#### CHAPTER VII

#### DYNAMITE AND OTHER HIGH EXPLOSIVES

#### Invention of Dynamite

Dynamite and the fulminate blasting cap both resulted from Alfred Nobel's effort to make nitroglycerin more safe and more convenient to use.1 Having discovered that nitroglycerin is exploded by the explosion of a small firecracker-like device filled with black powder, he tried the effect of mixing the two materials, and in 1863 was granted a patent 2 which covered the use of a liquid explosive, such as nitroglycerin or methyl or ethyl nitrate, in mixture with gunpowder in order to increase the effectiveness of the latter. The amount of the liquid was limited by the requirement that the mixtures should be dry and granular in character. The explosives were supposed to be actuated by fire, like black powder, but the liquid tended to slow down the rate of burning, and they were not notably successful. The same patent also covered the possibility of substituting a part of the saltpeter by nitroglycerin. Because this substance is insoluble in water and non-hygroscopic, it acts as a protective covering for the salt and makes the use of sodium nitrate possible in these mixtures.

Nobel's next patent,<sup>3</sup> granted in 1864, related to improvements in the manufacture of nitroglycerin and to the exploding of it by heating or by means of a detonating charge. He continued his experiments and in 1867 was granted a patent <sup>4</sup> for an explosive prepared by mixing nitroglycerin with a suitable non-explosive, porous absorbent such as charcoal or siliceous earth. The resulting material was much less sensitive to shock than nitroglycerin. It was known as *dynamite*, and was manufactured and sold also

<sup>&</sup>lt;sup>1</sup> For an account of Nobel and his inventions see de Mosenthal, Jour. Soc. Chem. Ind., 443 (1899).

<sup>&</sup>lt;sup>2</sup> Brit. Pat. 2359 (1863).

<sup>&</sup>lt;sup>3</sup> Brit. Pat. 1813 (1864).

<sup>&</sup>lt;sup>4</sup> Brit. Pat. 1345 (1867).

under the name of Nobel's Safety Powder. The absorbent which was finally chosen as being most satisfactory was diatomaceous earth or kieselguhr (guhr or fuller's earth). Nobel believed that dynamite could be exploded by a spark or by fire if it was confined closely, but preferred to explode it under all conditions by means of a special exploder or cap containing a strong charge of



FIGURE 83. Alfred Nobel (1833-1896). First manufactured and used nitroglycerin commercially, 1863; invented dynamite and the fulminate blasting cap, 1867; straight dynamite, 1869; blasting gelatin and gelatin dynamite, 1875; and ballistite, 1888. He left the major part of his large fortune for the endowment of prizes, now known as the Nobel Prizes, for notable achievements in physics, in chemistry, in physiology and medicine, in literature, and in the promotion of peace.

mercury fulminate, crimped tightly to the end of the fuse in order that it might detonate more strongly. He stated that the form of the cap might be varied greatly but that its action depended upon the sudden development of an intense pressure or shock.

Dynamite with an inactive base (guhr dynamite) is not manufactured commercially in this country. Small quantities are used for experimental purposes where a standard of comparison is needed in studies on the strength of various explosives.

The next important event in the development of these explosives was Nobel's invention of dynamite with an active base,<sup>5</sup> an explosive in which the nitroglycerin was absorbed by a mixture of materials which were themselves not explosive separately, such as potassium, sodium, or ammonium nitrate mixed with wood meal, charcoal, rosin, sugar, or starch. The nitroglycerin formed a thin coating upon the particles of the solid materials, and caused them to explode if a fulminate cap was used. The patent suggested a mixture of barium nitrate 70 parts, rosin or charcoal 10, and nitroglycerin 20, with or without the addition of sulfur, as an example of the invention. Nitroglycerin alone was evidently not enough to prevent the deliquescence of sodium and ammonium nitrate in these mixtures, for a later patent 6 of Nobel claimed the addition of small amounts of paraffin, ozokerite, stearine, naphthalene, or of any similar substance which is solid at ordinary temperatures and is of a fatty nature, as a coating for the particles to prevent the absorption of moisture by the explosive and the resulting danger from the exudation of nitroglycerin.

Dynamite with an active base is manufactured and used extensively in this country and in Canada and Mexico. It is known as straight dynamite, or simply as dynamite, presumably because its entire substance contributes to the energy of its explosion. The standard 40% straight dynamite which is used in comparative tests at the U. S. Bureau of Mines contains introglycerin 40%, sodium nitrate 44%, calcium carbonate (anti-acid) 1%, and wood pulp 15%. Since the time when this standard was adopted, the usage of the term "straight" has altered somewhat in consequence of changes in American manufacturing practice, with the result that this standard material is now better designated as 40% straight nitroglycerin (straight) dynamite. This name distinguishes it from 40% l. f. or 40% low-freezing (straight) dynamite which contains, instead of straight nitroglycerin, a mixture of nitric esters produced by nitrating a mix-

<sup>&</sup>lt;sup>5</sup> Brit. Pat. 442 (1869).

<sup>&</sup>lt;sup>6</sup> Brit. Pat. 1570 (1873).

<sup>&</sup>lt;sup>7</sup>C. A. Taylor and W. H. Rinkenbach, "Explosives, Their Materials, Constitution, and Analysis," U. S. Bur. Mines Bull. 219, Washington, 1923, p. 133.

ture of glycerin and glycol or of glycerin and sugar. Practically all active-base dynamites now manufactured in the United States, whether straight or ammonia or gelatin, are of this l. f. variety. American straight dynamites contain from 20 to 60% of mixed nitric esters absorbed on wood pulp and mixed with enough sodium or potassium nitrate to maintain the oxygen balance and to take care of the oxidation of part or occasionally of all the wood pulp.

Judson powder is a special, low-grade dynamite in which 5 to 15% of nitroglycerin is used as a coating on a granular dope made by mixing ground coal with sodium nitrate and sulfur, warming the materials together until the sulfur is melted, forming into grains which harden on cooling and are screened for size. It is intermediate in power between black powder and ordinary dynamite and is used principally for moving earth and soft rock in railroad work.

Nobel's inventions of blasting gelatin and gelatin dynamite are both covered by the same patent.8 Seven or 8% of collodion cotton dissolved in nitroglycerin converted it to a stiff jelly which was suitable for use as a powerful high explosive. Solvents, such as acetone, ether-alcohol, and nitrobenzene, facilitated the incorporation of the two substances in the cold, but Nobel reported that collodion cotton dissolved readily in nitroglycerin without additional solvent if the nitroglycerin was warmed gently on the water bath. A cheaper explosive of less power could be made by mixing the gelatinized nitroglycerin with black powder or with mixtures composed of an oxidizing agent, such as a nitrate or chlorate, and a combustible material, such as coal dust, sulfur, sawdust, sugar, starch, or rosin. A typical gelatin dynamite consists of nitroglycerin 62.5%, collodion cotton 2.5%, saltpeter 27.0%, and wood meal 8%. A softer jelly is used for making gelatin dynamite than is suitable for use by itself as a blasting gelatin, and somewhat less collodion is used in proportion to the amount of nitroglycerin.

All straight nitroglycerin explosives can be frozen. Straight dynamite when frozen becomes less sensitive to shock and to initiation, but blasting gelatin becomes slightly more sensitive.

<sup>&</sup>lt;sup>8</sup> Brit. Pat. 4179 (1875).

335

When the explosives are afterwards thawed, the nitroglycerin shows a tendency to exude.

#### Invention of Ammonium Nitrate Explosives

In 1867 two Swedish chemists, C. J. Ohlsson and J. H. Norrbin, patented an explosive, called ammoniakkrut, which consisted of ammonium nitrate either alone or in mixture with charcoal, sawdust, naphthalene, picric acid, nitroglycerin, or nitrobenzene. Theoretical calculations had shown that large quantities of heat and gas were given off by the explosions of these mixtures. The proportions of the materials were selected in such manner that all the carbon should be converted to carbon dioxide and all the hydrogen to water. Some of these explosives were difficult to ignite and to initiate, but the trouble was remedied by including some nitroglycerin in their compositions and by firing them with fulminate detonators. They were used to some extent in Sweden. Nobel purchased the invention from his fellow-countrymen early in the 1870's, and soon afterwards took out another patent 9 in connection with it, but still found that the hygroscopicity of the ammonium nitrate created real difficulty. He was not able to deal satisfactorily with the trouble until after the invention of gelatin dynamite. In present manufacturing practice in this country the tendency of the ammonium nitrate to take up water is counteracted by coating the particles with water-repelling substances, oils, or metallic soaps.

In 1879 Nobel took out a Swedish patent for extra-dynamite (ammon-gelatin-dynamit), one example of which was a fortified gelatin dynamite consisting of nitroglycerin 71%, collodion 4%, charcoal 2%, and ammonium nitrate 23%. Another contained much less nitroglycerin, namely, 25%, along with collodion 1%, charcoal 12%, and ammonium nitrate 62%, and was crumbly and plastic between the fingers rather than clearly gelatinous.

