CHAPTER V

NITRIC ESTERS

Nitric esters or *organic nitrates* contain the nitrate radical, —O—NO_2, attached to a carbon atom, or, to express the same idea in a different way, they contain the nitro group, —NO_2, attached to an oxygen atom which is attached to a carbon. In *nitro compounds,* strictly so called, the nitro group is attached directly to a carbon; in *nitroamines* or *nitramines* it is attached to an amino nitrogen atom, that is, to a nitrogen which is attached to a carbon. In the nitric esters and in the nitroamines alike, a single atom stands between the nitro group and the carbon atom of the organic molecule. Substances of the two classes are alike in their most characteristic reaction, namely, they are formed by the reversible nitration of alcohols and amines respectively.

During the nitration of glycerin by the action of strong nitric acid or of strong mixed acid upon it, nitro groups are introduced in place of three of the hydrogen atoms of the original molecule. There is therefore a certain propriety in thinking of the product as a nitro compound, and a reasonable warrant for the common practice of calling it by the name of trinitroglycerin or, more commonly, of *nitroglycerin.* The hydrogen atoms which are replaced were attached to oxygen atoms; the product is really a nitric ester, and its proper name is *glyceryl trinitrate.* Similarly, the substances which are commonly called nitroglycol, nitrostarch, nitrosugar, nitrolactose, nitrocotton, etc., are actually nitric esters.

The physical properties of the nitric esters resemble in a general way the physical properties of the alcohols from which they are derived. Thus, methyl and ethyl nitrate, like methyl and ethyl alcohol, are volatile liquids; nitroglycerin is a viscous oil, more viscous and less volatile than glycol dinitrate as glycerin is more viscous and less volatile than glycol. Nitrocellulose from fibrous cellulose yields a tough and plastic colloid, but nitrostarch remains from the evaporation of its solutions as a mass which is brittle and friable.

Methyl Nitrate

Methyl nitrate is a powerful explosive although its physical properties are such that it is not of practical use, and it is of interest only because it is the simplest of the nitric esters. Like ethyl and *n*-propyl nitrates, it may be prepared by the careful distillation of the alcohol with concentrated nitric acid (*d.* 1.42) from which, however, the last traces of nitrous acid must first have been removed by the addition of urea. It may also be prepared by adding the alcohol to strong mixed acid at low temperature, stirring, and separating and washing the product without distillation, by a process similar to that which is used for the preparation of nitroglycerin and nitroglycol except that the volatility of the product requires the stirring to be done by mechanical means and not by compressed air. It is a colorless limpid liquid somewhat less viscous than water, boiling point 65–66°, specific gravity 1.2322 at 5°, 1.2167 at 15°, and 1.2032 at 25°. Its vapors have a strongly aromatic odor resembling that of chloroform, and cause headache if they are inhaled. It dissolves collodion nitrocotton to form a jelly from which the methyl nitrate evaporates readily.

Methyl nitrate has a slightly higher energy content than nitroglycerin and a slightly greater explosive effect. Naoúm[1] reports that 10 grams of methyl nitrate in the Trauzl test with water tamping caused an expansion of 615 cc., while 10 grams of nitroglycerin under the same conditions gave 600 cc. Methyl nitrate is very much more sensitive to initiation than nitroglycerin, a fact which, like its higher velocity of detonation, is probably associated with its lower viscosity. It is less sensitive than nitroglycerin to the mechanical shock of the drop test. In the small lead block test, or lead block compression test, 100 grams of methyl nitrate under slight confinement in a shell of sheet lead 1 mm. thick and tamped with thin cork plates, gave a compres-

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[1] Phokion Naoúm, "Nitroglycerine and Nitroglycerine Explosives," trans. E. M. Symmes, Baltimore, The Williams and Wilkins Company, 1928, p. 205.

sion of 24.5 mm. while nitroglycol similarly gave 30 mm. and nitroglycerin 18.5 mm.

Methyl nitrate is easily inflammable and burns in an open dish with a large non-luminous flame. Its vapors explode when heated to about 150°.

Berthelot[2] measured the velocity of detonation of methyl nitrate in tubes of such small diameter that the maximum velocity of detonation was not secured, but he was able to make certain interesting inferences both as to the effect of the envelope and as to the effect of the physical state of the explosive. Some of his results are summarized in the table below. The data indicate that with tubes of the same internal diameter the velocity of detonation is greater in those cases in which the rupture of the tube is more difficult; it is greater in the tubes which have thicker walls and in the tubes which are made of the stronger materials. The extent to which the velocity of detonation builds up depends in some measure upon the pressure which builds up before the container is ruptured. By comparing these results with those from other explosive substances, Berthelot was able to make further inductions.

TUBE OF	INTERNAL DIAMETER, MILLIMETERS	EXTERNAL DIAMETER, MILLIMETERS	VELOCITY OF DETONATION, METERS PER SECOND
Rubber, canvas covered	5	12	1616
Glass	3	12	2482
Glass	3	7	2191
Glass	5	7	1890
Britannia metal	3	12.6	1230
Steel	3	15	2084
Steel	3	15	2094

> In fact, nitroglycerin in lead tubes 3 mm. internal diameter gave velocities in the neighborhood of 1300 meters per second, while dynamite in similar metallic tubes attained 2700 meters per second. This sets in evidence the influence of the structure of the explosive substance upon the velocity of propagation of the explosion, pure nitroglycerin, a viscous liquid, transmitting the shock which determines the detonation much more irregularly than the silica impregnated in

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[2] *Mém. poudres,* **4,** 13 (1891); *Ann. chim. phys.,* **23,** 485 (1901).

a uniform manner with the same liquid. Mica dynamite according to my observations produces effects which are still more considerable, a fact which could be foreseen from the crystalline structure of the mica, a substance which is less deformable than amorphous silica.

This last induction is confirmed by observations on nitromannite, a crystalline solid which appears by reason of this circumstance better suited than liquid methyl nitrate for transmitting detonation. It has in fact given practically constant velocities of 7700 meters per second in lead tubes of 1.9 mm. internal diameter at a density of loading of 1.9. Likewise picric acid, also crystalline, 6500 meters per second. . . .

