorate unless an anti-acid is present. In a moist atmosphere, the sulfuric acid, which is inevitably present on the sulfur, attacks the chlorate, liberating chlorine dioxide which further attacks the sulfur, producing more sulfuric acid, and causing a self-catalyzed *souring* which results first in the primer becoming slow in its response to the trigger (hang fire) and later in its becoming inert (misfire). It is evident that the presence of fulminate in the composition will tend to nullify the effect of the souring, and that it

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[64] Cf. Émile Monnin Chamot, "The Microscopy of Small Arms Primers," privately printed, Ithaca, New York, 1922.

is safest to avoid the use of sulfur with chlorate especially in non-fulminate mixtures. The second of the above-listed compositions is an undesirable one in this respect. In the third and fourth compositions, the cuprous thiocyanate serves both as a combustible and as an anti-acid, and it helps, particularly in the third mixture, by supplying copper oxide which is a solid vehicle for the transfer of heat. The first and the last of the above-listed mixtures are the best. They contain no sulfur, and they contain lead enough to supply plenty of solid particles of hot material.

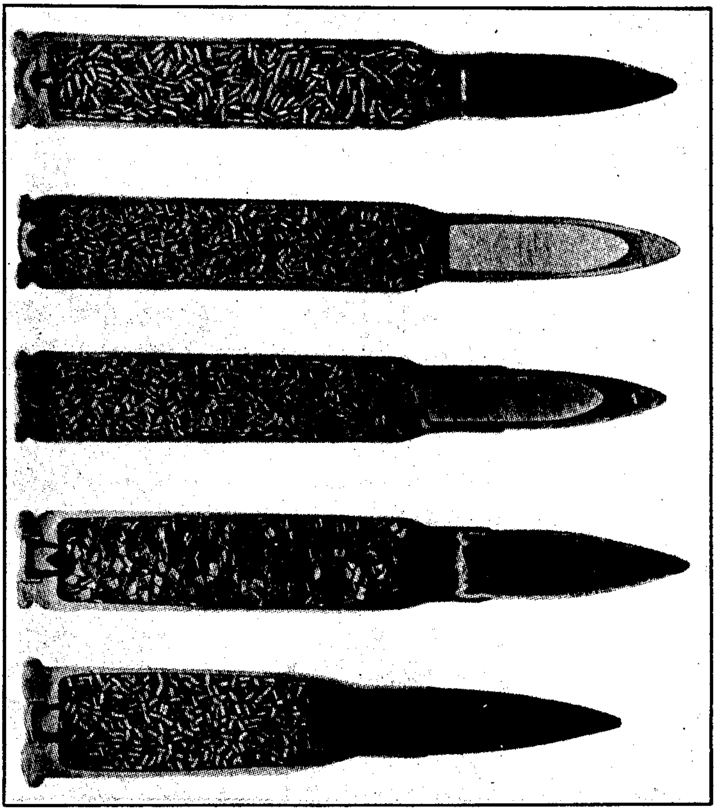

FIGURE 106. Longitudinal Sections of Military Rifle Ammunition of the First World War. (Courtesy Émile Monnin Chamot.) The cartridge at the bottom, French 9.0-mm. Lebel rifle, the one above it, German 7.9-mm. Mauser, and the one above that, Canadian .30 caliber, all have anvils of the Berdan type integrally one with the metal of the cartridge case.

Gunnery experts ascribe a large part of the erosion of shotgun and rifle barrels to the action of the soluble salts which are produced from the materials of the primer compositions, particularly to the chlorides which come from the chlorate, and to the sulfates which result from the combustion of the antimony sulfide. The following table lists several non-chlorate, non-erosive primer compositions. They contain no compounds of chlorine. They contain either lead or barium or both, and both of these metals form sulfates which are insoluble in water. Moreover, the soluble portions of the residues from the primers which contain barium nitrate are alkaline and are even capable of neutralizing any acidity which might arise from the smokeless powder.

Mercury fulminate	36	40	25	20	39
Antimony sulfide	20	25	15	20	9
Barium nitrate	..	25	25	40	41
Lead peroxide	..	..	35	10	..
Lead chromate	40	..	..	..	..
Barium carbonate	..	6	..	..	..
Picric acid	..	..	..	..	5
Powdered glass	4	4	..	..	6
Calcium silicide	..	..	..	10	..