In these explosives, and in the ammonium nitrate permissible explosives which contain still less nitroglycerin, it is supposed that the nitroglycerin or the nitroglycerin jelly, which coats the particles of ammonium nitrate, carries the explosive impulse originating in the detonator, that this causes the ammonium nitrate to decompose explosively to produce nitrogen and water

<sup>&</sup>lt;sup>9</sup> The above-cited Brit. Pat. 1570 (1873).

and oxygen, the last named of which enters into a further explosive reaction with the charcoal or other combustible material. Other explosive liquids or solids, such as liquid or solid DNT, TNT, or TNX, nitroglycol, nitrostarch, or nitrocellulose, may be used to sensitize the ammonium nitrate and to make the mixture more easily detonated by a blasting cap. Non-explosive combustible materials, such as rosin, coal, sulfur, cereal meal, and paraffin, also work as sensitizers for ammonium nitrate, and a different hypothesis is required to explain their action.

#### Guhr Dynamite

Guhr dynamite is used rather widely in Europe. It is not hygroscopic. Liquid water however, brought into contact with it, is absorbed by the kieselguhr and displaces the nitroglycerin which separates in the form of an oily liquid. The nitroglycerin thus set free in a wet bore hole might easily seep away into a fissure in the rock where it would later be exploded accidentally by a drill or by the blow of a pick. Water does not cause the separation of nitroglycerin from blasting gelatin or gelatin dynamite. It tends to dissolve the soluble salts which are present in straight dynamite and to liberate in the liquid state any nitroglycerin with which they may be coated.

Guhr dynamite, made from 1 part of kieselguhr and 3 parts of nitroglycerin, is not exploded by a blow of wood upon wood, but is exploded by a blow of iron or other metal upon iron. In the drop test it is exploded by the fall of a 1-kilogram weight through 12 to 15 cm., or by the fall of a 2-kilogram weight through 7 cm. The frozen material is less sensitive: a drop of more than 1 meter of the kilogram weight or of at least 20 cm. of the 2-kilogram weight is necessary to explode it. Frozen or unfrozen it is exploded in a paper cartridge by the impact of a bullet from a military rifle. A small sample will burn quietly in the open, but will explode if it is lighted within a confined space. A cartridge explodes if heated on a metal plate.

The velocity of detonation of guhr dynamite varies with the density of loading and with the diameter of the charge, but does not reach values equal to the maxima under best conditions for nitroglycerin and blasting gelatin. Velocities of 6650 to 6800 meters per second, at a density of loading of 1.50 (the highest

which is practical) have been reported. Naoúm, 10 working with charges in an iron pipe 34 mm. in internal diameter and at a density of loading of 1.30, found for nitroglycerin guhr dynamite a velocity of detonation of 5650 meters per second, and, under the same conditions, for nitroglycol guhr dynamite one of 6000 meters per second.



FIGURE 84. Determination of the Velocity of Detonation of Dynamite by the Dautriche Method. (Courtesy Hercules Powder Company.) Compare Figure 9, page 17.

Dynamites, like guhr dynamite and straight dynamite, which contain nitroglycerin in the subdivided but liquid state communicate explosion from cartridge to cartridge more readily, and in general are more easy to initiate, than blasting gelatin and gelatin dynamite in which no liquid nitroglycerin is present. A cartridge of guhr dynamite 30 mm. in diameter will propagate its explosion through a distance of 30 cm. to a similar cartridge.

<sup>10</sup> Phokion Naoúm, "Nitroglycerine and Nitroglycerine Explosives," trans E. M. Symmes, Baltimore, The Williams and Wilkins Company, 1928 p. 277.

## Straight Dynamite

Straight dynamite containing 60% or less of nixed nitric esters—but not more because of the danger of exudation—is used extensively in the United States, but has found little favor in

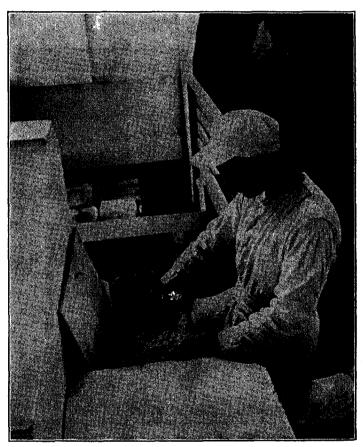


FIGURE 85. Dynamite Manufacture. (Courtesy Hercules Powder Company.) Rubbing the dry ingredients of dynamite through a screen into the bowl of a mixing machine.

Europe. It is made simply by mixing the explosive oil with the absorbent materials; the resulting loose, moist-appearing or greasy mass, from which oil ought not to exude under gentle pressure, is put up in cartridges or cylinders wrapped in paraffined paper and dipped into melted paraffin wax to seal them against moisture.

The strength of straight nitroglycerin dynamite is expressed by the per cent of nitroglycerin which it contains. Thus, "40% straight nitroglycerin dynamite" contains 40% of nitroglycerin, but "40% ammonia dynamite," "40% gelatin dynamite," etc., whatever their compositions may be, are supposed to have the same strength or explosive force as 40% straight nitroglycerin dynamite. Munroe and Hall 11 in 1915 reported for typical straight nitroglycerin dynamites the compositions which are

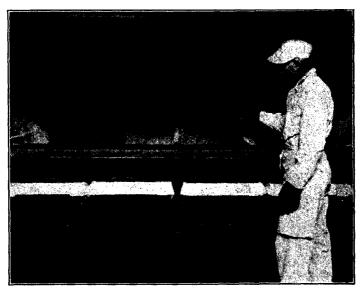


FIGURE 86. Dynamite Manufacture. (Courtesy Hercules Powder Company.) Hoppers underneath the mixing machine, showing the buggies which carry the mixed dynamite to the packing machines.

shown in the following table. Although these dynamites are not now manufactured commercially in the United States, their explosive properties, studied intensively at the U. S. Bureau of

	STRENGTH									
	15%	20%	25%	30%	35%	40%	45%	50%	55%	60%
Nitroglycerin	15	20	25	30	35	40	45	50	55	60
Combustible material	20	19	18	17	16	15	14	14	15	16
Sodium nitrate	64	60	5 <b>6</b>	52	48	44	40	35	29	23
Calcium or magne-										
sium carbonate	1	1	1	1	1	1	1	1	1	1

Mines and reported as a matter of interest, do not differ greatly from those of the l. f. dynamites by which they have been superseded in common use. The combustible material stated to be used in these compositions consists of a mixture of wood pulp,

<sup>11</sup> Charles E. Munroe and Clarence Hall, "A Primer on Explosives for Metal Miners and Quarrymen," U. S. Bur. Mines Bull. 80, Washington, 1915, p. 22.

flour, and brimstone for the grades below 40% strength, wood pulp alone for the 40% and stronger. In commercial practice the dope sometimes contains coarse combustible material, like rice hulls, sawdust, or bran, which makes the explosive more bulky and has the effect of reducing the velocity of detonation. Tests at the U. S. Bureau of Mines on standard straight dynamites in cartridges 1¼ inches in diameter showed for the 30% grade a velocity of detonation of 4548 meters per second, for the 40%

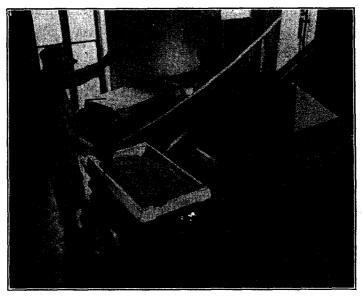


FIGURE 87. Dynamite Manufacture. (Courtesy Hercules Powder Company.) Dumping the mixed dynamite onto the conveyor belt which raises it to the hopper of the semi-automatic packing machine.

grade 4688 meters per second, and for the 60% grade 6246 meters per second. The 40% dynamite was exploded in one case out of three by an 11-cm. drop of a 2-kilogram weight, in no case out of five by a 10-cm. drop. Cartridges 1½ inches in diameter and 8 inches long transmitted explosion from one to another through a distance of 16 inches once in two trials, but not through a distance of 17 inches in three trials. The 40% dynamite gave a small lead block compression of 16.0 mm., and an expansion (average of three) in the Trauzl test of 278 cc.<sup>12</sup>

<sup>12</sup> Clarence Hall, W. O. Snelling, and S. P. Howell, "Investigations of Explosives Used in Coal Mines," U. S. Bur. Mines Bull. 15, Washington, 1912, pp. 171, 173.

Munroe and Hall <sup>18</sup> also reported the following compositions for typical ordinary and low-freezing ammonia dynamites, the combustible material in each case being a mixture of wood pulp, flour, and brimstone. Low-freezing dynamites at present in use in this country contain nitroglycol or nitrosugar instead of the above-mentioned nitrosubstitution compounds. In Europe dinitro-chlorohydrin, tetranitrodiglycerin, and other nitric esters are used.

Strength		0	rdina	ry		Low-Freezing				
Strength	30%	35%	40%	50%	60%	30%	35%	40%		60%
Nitroglycerin Nitrosubstitution com-		20	22	27	35	13	17	17	21	27
pounds	l .					3	4	4		6
Ammonium nitrate		15	20	25	30	15	15	20	25	30
Sodium nitrate	51	48	42	36	24	53	49	45	36	27
Combustible material	18	16	15	11	10	15	14	13	12	9
Calcium carbonate or zinc oxide	1	1	1	1	1	1	1	1	1	1

Three of the standard French ammonia dynamites, according to Naoúm,<sup>14</sup> have the compositions and explosive properties listed below.