The influence of the structure of the explosive substance on the course of the detonation being thus made evident, let us cite new facts which show the effect due to the containing envelope. . . . Compressed guncotton at such densities of loading as 1.0 and 1.27 in lead tubes 3.15 mm. internal diameter gave velocities of 5400 meters per second, while at a density of loading of practically one-half less (0.73) in a lead tube 3.77 mm. internal diameter, a velocity of 3800 meters per second was observed—a difference which is evidently due to the reduced continuity of the material. In supple cordeau, slightly resistant, formed by a single strand or braid, with a density of loading of 0.65, the velocity falls even to 2400 meters per second. But the feeble resistance of the envelope may be compensated by the mass of the explosive which opposes itself, especially in the central portion of the mass, to the instantaneous escape of the gas. Abel, in fact, with cartridges of compressed guncotton, of ten times the diameter of the above-mentioned cordeau, placed end to end, in the open air, has observed velocities of 5300 to 6000 meters per second.[3]

Other Alkyl Nitrates

Ethyl nitrate is a colorless liquid of agreeable odor, boiling point 87°, specific gravity (15°/15°) 1.1159 at 15°, and 1.1044 (25°/25°) at 25°. It has a less favorable oxygen balance than methyl nitrate, and is much less sensitive to initiation than the latter substance. It has only about 48% of the energy content of nitroglycerin, but its lower viscosity tends to give it a higher initial velocity of detonation than nitroglycerin and it performs about 58% as well as nitroglycerin in the sand test.[4] A No. 8

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[3] *Mém. poudres,* 4, 18–19 (1891).

[4] Naoúm, *op. cit.,* p. 207.

blasting cap will not detonate ethyl nitrate unless the explosive is tamped or confined. Mixed with fuller's earth in the proportion 70/30 or 60/40, it yields a brisant explosive which may be detonated without confinement.

n-Propyl nitrate, like ethyl nitrate, can be prepared by mixing the alcohol with nitric acid of density 1.42 or thereabouts, and carefully distilling the mixture. Ethyl alcohol and *n*-propyl alcohol, which contain the methylene group, are easily oxidized; if they are added to nitric acid of greater strength than density 1.42, or if they are added to strong mixed acid, they are likely to react with explosive violence and the abundant production of nitrous fumes, no matter how efficient the cooling. *n*-Propyl nitrate has a pleasant ethereal odor, boiling point 110.5°, specific gravity (15°/15°) 1.0631 at 15°, and (25°/25°) 1.0531 at 25°. It is less sensitive to detonation than ethyl nitrate. Ten grams in a Trauzl block, with water tamping and with a No. 8 blasting cap, detonated only partially and gave an expansion of 45 cc., or 15 cc. more than the cap alone, but 10 grams of it, mixed with 4 grams of fuller's earth to form a moist powder and exploded with a No. 8 cap, gave a sharp explosion and a net expansion of 230 cc.[5]

Isopropyl nitrate, b.p. 101–102°, specific gravity 1.054 at 0°, 1.036 at 19°, is prepared by the interaction of isopropyl iodide and silver nitrate. The hydrogen atom which is attached in isopropyl alcohol to the carbon atom carrying the hydroxyl group is so easily oxidized that it is not feasible to prepare the compound by the action of nitric acid on the alcohol.

Nitroglycerin (Glyceryl trinitrate, NG)

Nitroglycerin was first prepared late in the year 1846 or early in 1847 by the Italian chemist, Ascanio Sobrero (1812–1888), who was at the time professor of applied chemistry at the University of Torino. Sobrero had studied medicine in the same city, and in 1834 had been authorized to practice as a physician. After that he studied with Pelouze in Paris and served as his assistant in his private laboratory from 1840 to 1843. In 1843 he left Paris, studied for several months with Liebig at Giessen, and returned to Torino where he took up the duties of a teacher and in 1845

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[5] *Ibid.,* p. 209.

built and equipped a modest laboratory of his own. The earliest printed account of nitroglycerin appears in a letter which Sobrero wrote to Pelouze and which Pelouze caused to be published in *L'Institut* of February 15, 1847.[6] In the same month Sobrero presented to the Academy of Torino a paper, *Sopra alcuni nuovi composti fulminanti ottenuti col mezzo dell'azione dell'acido nitrico sulle sostanze organiche vegetali,*[7] in which he described nitroglycerin, nitromannite, and nitrated lactose. Later in the year he presented another paper, *Sulla Glicerina Fulminante o Piroglycerina,* before the chemistry section of the Ninth Italian Scientific Congress at Venice.[8]

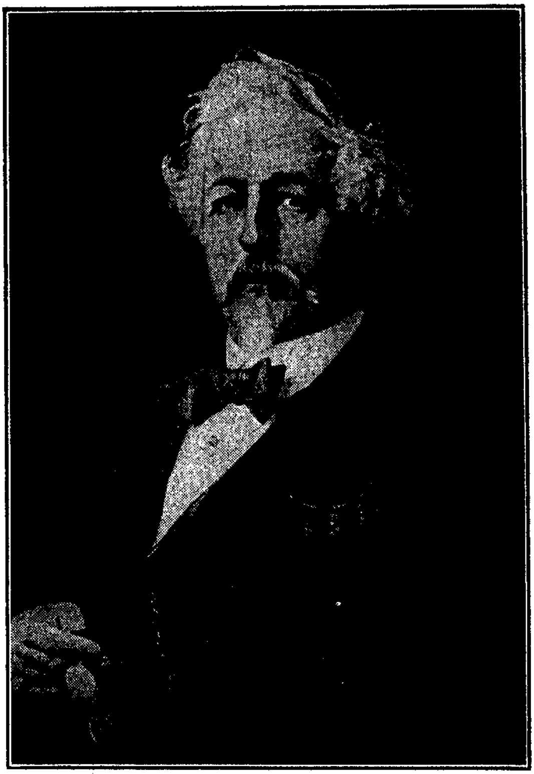

FIGURE 51. Ascanio Sobrero (1812-1888). First prepared nitroglycerin, nitromannite, and nitrolactose, 1846-1847.

Sobrero found that, if concentrated nitric acid or strong mixed acid is added to glycerin, a violent reaction ensues and red fumes

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[6] *L'Institut,* **15,** 53 (1847).

[7] *Mem. Acad. Torino,* [2] **10,** 195 (1847).