Nitroglycerin	40	20	22
Ammonium nitrate	45	75	75
Sodium nitrate	5		
Wood or cereal meal	10	5	• • •
Charcoal			3
Lead block expansion	400.0 cc.	335.0 cc.	330.0 сс.
Lead block crushing			
Density		1.20	1.33

Taylor and Rinkenbach <sup>15</sup> report typical analyses of American ammonium nitrate dynamite (I below) and ammonium nitrate sodium nitrate dynamite (II below). These formulas really represent ammonium nitrate permissible explosives, very close in their

<sup>&</sup>lt;sup>13</sup> Op. cit., p. 23.

<sup>14</sup> Op. cit., p. 285.

<sup>&</sup>lt;sup>15</sup> Op. cit., pp. 136, 138.

compositions to Monobel (III below) which is permissible in this country for use in coal mines. Naoúm 16 reports that this

	I	II	III
Nitroglycerin	9.50	9.50	10.0
Ammonium nitrate	79.45	69.25	80.0
Sodium nitrate		10.20	
Carbonaccous combustible material 17	9.75	9.65	
Wood meal			10.0
Anti-acid	0.40	0.50	
Moisture	0.90	0.90	

Monobel (density about 1.15) gives a lead block expansion of about 350 cc. and a lead block crushing of 12 mm. He states that

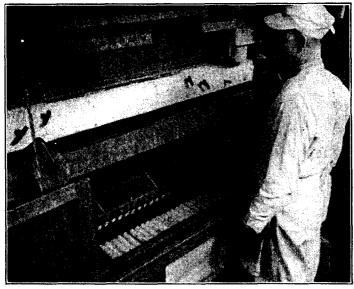


FIGURE 88. Dynamite Manufacture. (Courtesy Hercules Powder Company.) Cartridges of dynamite as they come from the semi-automatic packing machine.

Monobel belongs to the class of typical ammonium nitrate explosives rather than to the dynamites, and points out that no specific effect can be ascribed to the 10% nitroglycerin which it contains, for an explosive containing only a small quantity, say 4%,

<sup>16</sup> Op. cit., p. 286.

<sup>17</sup> The carbonaceous combustible material contains 0.40% grease or oil which was added to the ammonium nitrate to counteract its hygroscopicity. Note that the figures in the first two columns of the table represent results of analyses; those in the third column represent the formula according to which the explosive is mixed.

of nitroglycerin, or none at all, will give essentially the same performance. But the ammonium nitrate explosive with no nitroglycerin in it is safer to handle and more difficult to detonate.

# Blasting Gelatin

Blasting gelatin exists as a yellowish, translucent, elastic mass of density about 1.63. Strong pressure does not cause nitroglycerin to exude from it. Its surface is rendered milky by long contact with water, but its explosive strength is unaffected. It is less sensitive to shock, blows, and friction than nitroglycerin, guhr dynamite, and straight dynamite, for its elasticity enables it more readily to absorb the force of a blow, and a thin layer explodes under a hammer more easily than a thick one. Blasting gelatin freezes with difficulty. When frozen, it loses its elasticity and flexibility, and becomes a hard, white mass. Unlike guhr dynamite and straight dynamite, it is more sensitive to shock when frozen than when in the soft and unfrozen state.

Unlike nitroglycerin, blasting gelatin takes fire easily from a flame or from the spark of a fuse. Its combustion is rapid and violent, and is accompanied by a hissing sound. If a large quantity is burning, the combustion is likely to become an explosion, and the same result is likely to follow if even a small quantity of the frozen material is set on fire.

Pulverulent explosives or explosive mixtures are easier to initiate and propagate detonation for a greater distance than liquid explosives, especially viscous ones, and these are easier to detonate and propagate more readily than colloids. The stiffer the colloid the more difficult it becomes to initiate, until, with increasingly large proportions of nitrocellulose in the nitroglycerin gel, tough, horny colloids are formed, like ballistite and cordite, which in sizable aggregates can be detonated only with difficulty. Blasting gelatin is more difficult to detonate than any of the forms of dynamite in which the nitroglycerin exists in the liquid state. Naoúm 18 reports that a freshly prepared blasting gelatin made from 93 parts of nitroglycerin and 7 parts of collodion cotton is exploded by a No. 1 (the weakest) blasting cap and propagates detonation even in 25-mm. cartridges across a gap of about 10 mm. A blasting gelatin containing 9% of collodion cotton requires a No. 4 blasting cap to make it explode and propagates

<sup>18</sup> Op. cit., p. 316.

its explosion to an adjacent cartridge only when initiated by a No. 6 blasting cap.

Blasting gelatin and gelatin dynamite on keeping become less sensitive to detonation, and, after long storage in a warm climate, may even become incapable of being detonated. The effect has been thought to be due to the small air bubbles which make newly prepared blasting gelatin appear practically white but which disappear when the material is kept in storage and becomes translucent and yellowish. But this cannot be the whole cause of the effect, for the colloid becomes stiffer after keeping. The loss of sensitivity is accompanied by a rapid dropping off in the velocity of detonation and in the brisance. According to Naoúm, blasting gelatin containing 7% collodion cotton when newly prepared gave a lead block expansion of 600 cc., after 2 days 580 cc., and one containing 9% collodion gave when freshly made an expansion of 580 cc., after 2 days 545 cc.

Blasting gelatin under the most favorable conditions has a velocity of detonation of about 8000 meters per second. In iron pipes it attains this velocity only if its cross section exceeds 30 mm. in diameter, and it attains it only at a certain distance away from the point of initiation, so that in the Dautriche method where short lengths are used lower values are generally obtained. In tubes of 20–25 mm. diameter, and with samples of a sensitivity reduced either by storage or by an increased toughness of the colloid, values as low as 2000–2500 meters per second have been observed.

## Gelatin Dynamite

Blasting gelatin is not used very widely in the United States; the somewhat less powerful gelatin dynamite, or simply gelatin as it is called, is much more popular. Gelatin dynamite is essentially a straight dynamite in which a gel is used instead of the liquid nitroglycerin or l. f. mixture of nitric esters. It is a plastic mass which can be kneaded and shaped. The gel contains between 2 and 5.4% collodion cotton, and is not tough and really elastic like blasting gelatin. Correspondingly it is initiated more easily and has a higher velocity of detonation and better propagation. The gel is prepared by mixing the nitroglycerin and collodion cotton, allowing to stand at 40–45°C. for some hours or over

<sup>19</sup> Op. cit., p. 322.

night, and then incorporating mechanically with the dope materials which have been previously mixed together. Munroe and Hall <sup>20</sup> in 1915 gave the compositions listed below as typical of gelatin dynamites offered for sale at that time in this country. Instead of straight nitroglycerin, l. f. mixtures of nitric esters are now used.

	STRENGTH							
	30%	35%	40%	50%	55%	60%	70%	
Nitroglycerin	23.0	28.0	33.0	42.0	46.0	50.0	60.0	
Nitrocellulose	0.7	0.9	1.0	1.5	1.7	1.9	2.4	
Sodium nitrate	62.3	<b>58.1</b>	52.0	45.5	42.3	38.1	29.6	
Combustible material <sup>21</sup>	13.0	12.0	13.0	10.0	9.0	9.0	7.0	
Calcium carbonate	1.0	1.0	1.0	1.0	1.0	1.0	1.0	

The three standard explosives which are used in Great Britain are called respectively blasting gelatin, gelatin dynamite, and *Gelignite*. Gelignite, let us note, is a variety of gelatin dynamite as the latter term is used in this country. It is the most widely used of the three and may indeed be regarded as the standard explosive.

	BLASTING	GELATIN	
	GELATIN	DYNAMITE	GELIGNITE
Nitroglycerin	. 92	75	60
Collodion cotton	. 8	5	4
Wood meal		5	8
Potassium nitrate		15	28

The gelatin dynamites most widely used in Germany contain about 65 parts of gelatinized nitroglycerin and about 35 parts of dope or absorbent material. The dope for an explosive for domestic use consists of 76.9% sodium nitrate, 22.6% wood meal, and 0.5% chalk, and for one for export of 80% potassium nitrate, 19.5% wood meal, and 0.5% chalk. A weaker Gelignite II and certain high-strength gelatin dynamites, as tabulated below, are also manufactured for export.

	LIGNITE II	High-Strei	NGTH GELATIN 81%	DYNAMITE 75%
Nitroglycerin		75	75.8	70.4
Collodion cotton		7 <u>3,</u> 5	5.2	4.6
	-		5.2 15.2	
Potassium nitrate		15		19.3
		5	3.8	5.7
Rye meal	9.0			

<sup>20</sup> Op. cit., p. 23.

<sup>&</sup>lt;sup>21</sup> Wood pulp was used in the 60% and 70% grades. Flour, wood pulp, and, in some examples, rosin and brimstone were used in the other grades.