[8] *Proc. Ninth Ital. Sci. Congr.,* **3,** 105 (1848).

are evolved, but that, if syrupy glycerin is added to a mixture of two volumes of sulfuric acid (*d.* 1.84) and one volume of nitric acid (*d.* 1.50) with stirring while the mixture is kept below 0°, then the results are entirely different, the glycerin dissolves, and the solution when poured into water gives an oily precipitate of nitroglycerin. He collected the oil, washed it with water until free from acid, dried in a vacuum over sulfuric acid, and procured a transparent liquid of the color and appearance of olive oil. (Pure nitroglycerin is water-white.) Sobrero reported a value for the density which is very close to that which is now generally accepted, observed the ready solubility of nitroglycerin in alcohol and its reprecipitation by water, and reported a number of its chemical reactions—its comportments with acid and with alkali, that

> It detonates when brought into contact with metallic potassium, and evolves oxides of nitrogen in contact with phosphorus at 20° to 30°C., but at higher temperatures it ignites with an explosion. . . . When heated, nitroglycerin decomposes. A drop heated on platinum foil ignites and burns very fiercely. It has, however, the property of detonating under certain circumstances with great violence. On one occasion a small quantity of an ethereal solution of nitroglycerin was allowed to evaporate in a glass dish. The residue of nitroglycerin was certainly not more than 2 or 3 centigrams. On heating the dish over a spirit lamp a most violent explosion resulted, and the dish was broken to atoms. . . . The safest plan for demonstrating the explosive power of nitroglycerin is to place a drop upon a watch glass and detonate it by touching it with a piece of platinum wire heated to low redness. Nitroglycerin has a sharp, sweet, aromatic taste. It is advisable to take great care in testing this property. A trace of nitroglycerin placed upon the tongue, but not swallowed, gives rise to a most violent pulsating headache accompanied by great weakness of the limbs.

For many years Sobrero kept in his laboratory and guarded jealously a sample of the original nitroglycerin which he had prepared in 1847. In 1886 he washed this material with a dilute solution of sodium bicarbonate and took it to the Nobel-Avigliana factory, of which he was a consultant, where he gave verbal testimony of its authenticity and where it has since been stored in one of the magazines. Molinari and Quartieri[9] in a book published in 1913 state that the sample, consisting of about 200 cc. under water in a bottle, was at that time unaltered and that analyses gave values for nitrogen in the neighborhood of 18.35%, close to the theoretical.

Sobrero seems originally to have thought more highly of the solid crystalline nitromannite, which he thought might be used in percussion caps, than of the liquid nitroglycerin, but a spontaneous explosion of 400 grams of the former substance in the laboratory of the arsenal of Torino in 1853 and the extensive damage which resulted caused him to lose interest in the material. After Nobel's invention of dynamite and of the blasting cap had made the use of nitroglycerin safe and practical, Sobrero attempted in 1873 to establish a factory to be operated by Italian capital for the manufacture of an explosive called *melanina,* which was a kind of dynamite formed by absorbing nitroglycerin in a mixture of powdered charcoal and the silicious earth of Santa Fiora in Tuscany.[10] The project did not succeed. Shortly afterwards Sobrero accepted a position as consultant to the Nobel-Avigliana factory, a position which paid a generous salary during his life and a pension to his widow after his death. The high regard in which he was held by the Nobel company is indicated further by the bust of him which was unveiled in 1879 in the Avigliana factory.

Glycerin (glycerol) is a by-product of soap manufacture. All natural fats, whether of animal or vegetable origin, whether solid like beef suet or liquid like olive oil, are glyceryl esters of long-chain fatty acids containing an even number of carbon atoms. When they are warmed with an aqueous solution of strong alkali, they are saponified; soap, which is the alkali salt of the acids of the fats, is formed, and glycerin is produced which remains dissolved in the liquid. Glycerin is also formed from fats by the action of steam; the fatty acids, insoluble in water and generally of higher melting point than the fats, are formed at the same time.

Glycerin is a viscous liquid, colorless and odorless when pure, and possessing a sweet taste. It is hygroscopic, will absorb more

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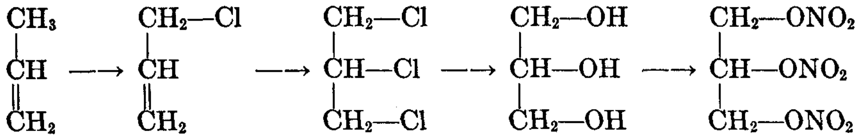
[9] Molinari and Quartieri, "Notizie sugli Esplodenti in Italia," Milano, 1913, p. 15.

[10] *Ibid.,* p. 33.

than half its own weight of moisture from the air, and does not evaporate. Glycerin will solidify in a freezing mixture, and when once frozen melts again at about 17°. It boils at atmospheric pressure at 290° with slight decomposition, and is best purified by distillation in vacuum. Its specific gravity is 1.265 at 15°. Perfectly pure and colorless glycerin yields a water-white nitroglycerin. Dynamite glycerin is a distilled product of high purity, density 1.262 or higher, and contains at least 99% of glycerin and less than 1% of water. It varies in color from pale yellow to dark brown, generally has a faint odor resembling that of burnt sugar, and yields a nitroglycerin of a pale yellow or pale brown color. The explosives makers consider a test nitration on a laboratory scale to be the surest way of estimating the quality of a sample of dynamite glycerin.

Small amounts of glycerin are produced during an ordinary alcoholic fermentation, but the quantity is greatly increased if a considerable amount of sodium sulfite is present. A commercial process based upon this principle was developed and used in Germany during the first World War, when the supply of glycerin from fats was insufficient to fill the needs of the explosives manufacturers, and similar processes have been used to some extent elsewhere and since that time. At the beginning of the second World War an effort was made to increase the production of whale oil for the manufacture of glycerin. Modern methods—harpoons shot from guns, fast Diesel-propelled steel ships—resulted immediately in a tremendous slaughter of whales, and whale oil again has become difficult to procure. Recent advances in synthetic chemistry make it probable that glycerin in the future will be prepared in large quantity from petroleum.

Cracking gas, which is produced when heavy petroleum is cracked to produce gasoline, consists in large part of olefins, particularly ethylene and propylene, and is being used more and more for the manufacture of such materials as glycol and glycerin, glycol dinitrate and nitroglycerin, mustard gas, ethanolamine and pentryl. The olefins under ordinary conditions combine with two atoms of chlorine, adding them readily to the unsaturated linkage, and thereafter react with chlorine, no further. It has been found that chlorine does not add to hot propylene in the gas phase, but substitutes instead, one of the hydrogen atoms of the methyl group being replaced and allyl chloride being formed. This at a lower temperature adds chlorine normally to form 1,2,3-trichloropropane which gives glycerin on hydrolysis.



$$\begin{array}{l}CH_3\\|\\CH\\\|\\CH_2\end{array} \longrightarrow \begin{array}{l}CH_2{-}Cl\\|\\CH\\\|\\CH_2\end{array} \longrightarrow \begin{array}{l}CH_2{-}Cl\\|\\CH{-}Cl\\|\\CH_2{-}Cl\end{array} \longrightarrow \begin{array}{l}CH_2{-}OH\\|\\CH{-}OH\\|\\CH_2{-}OH\end{array} \longrightarrow \begin{array}{l}CH_2{-}ONO_2\\|\\CH{-}ONO_2\\|\\CH_2{-}ONO_2\end{array}$$

Nitroglycerin is formed and remains in solution if glycerin is added to a large excess of strong nitric acid. Heat is evolved, and cooling is necessary. The nitroglycerin is thrown out as a heavy oil when the solution is diluted with water. A further quantity of the substance is procured by extracting the dilute acid liquors with chloroform. Naoúm[11] reports that 100 grams of glycerin treated in this manner with 1000 grams of 99% nitric acid yields 207.2 grams of nitroglycerin analyzing 18.16% nitrogen (calc. 18.50% N) and containing a small amount of dinitroglycerin (glyceryl dinitrate). The yield of the trinitrate may be improved by the addition to the nitric acid of dehydrating agents such as phosphorus pentoxide, calcium nitrate, or strong sulfuric acid.

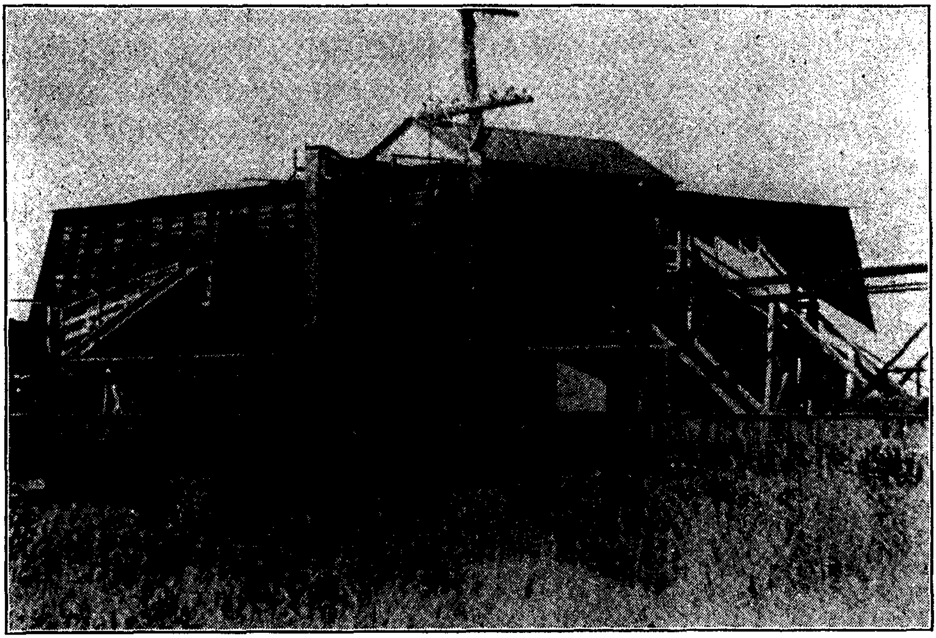


FIGURE 52. Nitroglycerin Nitrating House. (Courtesy E. I. du Pont de Nemours and Company, Inc.)

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[11] *Op. cit.*, pp. 25, 26.

Thus, if 100 grams of glycerin is added with cooling to a solution of 150 grams of phosphorus pentoxide in the strongest nitric acid, phosphoric acid precipitates as a heavy syrupy layer and the supernatant acid liquid on dilution yields about 200 grams of nitroglycerin. The yield is substantially the same if the glycerin is first dissolved in the nitric acid alone and if the phosphorus pentoxide is added afterwards. One hundred grams of glycerin in 500 grams of the strongest nitric acid, 400 grams of anhydrous calcium nitrate being added and the mixture allowed to stand for some hours, gives on drowning and purification 220 grams of nitroglycerin which contains about 10% of glyceryl dinitrate.

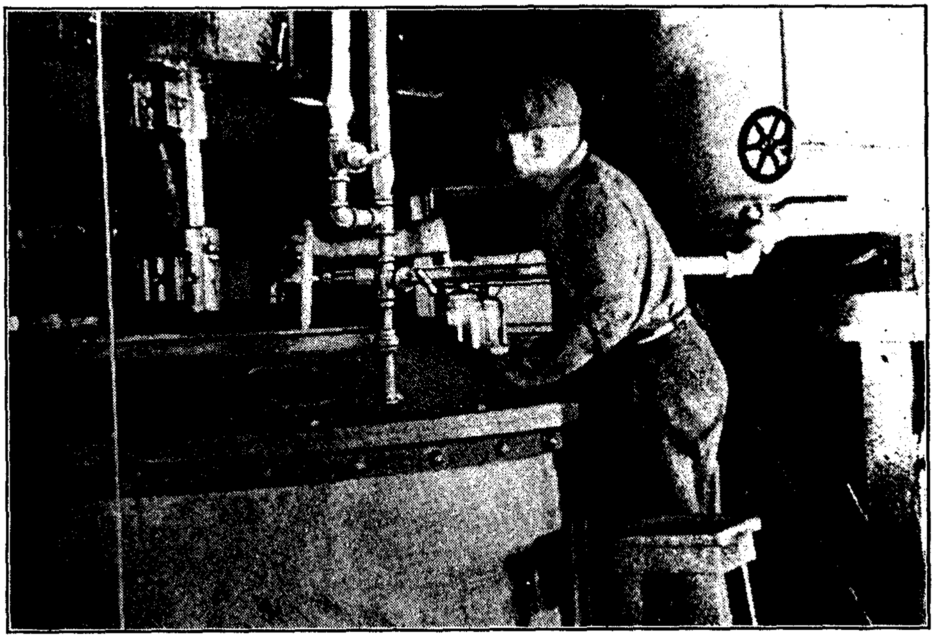

FIGURE 53. Nitroglycerin Nitrator. (Courtesy E. I. du Pont de Nemours and Company, Inc.)