The gelatin dynamites manufactured in Belgium are called *Forcites*. The reported compositions of several of them are tabulated below. *Forcite extra* is an ammonia gelatin dynamite.

		For-					,
		CITE	Su-		For-		For-
	For-	Su-	PER	For-	CITE	For-	CITE
	CITE	PER-	For-	CITE	No.	CITE	No.
	EXTRA	IEURE	CITE	No. 1	1P	No. 2	2P
Nitroglycerin	64	64	64	49	49	36	36
Collodion cotton	3.5	3	3	<b>2</b>	2	3	2
Sodium nitrate		24		36		35	
Potassium nitrate			23		37		46
Ammonium nitrate	25						
Wood meal	6.5	8	9	13	11	11	
Bran						14	15
Magnesium carbonate	1	1	1	1	1	1	1

In France gelatin dynamites are known by the names indicated in the following table where the reported compositions of several of them are tabulated.

	Dynamite-gomme- extra-forte	Dynamite-gomme- potasse	Dynamite-gomme- soude	Gélatine A	Gélatine B-potasse	Gélatine B-soude	Gomme E	Gélignite
Nitroglycerin	92–93 8–7 	82–83 6–5 9–10  2–3	82–83 6–5  9–10 2–3	64 3  24 ·8 	57.5 2.5 32.0  8.0	57 3  34 6 	49 2 36  10 3	58 2 28  9 3

## Permissible Explosives

The atmosphere of coal mines frequently contains enough methane (fire damp) to make it explode from the flame of a black powder or dynamite blast. Dust also produces an explosive atmosphere, and it may happen, if dust is not already present,

that one blast will stir up clouds of dust which the next blast will cause to explode. Accidents from this cause became more and more frequent as the industrial importance of coal increased during the nineteenth century and as the mines were dug deeper and contained more fire damp, until finally the various nations which were producers of coal appointed commissions to study and develop means of preventing them. The first of these was appointed in France in 1877, the British commission in 1879, the Prussian commission in 1881, and the Belgian and Austrian commissions at later dates. The Pittsburgh testing station of the U. S. Geological Survey was officially opened and regular work was commenced there on December 3, 1908, with the result that the first American list of explosives permissible for use in gaseous and dusty coal mines was issued May 15, 1909. On July 1, 1909, the station was taken over by the U.S. Bureau of Mines,22 which, since January 1, 1918, has conducted its tests at the Explosives Experiment Station at Bruceton, not far from Pittsburgh, in Pennsylvania.

Explosives which are approved for use in gaseous and dusty coal mines are known in this country as permissible explosives, in England as permitted explosives, and are to be distinguished from authorized explosives which conform to certain conditions with respect to safety in handling, in transport, etc. Explosives which are safe for use in coal mines are known in France as explosifs antigrisouteux, in Belgium as explosifs S. G. P. (sécurité, grisou, poussière), in Germany as schlagwettersichere Sprengstoffe while the adjective handhabungssichere is applied to those which are safe in handling. Both kinds, permissible and authorized, are safety explosives, explosifs de sûreté, Sicherheitssprengstoffe.

A mixture of air and methane is explosive if the methane content lies between 5 and 14%. A mixture which contains 9.5% of methane, in which the oxygen exactly suffices for complete combustion, is the one which explodes most violently, propagates the explosion most easily, and produces the highest temperature. This mixture ignites at about 650° to 700°. Since explosives in general produce temperatures which are considerably above 1000°, explo-

<sup>22</sup> A few of the interesting and important publications of the U. S. Bureau of Mines are listed in the footnote, Vol. I, pp. 22-23,

sive mixtures of methane and air would always be exploded by them if it were not for the circumstance, discovered by Mallard and Le Chatelier,28 that there is a certain delay or period of induction before the gaseous mixture actually explodes. At 650° this amounts to about 10 seconds, at 1000° to about 1 second, and at 2200° there is no appreciable delay and the explosion is presumed to follow instantaneously after the application of this temperature however momentary. Mallard and Le Chatelier concluded that an explosive having a temperature of explosion of 2200° or higher would invariably ignite fire damp. The French commission which was studying these questions at first decided that the essential characteristic of a permissible explosive should be that its calculated temperature of explosion should be not greater than 2200°, and later designated a temperature of 1500° as the maximum for explosives permissible in coal seams and 1900° for those intended to be used in the accompanying rock.

The flame which is produced by the explosion of a brisant explosive is of extremely short duration, and its high temperature continues only for a small fraction of a second, for the hot gases by expanding and by doing work immediately commence to cool themselves. If they are produced in the first place at a temperature below that of the instantaneous inflammation of fire damp, they may be cooled to such an extent that they are not sufficiently warm for a sufficiently long time to ignite fire damp at all. Black powder, burning slowly, always ignites explosive gas mixtures. But any high explosive may be made safe for use in gaseous mines by the addition to it of materials which reduce the initial temperature of the products of its explosion. Or, in cases where this initial temperature is not too high, the same safety may be secured by limiting the size of the charge and by firing the shot in a well-tamped bore hole under such conditions that the gases are obliged to do more mechanical work and are cooled the more in consequence.

Permissible explosives may be divided into two principal classes: (1) those which are and (2) those which are not based upon a high explosive which is cool in itself, such as ammonium nitrate, or guanidine nitrate, or nitroguanidine. The second class may be subdivided further, according to composition, into as

<sup>&</sup>lt;sup>23</sup> Ann. Min., [8] 11, 274 (1887).

many classes as there are varieties in the compositions of high explosives, or it may be subdivided, irrespective of composition, according to the means which are used to reduce the explosion temperature. Thus, an explosive containing nitroglycerin, nitrostarch, chlorate or perchlorate, or tetranitronaphthalene, or an explosive which is essentially black powder, may have its temperature of explosion reduced by reason of the fact that (a) it contains an excess of carbonaceous material, (b) it contains water physically or chemically held in the mixture, or (c) it contains volatile salts or substances which are decomposed by heat. Ammonium nitrate may also be used as a means of lowering the temperature of explosion, and thus defines another subdivision (d) which corresponds to an overlapping of the two principal classes, (a) and (b).

Ammonium nitrate, although it is often not regarded as an explosive, may nevertheless be exploded by a suitable initiator. On complete detonation it decomposes in accordance with the equation  $2NH_4NO_3 \longrightarrow 4H_2O + 2N_2 + O_2$ 

but the effect of feeble initiation is to cause decomposition in another manner with the production of oxides of nitrogen. By using a booster of 20–30 grams of Bellite (an explosive consisting of a mixture of ammonium nitrate and dinitrobenzene) and a detonator containing 1 gram of mercury fulminate, Lobry de Bruyn <sup>24</sup> succeeded in detonating 180 grams of ammonium nitrate compressed in a 8-cm. shell. The shell was broken into many fragments. A detonator containing 3 grams of mercury fulminate, used without the booster of Bellite, produced only incomplete detonation. Lheure <sup>25</sup> secured complete detonation of cartridges of ammonium nitrate <sup>26</sup> loaded in bore holes in rock by means of a trinitrotoluene detonating fuse which passed completely through them.

The sensitiveness of ammonium nitrate to initiation is increased by the addition to it of explosive substances, such as nitroglycerin, nitrocellulose, or aromatic nitro compounds, or of

<sup>&</sup>lt;sup>24</sup> Rec. trav. chim., 10, 127 (1891).

<sup>&</sup>lt;sup>25</sup> Ann. Min., [10] 12, 169 (1907).

<sup>&</sup>lt;sup>26</sup> On the explosibility of ammonium nitrate, see also Munroe, Chem. Met. Eng., 26, 535 (1922); Cook, ibid., 31, 231 (1924); Sherrick, Army Ordnance, 4, 237, 329 (1924).

non-explosive combustible materials, such as rosin, sulfur, charcoal, flour, sugar, oil, or paraffin. Substances of the latter class react with the oxygen which the ammonium nitrate would otherwise liberate; they produce additional gas and heat, and increase both the power of the explosive and the temperature of its explosion. Pure ammonium nitrate has a temperature of explosion of about 1120° to 1130°. Ammonium nitrate explosives permissible in the United States generally produce instantaneous temperatures between 1500° and 2000°.

Among the first permissible explosives developed in France were certain ones of the Belgian Favier type which contained no nitroglycerin and consisted essentially of ammonium nitrate, sometimes with other nitrates, along with a combustible material such as naphthalene or nitrated naphthalene or other aromatic nitro compounds. These explosives have remained the favorites in France for use in coal mines. The method of manufacture is simple. The materials are ground together in a wheel mill, and the mass is broken up, sifted, and packed in paraffined paper cartridges. The compositions of the mixtures are those which calculations show to give the desired temperatures of explosion. Grisourites roches, permissible for use in rock, have temperatures of explosion between 1500° and 1900°; Grisounites couches, for use in coal, below 1500°. Several typical compositions are listed below.