All these methods are too expensive, for the excess of nitric acid is lost or has to be recovered from dilute solution. A process in which the nitroglycerin comes out as a separate phase without the spent acid being diluted is preferable—and it is indeed true that the addition of strong sulfuric acid to a solution of glycerin in strong nitric acid completes the esterification and causes the nitroglycerin to separate out. Since the strongest nitric acid is expensive to manufacture, and since a mixture of less strong nitric acid with oleum (sulfuric acid containing free sulfur trioxide) may be identical in all respects with a mixture of strong nitric and strong sulfuric acids, glycerin is universally nitrated in commercial practice by means of acid already mixed, and the nitroglycerin is procured by means of gravity separation of the phases. One hundred parts by weight of glycerin yield 225 to 235 parts of nitroglycerin.

One part of glycerin is nitrated with about 6 parts of mixed acid, made up by the use of oleum and containing about 40.0% of nitric acid, 59.5% of sulfuric acid, and 0.5% of water. The nitration in this country is carried out in cast iron or steel nitrators, in Europe in nitrators of lead. The glycerin is commonly added from a cock, controlled by hand, in a stream about the size of a man's finger. The mixture is stirred by compressed air, and the temperature is controlled carefully by means of brine coils, there being usually two thermometers, one in the liquid, one in the gas phase above it. In Great Britain the temperature of the nitration mixture is not allowed to rise above 22°C., in this country generally not above 25°. If the temperature for any reason gets out of control, or if the workman sees red fumes through the window in the nitrator, then the charge is dumped

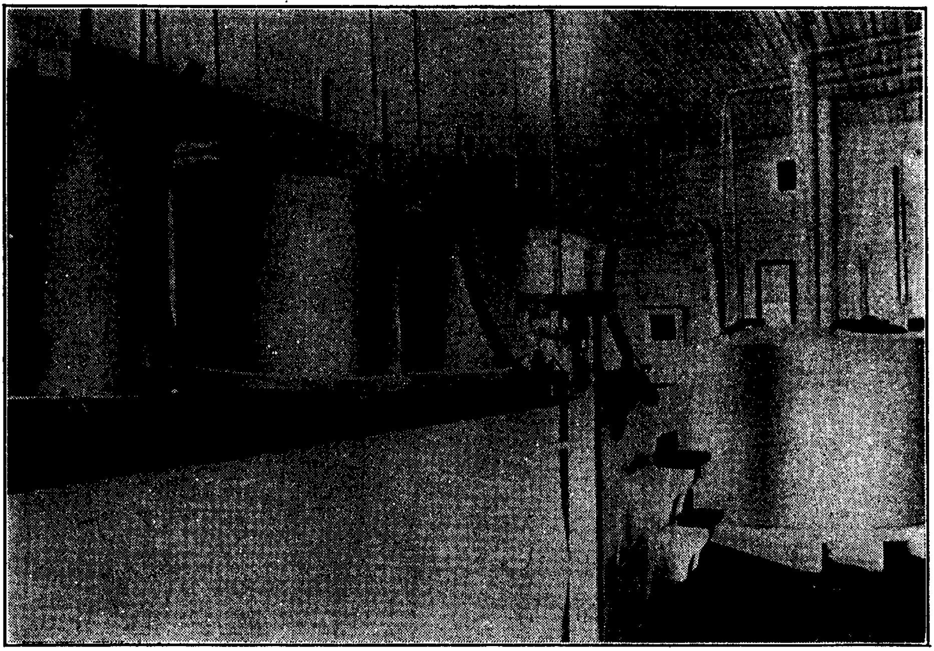

FIGURE 54. Interior of Nitroglycerin Storage House. (Courtesy E. I. du Pont de Nemours and Company, Inc.)

quickly into a drowning tank and the danger is averted. The safety precautions which are everywhere exercised are such that the explosion of a nitroglycerin plant is a rare occurrence. After all the glycerin has been added to the nitrator, agitation and cooling are continued until the temperature drops to about 15°, and the mixture is then run off to the *separator* where the nitroglycerin rises to the top. The spent acid contains 9 to 10% of nitric acid, 72 to 74% of sulfuric acid, and 16 to 18% of water.

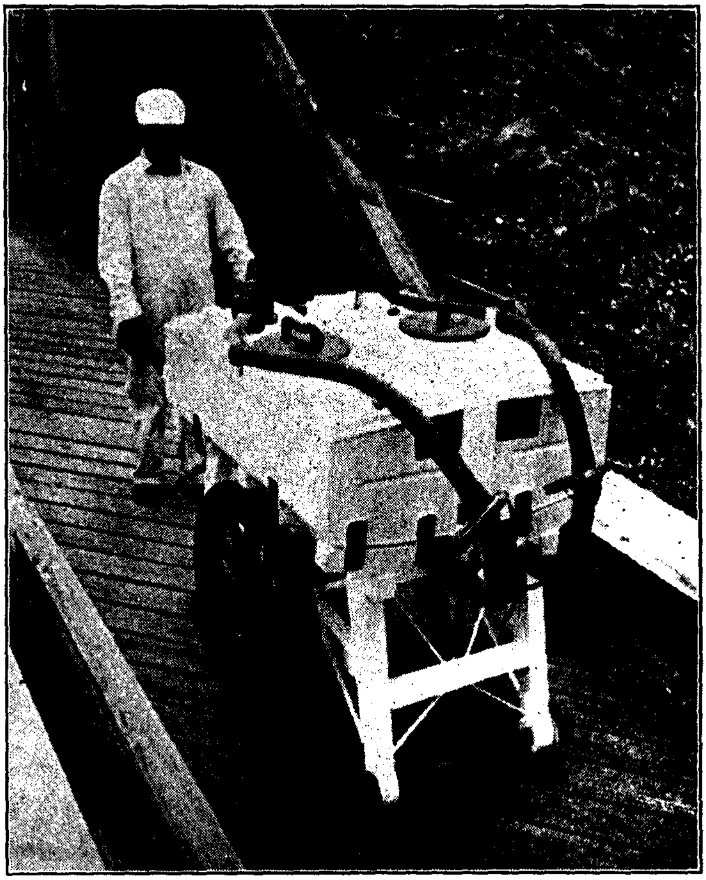

FIGURE 55. Nitroglycerin Buggy. (Courtesy Hercules Powder Company.) For transporting nitroglycerin from the storage house to the house where it is mixed with the other ingredients of dynamite. Note the absence of valves and the use of wooden hose clamps as a safety precaution.