	Grisou- naphtalite- roche	Grisou- naphtalite- roche salpêtrée	Grisou- naphtalite- couche	Grisou- naphtalite- couche salpêtrée	Grisou- tétrylite- couche
Ammonium					
nitrate	91.5	86.5	95	90	88
Potassium			1		
nitrate	• •	5.0		5	5
Dinitro-					
naphthalene.	8.5	8.5			• •
Trinitro-					-, •
naphthalene.			5	5	
Tetryl			_	١	7
	•	• •	• •	••	•
				i i	

The French also have permissible explosives containing both ammonium nitrate and nitroglycerin (gelatinized), with and without saltpeter. These are called *Grisou-dynamites* or *Grisoutines*.

	Grisou- dynamite- roche	Grisou- dynamite- roche salpêtrée	Grisou- dynamite- couche	Grisou- dynamite- couche salpêtrée
Nitroglycerin Collodion cotton Ammonium nitrate. Potassium nitrate	29.0 1.0 70.0	29.0 1.0 65.0 5.0	12.0 0.5 87.5	12.0 0.5 82.5 5.0

The effect of ammonium nitrate in lowering the temperature of explosion of nitroglycerin mixtures is nicely illustrated by the data of Naoúm <sup>27</sup> who reports that guhr dynamite (75% actual nitroglycerin) gives a temperature of 2940°, a mixture of equal amounts of guhr dynamite and ammonium nitrate 2090°, and a mixture of 1 part of guhr dynamite and 4 of ammonium nitrate 1468°.

In ammonium nitrate explosives in which the ingredients are not intimately incorporated as they are in the Favier explosives, but in which the granular particles retain their individual form, the velocity of detonation may be regulated by the size of the nitrate grains. A relatively slow explosive for producing lump coal is made with coarse-grained ammonium nitrate, and a faster explosive for the procurement of coking coal is made with fine-grained material.

The first explosives to be listed as permissible by the U. S. Bureau of Mines were certain *Monobels* and *Carbonites*, and Monobels are still among the most important of American permissibles. Monobels contain about 10% nitroglycerin, about 10% carbonaceous material, wood pulp, flour, sawdust, etc., by the physical properties of which the characteristics of the explosive are somewhat modified, and about 80% ammonium nitrate of which, however, a portion, say 10%, may be substituted by a volatile salt such as sodium chloride.

<sup>&</sup>lt;sup>27</sup> Op. cit., p. 403.

In Europe the tendency is to use a smaller amount of nitroglycerin, say 4 to 6%, or, as in the Favier explosives, to omit it altogether. Ammonium nitrate permissible explosives which contain nitroglycerin may be divided broadly into two principal classes, those of low ammonium nitrate content in which the oxygen is balanced rather accurately against the carbonaceous material and which are cooled by the inclusion of salts, and those which have a high ammonium nitrate content but whose temperature of explosion is low because of an incomplete utilization of the oxygen by a relatively small amount of carbonaceous material. Explosives of the latter class are more popular in England and in Germany. Several examples of commercial explosives of each sort are listed in the following table.

	I	$\mathbf{II}$	III	IV	$\mathbf{v}$	VI	VII	VIII
Ammonium nitrate	<b>52.0</b>	53.0	60.0	61.0	66.0	73.0	78.0	83.0
Potassium nitrate	21.0					2.8	5.0	7.0
Sodium nitrate		12.0	5.0	3.0				
Barium nitrate								2.0
Na or K chloride			21.0	20.5	22.0	15.0	8.0	
Hydrated ammonium								
oxalate	16.0	19.0						
Ammonium chloride	6.0							
Cereal or wood meal		4.0	4.0	7.5	2.0	1.0	5.0	2.0
Glycerin		• • •		3.0				
Powdered coal					4.0			
Nitrotoluene			6.0	1.0				
Dinitrotoluene	• • •					5.0		
Trinitrotoluene		6.0						2.0
Nitroglycerin	5.0	5.0	4.0	4.0	4.0	3.2	4.0	4.0

The Carbonites which are permissible are straight dynamites whose temperatures of explosion are lowered by the excess of carbon which they contain. As a class they merge, through the Ammon-Carbonites, with the class of ammonium nitrate explosives. The Carbonites, have the disadvantage that they produce gases which contain carbon monoxide, and for that reason have largely given way for use in coal mines to ammonium nitrate permissibles which contain an excess of oxygen. Naoúm <sup>28</sup> reports the compositions and explosive characteristics of four German Carbonites as follows.

<sup>&</sup>lt;sup>28</sup> Op. cit., p. 401.

	I	II	III	IV
Nitroglycerin	25.0	25.0	25.0	30.0
Potassium nitrate	30.5	34.0		
Sodium nitrate			30.5	24.5
Barium nitrate	4.0	1.0		
Spent tan bark meal	40.0	1.0		
Meal		38.5	39.5	40.5
Potassium dichromate			5.0	5.0
Sodium carbonate	0,5	0.5		
Heat of explosion, Cal./kg	576	506	536	602
Temperature of explosion	1874°	1561°	1666°	1639°
Velocity of detonation, meters/sec	2443	2700	3042	2472
Lead block expansion	- 235 cc.	213 cc.	240 cc.	258 сс.

The salts which are most frequently used in permissible explosives are sodium chloride and potassium chloride, both of which are volatile (the potassium chloride more readily so), ammonium chloride and ammonium sulfate, which decompose to form gases, and the hydrated salts, alum Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·K<sub>2</sub>SO<sub>4</sub>·24H<sub>2</sub>O; ammonium alum Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>·24H<sub>2</sub>O; chrome alum Cr<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·K<sub>2</sub>SO<sub>4</sub>·24H<sub>2</sub>O; aluminum sulfate Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·18H<sub>2</sub>O; ammonium oxalate (NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub>·H<sub>2</sub>O; blue vitriol CuSO<sub>4</sub>·5H<sub>2</sub>O; borax Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·10H<sub>2</sub>O; Epsom salt MgSO<sub>4</sub>·7H<sub>2</sub>O; Glauber's salt Na<sub>2</sub>SO<sub>4</sub>·10H<sub>2</sub>O; and gypsum CaSO<sub>4</sub>·2H<sub>2</sub>O, all of which give off water, while the ammonium salts among them yield other volatile products in addition. Hydrated sodium carbonate is not suitable for use because it attacks both ammonium nitrate and nitroglycerin.<sup>29</sup>

## Sprengel Explosives

Explosives of a new type were introduced in 1871 by Hermann Sprengel, the inventor of the mercury high-vacuum pump, who patented <sup>30</sup> a whole series of mining explosives which were prepared by mixing an oxidizing substance with a combustible one "in such proportions that their mutual oxidation and de-oxidation should be theoretically complete." The essential novelty of his invention lay in the fact that the materials were mixed just before the explosive was used, and the resultant explosive mixture was

<sup>&</sup>lt;sup>29</sup> C. G. Storm, "The Analysis of Permissible Explosives," U. S. Bur. Mines Bull. 96, Washington, 1916.

<sup>&</sup>lt;sup>30</sup> Brit. Pats. 921, 2642 (1871).

fired by means of a blasting cap. Among the oxidizing agents which he mentioned were potassium chlorate, strong nitric acid, and liquid nitrogen dioxide; among the combustible materials nitrobenzene, nitronaphthalene, carbon disulfide, petroleum, and picric acid. Strong nitric acid is an inconvenient and unpleasant material to handle. It can eat through the copper capsule of a blasting cap and cause the fulminate to explode. Yet several explosives containing it have been patented, Oxonite, for example, consisting of 58 parts of picric acid and 42 of fuming nitric acid, and Hellhoffite, 28 parts of nitrobenzene and 72 of nitric acid. These explosives are about as powerful as 70% dynamite, but are distinctly more sensitive to shock and to blows. Hellhoffite was sometimes absorbed on kieselguhr to form a plastic mass, but it still had the disadvantage that it was intensely corrosive and attacked paper, wood, and the common metals.

The peculiarities of the explosives recommended by Sprengel so set them apart from all others that they define a class; explosives which contain a large proportion of a liquid ingredient and which are mixed in situ immediately before use are now known as Sprengel explosives. They have had no success in England, for the reason that the mixing of the ingredients has been held to constitute manufacture within the meaning of the Explosives Act of 1875 and as such could be carried out lawfully only on licensed premises. Sprengel explosives have been used in the United States, in France, and in Italy, and were introduced into Siberia and China by American engineers when the first railroads were built in those countries. Rack-a-rock, patented by S. R. Divine, 32 is particularly well known because it was used for blasting out Hell Gate Channel in New York Harbor. On October 10, 1885, 240,399 pounds of it, along with 42,331 pounds of dynamite, was exploded for that purpose in a single blast. It was prepared for use by adding 21 parts of nitrobenzene to 79 parts of potassium chlorate contained in water-tight copper cartridges.

<sup>31</sup> Sprengel was aware in 1871 that picric acid alone could be detonated by means of fulminate but realized also that more explosive force could be had from it if it were mixed with an oxidizing agent. Picric acid alone was evidently not used practically as an explosive until after Turpin in 1886 had proposed it as a bursting charge for shells.

<sup>32</sup> Brit. Pats. 5584, 5596 (1881); 1461 (1882); 5624, 5625 (1883).

The Prométhées, authorized in France under the name of explosifs O No. 3, are prepared by dipping cartridges of a compressed oxidizing mixture of potassium chlorate 80 to 95% and manganese dioxide 5 to 20% into a liquid prepared by mixing nitrobenzene, turpentine, and naphtha in the proportions 50/20/30 or 60/15/25. The most serious disadvantage of these explosives was an irregularity of behavior resulting from the circumstance that different cartridges absorbed different quantities of the combustible oil, generally between 8 and 13%, and that the absorption was uneven and sometimes caused incomplete detonation. Similar explosives are those of Kirsanov, a mixture of 90 parts of turpentine and 10 of phenol absorbed by a mixture of 80 parts of potassium chlorate and 20 of manganese dioxide, and of Fielder, a liquid containing 80 parts of nitrobenzene and 20 of turpentine absorbed by a mixture of 70 parts of potassium chlorate and 30 of potassium permanganate.

The Panclastites, proposed by Turpin in 1881, are made by mixing liquid nitrogen dioxide with such combustible liquids as carbon disulfide, nitrobenzene, nitrotoluene, or gasoline. They are very sensitive to shock and must be handled with the greatest caution after they have once been mixed. In the first World War the French used certain ones of them, under the name of Anilites, in small bombs which were dropped from airplanes for the purpose of destroying personnel. The two liquids were enclosed in separate compartments of the bomb, which therefore contained no explosive and was safe while the airplane was carrying it. When the bomb was released, a little propeller on its nose, actuated by the passage through the air, opened a valve which permitted the two liquids to mix in such fashion that the bomb was then filled with a powerful high explosive which was so sensitive that it needed no fuze but exploded immediately upon impact with the target.

# Liquid Oxygen Explosives

Liquid oxygen explosives were invented in 1895 by Linde who had developed a successful machine for the liquefaction of gases. The Oxyliquits, as he called them, prepared by impregnating cartridges of porous combustible material with liquid oxygen or liquid air are members of the general class of Sprengel explosives, and have the unusual advantage from the point of view of safety

that they rapidly lose their explosiveness as they lose their liquid oxygen by evaporation. If they have failed to fire in a bore hole, the workmen need have no fear of going into the place with a pick or a drill after an hour or so has elapsed.

Liquid oxygen explosives often explode from flame or from the spurt of sparks from a miner's fuse, and frequently need no detonator, or, putting the matter otherwise, some of them are themselves satisfactory detonators. Like other detonating explosives, they may explode from shock. Liquid oxygen explosives made from carbonized cork and from kieselguhr mixed with petroleum were used in the blasting of the Simplon tunnel in 1899. The explosive which results when a cartridge of spongy metallic aluminum absorbs liquid oxygen is of theoretical interest because its explosion yields no gas; it yields only solid aluminum oxide and heat, much heat, which causes the extremely rapid gasification of the excess of liquid oxygen and it is this which produces the explosive effect. Lampblack is the absorbent most commonly used in this country.

Liquid oxygen explosives were at first made up from liquid air more or less self-enriched by standing, the nitrogen (b.p. -195°) evaporating faster than the oxygen (b.p.  $-183^{\circ}$ ), but it was later shown that much better results followed from the use of pure liquid oxygen. Rice reports 33 that explosives made from liquid oxygen and an absorbent of crude oil on kieselguhr mixed with lampblack or wood pulp and enclosed in a cheesecloth bag within a corrugated pasteboard insulator were 4 to 12% stronger than 40% straight nitroglycerin dynamite in the standard Bureau of Mines test with the ballistic pendulum. They had a velocity of detonation of about 3000 meters per second. They caused the ignition of fire damp and produced a flame which lasted for 7.125 milliseconds as compared with 0.342 for an average permissible explosive (no permissible producing a flame of more than 1 millisecond duration). The length of the flame was 2½ times that of the flame of the average permissible. In the Trauzl lead block an explosive made up from a liquid air (i.e., a mixture of liquid

<sup>33</sup> George S. Rice, "Development of Liquid Oxygen Explosives during the War," U. S. Bur. Mines Tech. Paper 243, Washington, 1920, pp. 14-16. Also, S. P. Howell, J. W. Paul, and J. L. Sherrick, "Progress of Investigations on Liquid Oxygen Explosives," U. S. Bur. Mines Tech. Paper 294, Washington, 1923, pp. 33, 35, 51.

oxygen and liquid nitrogen) containing 33% of oxygen gave no explosion; with 40% oxygen an enlargement of 9 cc.; with 50% 80 cc., with 55% 147 cc.; and with 98% oxygen an enlargement of 384 cc., about 20% greater than the enlargement produced by 60% straight dynamite. The higher temperatures of explosion of the liquid oxygen explosives cause them to give higher results in the Trauzl test than correspond to their actual explosive power.

Liquid oxygen explosives are used in this country for open-cut mining or strip mining, not underground, and are generally prepared near the place where they are to be used. The cartridges are commonly left in the "soaking box" for 30 minutes, and on occasions have been transported in this box for several miles.

One of the most serious faults of liquid oxygen explosives is the ease with which they inflame and the rapidity with which they burn, amounting practically and in the majority of cases to their exploding from fire. Denues 34 has found that treatment of the granular carbonaceous absorbent with an aqueous solution of phosphoric acid results in an explosive which is non-inflammable by cigarettes, matches, and other igniting agents. Monoand diammonium phosphate, ammonium chloride, and phosphoric acid were found to be suitable for fireproofing the canvas wrappers. Liquid oxygen explosives made up from the fireproofed absorbent are still capable of being detonated by a blasting cap. Their strength, velocity of detonation, and length of life after impregnation are slightly but not significantly shorter than those of explosives made up from ordinary non-fireproofed absorbents containing the same amount of moisture.

## Chlorate and Perchlorate Explosives

The history of chlorate explosives goes back as far as 1788 when Berthollet attempted to make a new and more powerful gunpowder by incorporating in a stamp mill a mixture of potassium chlorate with sulfur and charcoal. He used the materials in the proportion 6/1/1. A party had been organized to witness the manufacture, M. and Mme. Lavoisier, Berthollet, the Commissaire M. de Chevraud and his daughter, the engineer M. Lefort, and others. The mill was started, and the party went away for

<sup>&</sup>lt;sup>34</sup> A. R. T. Denues, "Fire Retardant Treatments of Liquid Oxygen Explosives," U. S. Bur. Mines Bull. 429, Washington, 1940.

breakfast. Lefort and Mlle. de Chevraud were the first to return. The material exploded, throwing them to a considerable distance and causing such injuries that they both died within a few minutes. In 1849 the problem of chlorate gunpowder was again attacked by Augendre vho invented a white powder made from potassium chlorate 4 parts, cane sugar 1 part, and potassium ferrocyanide 1 part. However, no satisfactory propellent powder for use in guns has yet been made from chlorate. Chlorate powders are used in toy salutes, maroons, etc., where a sharp explosion accompanied by noise is desired, and chlorate is used in primer compositions and in practical high explosives of the Sprengel type (described above) and in the Cheddites and Silesia explosives.

Many chlorate mixtures, particularly those which contain sulfur, sulfides, and picric acid, are extremely sensitive to blows and to friction. In the *Street explosives*, later called Cheddites because they were manufactured at Chedde in France, the chlorate is phlegmatized by means of castor oil, a substance which appears to have remarkable powers in this respect. The French *Commission des Substances Explosives* in 1897 commenced its first investigation of these explosives by a study of those which are listed below, and concluded <sup>35</sup> that their sensitivity to shock is

	I	$\mathbf{II}$	III
Potassium chlorate	75.0	74.6	80.0
Picronitronaphthalene	20.0		• • •
Nitronaphthalene		5.5	12.0
Starch		14.9	
Castor oil	5.0	5.0	8.0

less than that of No. 1 dynamite (75% guhr dynamite) and that when exploded by a fulminate cap they show a considerable brisance which however is less than that of dynamite. Later studies showed that the Cheddites had slightly more force than No. 1 dynamite, although they were markedly less brisant because of their lower velocity of detonation. After further experimentation four Cheddites were approved for manufacture in France, but the output of the Poudrerie de Vonges where they were made consisted principally of Cheddites No. 1 and No. 4.

<sup>&</sup>lt;sup>35</sup> Mém. Poudres, 9, 144 (1897–1898); 11, 22 (1901); 12, 117, 122 (1903–1904); 13, 144, 282 (1905–1906); 15, 135 (1909–1910); 16, 66 (1911–1912).

	O No. 1 Formula 41	O No. 1 Formula 60 bis	O No. 2 Formula 60 bis M Cheddite No. 4	O No. 5 Cheddite No. 1
Potassium chlorate	80  12  8	80  13 2 5	79  1 15 5	79  16 5

The Cheddites are manufactured by melting the nitro compounds in the castor oil at 80°, adding little by little the pulverized chlorate dried and still warm, and mixing thoroughly. The mixture is emptied out onto a table, and rolled to a thin layer which hardens on cooling and breaks up under the roller and is then sifted and screened.