The nitroglycerin from the separator contains about 10% of its weight of dissolved acid (about 8% nitric and about 2% sulfuric). Most of this is removed by a *drowning wash* or *prewash* carried out, in Europe with water at about 15°, in this country with water at 38° to 43°, while the mixture is agitated with compressed air. The higher temperature reduces the viscosity of the nitroglycerin and increases greatly the efficiency of the washing. The nitroglycerin is heavier than water and sinks rapidly to the bottom. It is washed again with water, then with sodium carbonate solution (2 or 3%), and then with water until the washings give no color with phenolphthalein and the nitroglycerin itself is neutral to litmus paper. In this country the nitroglycerin is sometimes given a final wash with a concentrated solution of common salt. This reduces the moisture which is suspended in it, to about the same extent as the filtration to which it is commonly subjected in European practice. The nitroglycerin then goes to storage tanks in a heated building where there is no danger of freezing. It has a milky appearance at first, but this quickly disappears. After one day of storage it generally contains not more than 0.3 or 0.4% of moisture, and this amount does not interfere with its use for the manufacture of dynamite.

Pure nitroglycerin is odorless at ordinary temperatures, but has a faint and characteristic odor at temperatures above 50°. Its specific gravity is 1.6009 at 15° and 1.5910 at 25°.[12] It contracts on freezing. Its vapor pressure has been reported by Marshall and Peace[13] to be 0.00025 mm. at 20°, 0.00083 mm. at 30°, 0.0024 at 40°, 0.0072 at 50°, 0.0188 at 60°, 0.043 at 70°, 0.098 at 80°, and 0.29 mm. at 93.3°. About 5 cc. of nitroglycerin passes over with one liter of water in a steam distillation. Snelling and Storm[14] heated nitroglycerin at atmospheric pressure in a distillation apparatus behind an adequate barricade. They reported that

> Nitroglycerin begins to decompose at temperatures as low as 50° or 60°C. . . . At a temperature of about 135°C. the decomposition of nitroglycerin is so rapid as to cause the liquid to become of a strongly reddish color, owing to the absorption of the nitrous fumes resulting from that which is decomposed; and at a temperature of about 145°C. the evolution of decomposition products is so rapid that, at atmospheric pressures, ebullition begins, and the liquid

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[12] Perkin, *J. Chem. Soc.*, **55**, 685 (1879).

[13] *J. Soc. Chem. Ind.*, **109**, 298 (1916).

[14] *U. S. Bur. Mines Tech. Paper* 12, "The Behavior of Nitroglycerine When Heated," Washington, 1912.

"boils" strongly. This "boiling" is due in part to the evolution of decomposition products (mainly oxides of nitrogen and water vapor) and in part to the actual volatilization of nitroglycerin itself.

FIGURE 56. C. G. Storm. Author of numerous articles and government publications on the properties, testing, and analysis of smokeless powder and high explosives. Explosives Chemist at Navy Powder Works, 1901-1909, at U. S. Bureau of Mines, 1909-1915; Directing Chemist, Aetna Explosives Company, 1915-1917; Major and Lieutenant-Colonel, Ordnance Department, 1917-1919; Research Chemist, Trojan Powder Company, 1919; Chief Explosives Chemical Engineer, Office of the Chief of Ordnance, War Department, 1919-1942; since early in 1942, Technical Director, National Fireworks, Inc.

. . . At temperatures between 145° and 215°C. the ebullition of nitroglycerin becomes more and more violent; at higher temperatures the amount of heat produced by the

> decomposing liquid becomes proportionately greater, and at about 218°C. nitroglycerin explodes.[15]
>
> When nitroglycerin is maintained at a temperature between 145° and 210°C., its decomposition goes on rapidly, accompanied by much volatilization, and under these conditions nitroglycerin may be readily distilled. The distillate consists of nitroglycerin, nitric acid, water, and other decomposition products. The residue that remains after heating nitroglycerin under such conditions for some time probably consists mainly of glycerin, with small amounts of dinitroglycerin, mononitroglycerin, and other decomposition products. These substances are far less explosive than ordinary nitroglycerin, and accordingly by heating nitroglycerin slowly it can be caused to "boil" away until the residue consists of products that are practically non-explosive. In a number of experiments nitroglycerin was thus heated, and a copious residue was obtained. By carefully raising the temperature this residue could be made to char without explosion.

Belyaev and Yuzefovich[16] heated nitroglycerin and other explosives in vacuum; and procured the results summarized in the following table. The fact that ignition temperatures are fairly close to probable boiling points indicates that high concentrations of vapor exist at the moment when the substances ignite. The authors point out that TNT, PETN, and picric acid neither detonate nor burn in vacuum and suggest that this is probably

	B.P. (2 mm.) Experimental, °C.	B.P. (50 mm.) Experimental, °C.	B.P. (760 mm.) Most Probable Value, °C.	Ignition Temperature, °C.
Methyl nitrate	...	5	66	...
Glycol dinitrate	70	125	197 ± 3	195–200
TNT	190	245–250	300 ± 10	295–300
Picric acid	195	255	325 ± 10	300–310
TNB	175	250	315 ± 10	...
PETN	160	180	200 ± 10	215
Nitroglycerin	125	180	245 ± 5	200

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[15] Munroe had found the "firing temperature" of nitroglycerin to be 203 to 205°, *J. Am. Chem. Soc.*, 12, 57 (1890).

[16] *Comp. rend. acad. sci. U.S.S.R.*, 27, 133 (1940).

because the boiling points in vacuum are considerably below the ignition temperatures.

Nitroglycerin crystallizes in two forms, a stable form, dipyramidal rhombic crystals, which melt or freeze at 13.2–13.5°, and a labile form, glassy-appearing triclinic crystals, m.p. 1.9–2.2°. It does not freeze readily or quickly. When cooled rapidly, it becomes more and more viscous and finally assumes the state of a hard glassy mass, but this is not true freezing, and the glassy mass becomes a liquid again at a temperature distinctly below the melting point of the crystalline substance. Nitroglycerin in dynamite freezes in crystals if the explosive is stored for a considerable length of time at low temperatures, the form in which it solidifies being determined apparently by the nature of the materials with which it is mixed.[17] If liquid nitroglycerin is cooled strongly, say to $-20°$ or $-60°$, stirred with a glass rod, and seeded with particles of one or the other form, then it crystallizes in the form with which it has been seeded. If the solid is melted by warming, but not warmed more than a few degrees above its melting point, it will on being cooled solidify in the form, whether labile or stable, from which it had been melted. If, however, it is warmed for some time at 50°, it loses all preference for crystallizing in one form rather than in the other, and now shows the usual phenomena of supercooling when it is chilled. Crystals of the labile form may be preserved sensibly unchanged for a week or two, but gradually lose their transparency and change over to the stable form. Crystals of the stable form cannot be changed to the labile form except by melting, warming above the melting point, and seeding with the labile form.

Nitroglycerin is miscible in all proportions at ordinary temperatures with methyl alcohol, acetone, ethyl ether, ethyl acetate, glacial acetic acid, benzene, toluene, nitrobenzene, phenol, chloroform, and ethylene chloride, and with homologous nitric esters such as dinitroglycerin, dinitrochlorohydrin, nitroglycol, and trimethyleneglycol dinitrate. Absolute ethyl, propyl, isopropyl, and amyl alcohols mix with nitroglycerin in all proportions if they are hot, but their solvent power falls off rapidly at lower temperatures. One hundred grams of absolute ethyl alcohol dissolves

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[17] Hibbert, *Z. ges. Schiess- u. Sprengstoffw.*, **9**, 83 (1914).

37.5 grams of nitroglycerin at 0°, 54.0 grams at 20°. One hundred grams of nitroglycerin on the other hand dissolves 3.4 grams of ethyl alcohol at 0°, 5.5 grams at 20°.

Nitroglycerin dissolves aromatic nitro compounds, such as dinitrotoluene and trinitrotoluene, in all proportions when warm. When the liquids are cooled, 100 grams of nitroglycerin at 20° still holds in solution 35 grams of DNT or 30 grams of TNT. Both nitroglycerin and the polynitro aromatic compounds are solvents or gelatinizing agents for nitrocellulose.

Nitroglycerin dissolves in concentrated sulfuric acid with the liberation of its nitric acid, and may therefore be analyzed by means of the nitrometer (see below).

Nitroglycerin is destroyed by boiling with alcoholic sodium or potassium hydroxide, but glycerin is not formed; the reaction appears to be in accordance with the following equation.

$$C_3H_5(ONO_2)_3 + 5KOH \longrightarrow KNO_3 + 2KNO_2 + H{-}COOK + CH_3{-}COOK + 3H_2O$$

This however is not the whole story, for resinous products, oxalic acid, and ammonia are also formed. If the reaction with caustic alkali is carried out in the presence of thiophenol, some glycerin is formed and the thiophenol is oxidized to diphenyl sulfide. Alkali sulfides, K_2S, KHS, and CaS, also yield glycerin.

Nitroglycerin vapors cause severe and persistent headache. A workman who is exposed to them constantly soon acquires an immunity. If he is transferred to another part of the plant, he may retain his immunity by paying a short visit every few days to the area in which the nitroglycerin is being used. Workmen appear to suffer no ill effects from handling the explosive continually with the naked hands. Nitroglycerin relaxes the arteries, and is used in medicine under the name of *glonoin*. *Spirit of glonoin* is a 1% solution of nitroglycerin in alcohol. The usual dose for angina pectoris is one drop of this spirit taken in water, or one lactose or dextrose pellet, containing 1/100 grain (0.0006 gram) of nitroglycerin, dissolved under the tongue.

Nitroglycerin is not easily inflammable. If a small quantity is ignited, it burns with a slight crackling and a pale green flame—and may be extinguished readily before all is burned. If a larger amount is burned in such manner that the heat accumulates and the temperature rises greatly, or if local overheating occurs as by burning in an iron pot, then an explosion ensues. The explosion of nitroglycerin by heat is conveniently demonstrated by heating a stout steel plate to dull redness, removing the source of heat, and allowing the nitroglycerin to fall drop by drop slowly onto the plate while it is cooling. At first the drops assume the spheroidal condition when they strike the plate and deflagrate or burn with a flash, but when the plate cools somewhat each drop yields a violent explosion.

Nitroglycerin is very sensitive to shock, and its sensitivity is greater if it is warm. A drop of the liquid on a steel anvil, or a drop absorbed by filter paper and the paper placed upon the anvil, is detonated by the blow of a steel hammer. The shock of iron striking against stone, or of porcelain against porcelain, also explodes nitroglycerin, that of bronze against bronze less readily, and of wood against wood much less so. Stettbacher[18] reports drop tests with a 2-kilogram weight: mercury fulminate 4.5 cm., lead azide 9 cm., nitroglycerin 10–12 cm., blasting gelatin 12–15 cm., and tetryl 30–35 cm. He also reports the observations of Kast and Will and of Will that nitroglycerin at 90° requires only half as much drop to explode it as nitroglycerin at ordinary temperature, while the frozen material requires about three times as much.

Nitroglycerin and nitroglycerin explosives, like all other high explosives, show different velocities of detonation under different conditions of initiation and loading. They are sometimes described as having low and high velocities of detonation. Berthelot found for nitroglycerin a velocity of 1300 meters per second in lead or tin tubes of 3 mm. internal diameter. Abel[19] found 1525 meters per second in lead pipe 30 mm. internal diameter, while Mettegang[20] found 2050 meters per second in iron pipes of the same internal diameter. Comey and Holmes[21] working with pipes of 25–37.5 mm. internal diameter found values varying from 1300–1500 to 8000–8500 meters per second, and, with especially strong detonators, they regularly found velocities between 6700

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[18] Stettbacher, "Die Schiess- und Sprengstoffe," Leipzig, 1919, p. 124.

[19] *Phil. Trans.*, **156**, 269 (1866); **157**, 181 (1867).

[20] *Internat. Congr.*, **2**, 322 (1903).