Sodium chlorate contains more oxygen than potassium chlorate, but has the disadvantage of being hygroscopic. Neither salt ought to be used in mixtures which contain ammonium nitrate or ammonium perchlorate, for double decomposition might occur with the formation of dangerous ammonium chlorate. Potassium chlorate is one of the chlorates least soluble in water, potassium perchlorate one of the least soluble of the perchlorates. The latter salt is practically insoluble in alcohol. The perchlorates are intrinsically more stable and less reactive than the chlorates, and are much safer in contact with combustible substances. Unlike the chlorates they are not decomposed by hydrochloric acid, and they do not yield an explosive gas when warmed with concentrated sulfuric acid. The perchlorates require a higher temperature for their decomposition than do the corresponding chlorates.

SOLUBILITY: PARTS PER 100 PARTS OF WATER

	$KClO_3$	$NaClO_3$	KClO₄	NH <sub>4</sub> ClO <sub>4</sub>
At 0°	3.3	<b>82</b> .	0.7	12.4
At 100°	<b>56</b> .	204.	18.7	88.2

Mixtures of aromatic nitro compounds with chlorate are dangerously sensitive unless they are phlegmatized with castor oil or a similar material, but there are other substances, such as rosin, animal and vegetable oils, and petroleum products, which give mixtures which are not unduly sensitive to shock and friction and may be handled with reasonable safety. Some of these, such as Pyrodialyte 36 and the Steelites, 37 were studied by the Commission des Substances Explosives. The former consisted of 85 parts of potassium chlorate and 15 of rosin, 2 parts of alcohol being used during the incorporation. The latter, invented by Everard Steele of Chester, England, contained an oxidized rosin (résidée in French) which was made by treating a mixture of 90 parts of colophony and 10 of starch with 42 Bé nitric acid. After washing, drying, and powdering, the résidée was mixed with powdered potassium chlorate, moistened with methyl alcohol, warmed, and stirred gently while the alcohol was evaporated. Colliery Steelite

	STEELITE No. 3	Steelite No. 5	STEELITE No. 7	Colliery Steelite
Potassium chlorate	75	83.33	87.50	72.5-75.5
Résidée	25	16.67	12.50	23.5-26.5
Aluminum		5.00		
Castor oil				0.5-1.0
Moisture				0-1

passed the Woolwich test for safety explosives and was formerly on the British permitted list but failed in the Rotherham test. In Germany the Silesia explosives have been used to some extent. Silesia No. 4 consists of 80 parts of potassium chlorate and 20 of rosin, and Silesia IV 22, 70 parts of potassium chlorate, 8 of rosin, and 22 of sodium chloride, is cooled by the addition of the volatile salt and is on the permissible list.

The Sebomites,<sup>38</sup> invented by Eugène Louis, contained animal fat which was solid at ordinary temperature, and were inferior to the Cheddites in their ability to transmit detonation. Explosifs P (potasse) and S (soude)<sup>39</sup> and the Minélites,<sup>40</sup> containing petroleum hydrocarbons, were studied in considerable detail by Dautriche, some of whose results for velocities of detonation are reported in the table on pages 362–363 where they are compared with

<sup>36</sup> Mém. Poudres, 11, 53 (1901).

<sup>&</sup>lt;sup>37</sup> Ibid., 15, 181 (1909–1910).

<sup>&</sup>lt;sup>38</sup> Ibid., 13, 280 (1905–1906); 15, 137 (1909–1910).

<sup>&</sup>lt;sup>39</sup> *Ibid.*, **15**, 212 (1909–1910). <sup>40</sup> *Ibid.*, **16**, 224 (1911–1912).

his results for Cheddite 60, fourth formula.<sup>41</sup> His experimental results <sup>42</sup> illustrate very clearly the principle that there is an optimum density of loading at which the velocity of detonation is greatest and that at higher densities the velocity drops and the detonation is incomplete and poorly propagated. The Cheddite 60,

	Explosifs		Minélites		ES
	P	$\mathbf{s}$	A	$\mathbf{B}$	$\mathbf{C}$
Potassium chlorate	90		90	90	89
Sodium chlorate					
Heavy petroleum oil			3		٠.
Vaseline				. 3	4
Paraffin		11	-	7	5
Pitch	• •				2

fourth formula, when ignited burns slowly with a smoky flame. Explosifs P and S and the Minélites burn while the flame of a Bunsen burner is played upon them but, in general, go out when the flame is removed. Minélite B, under the designation O No. 6 B, was used by the French during the first World War in grenades and mines. A similar explosive containing 90 parts of sodium chlorate instead of 90 of potassium chlorate was used in grenades and in trench mortar bombs.

Chlorate explosives which contain aromatic nitro compounds have higher velocities of detonation and are more brisant than those whose carbonaceous material is merely combustible. The addition of a small amount of nitroglycerin increases the velocity of detonation still farther. Brisant chlorate explosives of this sort were developed in Germany during the first World War and were known as Koronit and Albit (Gesteinskoronit, Kohlenkoronit, Wetteralbit, etc.). They found considerable use for a time but have now been largely superseded by low-percentage dynamites and by perchlorate explosives. Two of them, manufactured by the Dynamit A.-G., had according to Naoúm 43 the compositions and explosive characteristics which are indicated

<sup>&</sup>lt;sup>41</sup> The composition of this explosive was the same as that which is given in the table on page 359 as that of O No. 2, formula 60 bis M, or Cheddite No. 4.

<sup>&</sup>lt;sup>42</sup> In several cases Dautriche reported temperatures, but the velocity of detonation appears to be unaffected by such temperature variations as those between summer and winter.

<sup>43</sup> Op. cit., p. 428.

Explosive	In Tubes of	Diameter	DENSITY OF LOADING	Velocity of Detonation, M./Sec.
Explosif P	copper	20–22 mm.	0.62 1.00 1.05 1.36 1.48 1.54 0.99 1.24 1.45	2137 3044 3185 3621 3475 Incomplete 2940 3457 3565
Explosif P	paper	29 mm.	$\begin{cases} 0.95 \\ 1.30 \\ 1.35 \\ 0.90 \\ 1.21 \\ 1.36 \\ 1.41 \end{cases}$	Incomplete 2752 3406 3340 2688 3308 3259 Incomplete
Explosif S	copper	20–22 mm.	0.88 1.25 0.81 0.92 1.33 1.45 1.54 1.56 1.58	2480 2915 2191 2457 2966 2940 2688 Incomplete Incomplete
Explosif S	paper	29 mm.	$\begin{cases} 1.05 \\ 1.16 \\ 1.29 \\ 1.39 \\ 1.47 \end{cases}$	2335 2443 2443 Incomplete Incomplete
Cheddite 60 4th formula	copper	20–22 mm.	$\begin{cases} 1.51 \\ 1.62 \\ 0.84 \\ 1.39 \\ 1.48 \end{cases}$	3099 2820 2457 3045 3156
Cheddite 60 4th formula	paper	29 mm.	$\begin{cases} 1.25 \\ 1.31 \\ 1.40 \\ 1.50 \end{cases}$	2774 2915 2843 Incomplete

			ر0.87	2800
			0.99	2930
			1.17	3125
			1.24	3235
			1.38	Incomplete
			1.52	Incomplete
Minélite A			0.89	2435
in powder	$\operatorname{copper}$	$20$ – $22 \mathrm{mm}$ .	0.95	2835
•			1.20	3235
			1.39	3125
			1.45	Incomplete
			0.87	2395
			1.27	3355
		**	$\lfloor 1.39 \rfloor$	Incomplete
			r 1.08	2670
			1.19	2835
Minélite A			1.25	Incomplete
in powder	paper	29  mm.	1.28	Incomplete
in powder			1.19	289 <b>5</b>
			1.19	Incomplete
			$\{0.87$	2150
			1.12	2415
			1.20	2550
1.62 - 6724 - A			1.29	3025
Minélite A	copper	$20-22 \mathrm{mm}$ .	1.33	2480
in grains			1.35	Incomplete
			1.30	2895
			0.85	2100
			1.17	2415
			1.27	2750
			0.97	2350
			1.07	2895
			1.24	3235
			1.33	3090
			1.45	Incomplete
			1.57	Incomplete
$\it Min\'elite~B$	gonnor	20-22 mm.	1.00	2925
in powder	copper	20-22 IIIII.	1.12	2925
			1.26	3165
			1.02	2585
			1.14	2910
			1.30	3180
			1.41	Complete
			1.38	3160
Min Hit - O			(1.28	3125
Minélite C	copper	20-22 mm.	₹ 1.37	Incomplete
in powder	- F F =-		1.48	Incomplete
			(0	-month proof

below. It is interesting that the explosive which contained a small amount of nitroglycerin was more brisant, as well as softer and more plastic, and less sensitive to shock, to friction, and to initiation than the drier explosive which contained no nitroglycerin. It required a No. 3 blasting cap to explode it, but the material which contained no nitroglycerin was exploded by a weak No. 1.

	Gesteins- Koronit T1	Gesteins- Koronit T2
Sodium chlorate	72.0	75.0
Vegetable meal	1.0-2.0	1.0-2.0
Di- and trinitrotoluene	20.0	20.0
Paraffin	3.0-4.0	3.0-4.0
Nitroglycerin	3.0-4.0	• • •
Heat of explosion, Cal./kg	1219.0	1241.0
Temperature of explosion	3265.0°	3300.0°
Velocity of detonation, m./sec	5000.0	4300.0
Density of cartridge	1.57	1.46
Lead block expansion	$290.0 \ cc.$	$280.0 \ \mathrm{cc}$ .
Lead block crushing	$20.0~\mathrm{mm}$ .	19.5 mm.

During the first World War when Germany needed to conserve as much as possible its material for military explosives, blasting explosives made from perchlorate came into extensive use. The Germans had used in their trench mortar bombs an explosive, called Perdit, which consisted of a mixture of potassium perchlorate 56%, with dinitrobenzene 32% and dinitronaphthalene 12%. After the War, the perchlorate recovered from these bombs and that from the reserve stock came onto the market, and perchlorate explosives, Perchlorit, Perchloratit, Persalit, Perkoronit, etc., were used more widely than ever. The sale of these explosives later ceased because the old supply of perchlorate became exhausted and the new perchlorate was too high in price. Each of these explosives required a No. 3 cap for its initiation. Perchlorate explosives in general are somewhat less sensitive to initiation than chlorate explosives. A small amount of nitroglycerin in perchlorate explosives plays a significant part in propagating the explosive wave and is more important in these compositions than it is in ammonium nitrate explosives. Naoúm 44 reports the following particulars concerning two of the Perkoronites.

<sup>44</sup> Op. cit., p. 430.

	PERKORONIT A	Perkoronit B
Potassium perchlorate	58	59
Ammonium nitrate	8	10
Di- and trinitrotoluene, vegetable meal	30	31
Nitroglycerin	4	•••
Heat of explosion, Cal./kg	1170.0	1160.0
Temperature of explosion	3145.0°	3115.0°
Velocity of detonation, m./sec	5000.0	4400.0
Density of cartridge	1.58	1.52
Lead block expansion	340.0 cc.	330.0 cc.
Lead block crushing	20.0 mm.	18.0 mm.

Potassium perchlorate and ammonium perchlorate permissible explosives, cooled by means of common salt, ammonium oxalate, etc., and containing either ammonium nitrate or alkali metal nitrate with or without nitroglycerin, are used in England, Belgium, and elsewhere. They possess no novel features beyond the explosives already described. Explosives containing ammonium perchlorate yield fumes which contain hydrogen chloride. Potassium perchlorate produces potassium chloride.

Early in the history of these explosives the French Commission des Substances Explosives published a report on two ammonium perchlorate Cheddites.<sup>45</sup> The manufacture of these explosives,

	I	II
Ammonium perchlorate	82	50
Sodium nitrate		30
Dinitrotoluene	13	15
Castor oil	5	5

however, was not approved for the reason that the use of castor oil for phlegmatizing was found to be unnecessary. Number I took fire easily and burned in an 18-mm. copper gutter at a rate of 4.5 mm. per second, and produced a choking white smoke. Cheddite 60, for comparison, burned irregularly in the copper gutter, with a smoke which was generally black, at a rate of 0.4-0.5 mm. per second. Number II took fire only with the greatest difficulty, and did not maintain its own combustion. The maximum velocities of detonation in zinc tubes 20 mm. in diameter were about 4020 meters per second for No. I and about 3360 for No. II.

<sup>45</sup> Mém. poudres, 14, 206 (1907-1908).

The Commission published in the same report a number of interesting observations on ammonium perchlorate. Pieces of cotton cloth dipped into a solution of ammonium perchlorate and dried were found to burn more rapidly than when similarly treated with potassium chlorate and less rapidly than when similarly treated with sodium chlorate. Ammonium perchlorate inflamed in contact with a hot wire and burned vigorously with the production of choking white fumes, but the combustion ceased as soon as the hot wire was removed. Its sensitivity to shock, as determined by the drop test, was about the same as that of picric acid, but its sensitivity to initiation was distinctly less. A 50-cm. drop of a 5-kilogram weight caused explosions in about 50% of the trials. A cartridge, 16 cm. long and 26 mm. in diameter, was filled with ammonium perchlorate gently tamped into place (density of loading about 1.10) and was primed with a cartridge of the same diameter containing 25 grams of powdered picric acid (density of loading about 0.95) and placed in contact with one end of it. When the picric acid booster was exploded, the cartridge of perchlorate detonated only for about 20 mm. of its length and produced merely a slight and decreasing furrow in the lead plate on which it was resting. When a booster of 75 grams of picric acid was used, the detonation was propagated in the perchlorate for 35 mm. The temperature of explosion of ammonium perchlorate was calculated to be 1084°.

The French used two ammonium perchlorate explosives during the first World War.

	I	$\Pi$
Ammonium perchlorate	86	61.5
Sodium nitrate		30.0
Paraffin	14	8.5

The first of these was used in 75-mm. shells, the second in 58-mm. trench mortar bombs.

Hydrazine perchlorate melts at 131–132°, burns tranquilly, and explodes violently from shock.

Guanidine perchlorate is relatively stable to heat and to mechanical shock but possesses extraordinary explosive power and sensitivity to initiation. Naoúm <sup>46</sup> states that it gives a lead block expansion of about 400 cc. and has a velocity of detonation of about 6000 meters per second at a density of loading of 1.15.

<sup>46</sup> Naoum, "Schiess- und Sprengstoffe," Dresden and Leipzig, 1927, p. 137.

#### Ammonium Nitrate Military Explosives

The Schneiderite (Explosif S or Sc) which the French used during the first World War in small and medium-size high-explosive shells, especially in the 75 mm., was made by incorporating 7 parts of ammonium nitrate and 1 of dinitronaphthalene in a wheel mill, and was loaded by compression. Other mixtures, made in the same way, were used in place of Schneiderite or as a substitute for it.

05010000 101 10.	NX	NT	NTN	NDNT	N2TN
Ammonium nitrate	77	70	80	85	50
Sodium nitrate				• •	30
Trinitrotoluene		30		5	
Trinitroxylene	23	-			
Dinitronaphthalene				10	
Trinitronaphthalene					20

Amatol, developed by the British during the first World War, is made by mixing granulated ammonium nitrate with melted trinitrotoluene, and pouring or extruding the mixture into the shells where it solidifies. The booster cavity is afterwards drilled out from the casting. The explosive can be cut with a hand saw. It is insensitive to friction and is less sensitive to initiation and more sensitive to impact than trinitrotoluene. It is hygroscopic, and in the presence of moisture attacks copper, brass, and bronze.

Amatol is made up in various proportions of ammonium nitrate to trinitrotoluene, such as 50/50, 60/40, and 80/20. The granulated, dried, and sifted ammonium nitrate, warmed to about 90°, is added to melted trinitrotoluene at about 90°, and the warm mixture, if 50/50 or 60/40, is ladled into the shells which have been previously warmed somewhat in order that solidification may not be too rapid, or, if 80/20, is stemmed or extruded into the shells by means of a screw operating within a steel tube. Synthetic ammonium nitrate is preferred for the preparation of amatol. The pyridine which is generally present in gas liquor and tar liquor ammonia remains in the ammonium nitrate which is made from these liquors and causes frothing and the formation of bubbles in the warm amatol—with the consequent probability of cavitation in the charge. Thiocvanates which are often present in ammonia from the same sources likewise cause frothing, and phenols if present tend to promote exudation.

The velocity of detonation of TNT-ammonium nitrate mixtures decreases regularly with increasing amounts of ammonium nitrate, varying from about 6700 meters per second for TNT to about 4500 meters per second for 80/20 amatol. The greater the proportion of ammonium nitrate the less the brisance and the greater the heaving power of the amatol. 50/50 Amatol does not contain oxygen enough for the complete combustion of its trinitrotoluene, and gives a smoke which is dark colored but less black than the smoke from straight TNT. 80/20 Amatol is less brisant than TNT. It gives an insignificant white smoke. Smoke boxes are usually loaded with 80/20 amatol in order that the artilleryman may observe the bursting of his shells. The best smoke compositions for this purpose contain a large proportion of aluminum and provide smoke by day and a brilliant flash of light by night.

The name of ammonal is applied both to certain blasting explosives which contain aluminum and to military explosives, based upon ammonium nitrate, which contain this metal. Military ammonals are brisant and powerful explosives which explode with a bright flash. They are hygroscopic, but the flake aluminum which they contain behaves somewhat in the manner of the shingles on a roof and helps materially to exclude moisture. At the beginning of the first World War the Germans were using in major caliber shells an ammonal having the first of the compositions listed below. After the War had advanced and TNT

	GERMAN	AMMONAL	FRENCH	
	I	II	Ammonal	
Ammonium nitrate	. 54	72	86	
Trinitrotoluene	. 30	12		
Aluminum flakes	. 16	16	8	
Stearic acid			6	

had become more scarce, ammonal of the second formula was adopted. The French also used ammonal in major caliber shells during the first World War. All three of the above-listed explosives were loaded by compression. Experiments have been tried with an ammonal containing ammonium thiocyanate; the mixture was melted, and loaded by pouring but was found to be unsatisfactory because of its rapid decomposition. Ammonal yields a flame which is particularly hot, and consequently gives an unduly high result in the Trauzl lead block test.