[21] *Z. ges. Schiess- u. Sprengstoffw.*, **8**, 306 (1913).

and 7500 meters per second. Naoúm[22] reports that blasting gelatin (92–93% NG, 7–8% collodion nitrocotton) has a low velocity of 1600–2000 meters per second and a high velocity of about 8000. Blasting gelatin filled with air bubbles always shows the higher velocity, while clear and transparent blasting gelatin almost always shows the lower velocity of detonation. Frozen dynamite is more difficult to initiate, but always detonates at the high velocity.[23]

Certain properties of nitroglycerin and of other explosives, reported by Brunswig,[24] are tabulated below and compared in a manner to show the relative power of the substances. The specific volume is the volume, at 0° and 760 mm., of the gaseous products of the explosion. This number multiplied by the heat of explosion gives the *characteristic product* which Berthelot considered to be a measure of the mechanical work performed by the explosion. The mechanical work has also been estimated, differently, in kilogram-meters by multiplying the heat of explosion by 425, the mechanical equivalent of heat.

	Specific Volume, Liters	Explosion Temperature, °C.	Heat of Explosion, Calories	Characteristic Product
Nitroglycerin	712	3470	1580	1,125,000
Nitromannite	723	3430	1520	1,099,000
Blasting gelatin (93% NG, 7% NC)	710	3540	1640	1,164,000
75% Guhr dynamite	628	3160	1290	810,000
Nitrocotton (13% N)	859	2710	1100	945,000
Picric acid	877	2430	810	710,000
Black powder	285	2770	685	195,000
Ammonium nitrate	937	2120	630	590,000
Mercury fulminate	314	3530	410	129,000

Naoúm[25] reports the results of his own experiments with nitroglycerin and with other explosives in the Trauzl lead block test (sand tamping), 10-gram samples, as shown below. The Trauzl test is essentially a measure of brisance, but for explosives of similar

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[22] *Op. cit.*, p. 145.

[23] Herlin, *Z. ges. Schiess- u. Sprengstoffw.*, **9**, 401 (1914).

[24] Brunswig, "Explosivstoffe," 1909, cited by Naoúm, *op. cit.*, p. 152.

[25] *Op. cit.*, p. 156.

velocities of detonation it supplies a basis for the comparison of their total energies.

	EXPANSION, CUBIC CENTIMETERS
Nitroglycerin	550
Nitromannite	560
Compressed guncotton (13.2% N)	420
Blasting gelatin	580
65% Gelatin dynamite	410
75% Guhr dynamite	325
Tetryl	360
Picric acid	300
Trinitrotoluene	285
Mercury fulminate	150

For several years after the discovery of nitroglycerin, the possibility of using it as an explosive attracted very little interest. Indeed, it first came into use as a medicine, and the first serious study on its preparation, after the work of Sobrero, was made by J. E. de Vrij, professor of chemistry in the Medical School at Rotterdam, and published in the Dutch journal of pharmacy, *Tijdschrift voor wetensch. pharm.*, in 1855. The next significant work was done by Alfred Nobel who in 1864 patented[26] improvements both in the process of manufacturing nitroglycerin and in the method of exploding it. No liquid explosive had been successful in practical use. Nobel believed that he had solved the difficulty by taking advantage of the property of nitroglycerin of exploding from heat or from the shock of an explosion. A small glass vessel containing black powder was to be immersed in the nitroglycerin and exploded. Another method was by the local heat of an electric spark or of a wire electrically heated under the surface of the nitroglycerin. And another was the percussion cap. Nobel used black powder first in glass bulbs, later in hollow wooden cylinders closed with cork stoppers, then a mixture of black powder and mercury fulminate, and later fulminate in small lead capsules and finally in the copper detonators which are still in general use. The invention of the blasting cap depended upon the discovery of the phenomenon of initiation, and signalized the beginning of a new era in the history of

[26] Brit. Pat. 1813 (1864).

explosives. Blasting caps were used first for the safe and certain explosion of the dangerous liquid nitroglycerin, but presently they were found to be exactly what was needed for the explosion of the safer and less sensitive dynamites which Nobel also invented.

The first establishment for the manufacture of nitroglycerin in industrial quantities was a laboratory set up by Alfred Nobel and his father, Immanuel Nobel, probably in the autumn of 1863, near the latter's home at Heleneborg near Stockholm. An explosion which occurred there in September, 1864, cost the life of Alfred's younger brother, Emil, and of four other persons. The manufacture of nitroglycerin was prohibited within the city area, but the explosive was already in practical use for the tunnelling operations of the State Railway, and it was desirable to continue its manufacture. The manufacture was removed to a pontoon moored in Malar Lake and was continued there during the late autumn of 1864 and during the following winter until March, 1865, when it was transferred to a new factory, the first real nitroglycerin factory in the world, at Winterwik near Stockholm. Later in the same year the Nobel company commenced manufacturing nitroglycerin in Germany, at a plant near Hamburg, and within a few years was operating explosives factories in the United States and in all the principal countries of Europe.[27]

The first considerable engineering operation in the United States to be accomplished by means of nitroglycerin was the blasting out of the Hoosac tunnel in Massachusetts. The work had been progressing slowly until George M. Mowbray,[28] an "operative chemist" of North Adams, was engaged to manufacture nitroglycerin at the site of the work and to supervise its use. Twenty-six feet of tunnel was driven during May, 1868, 21 during June, 47 during July when the use of nitroglycerin commenced, 44 during August, and 51 feet during September. Mowbray profited by the observation of W. P. Granger that frozen nitroglycerin could not be detonated, and accordingly transported his

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[27] Cf. Schück and Sohlman, "The Life of Alfred Nobel," London, William Heinemann, Ltd., 1929.

[28] His experiences and methods are told in a very interesting manner in his book, "Tri-Nitro-Glycerine, as Applied in the Hoosac Tunnel," third edition, rewritten, New York and North Adams, 1874.

material in safety in the frozen condition.[29] He described an explosion which occurred in December, 1870, in which the life of a foreman was lost, and another in March, 1871, in which a large amount of frozen nitroglycerin failed to explode.

> The new magazine had hardly been completed, and stored with nitroglycerine, when, on Sunday morning, at half past six o'clock, March twelfth, 1871, the neighborhood was startled by another explosion of sixteen hundred pounds of nitroglycerine. The cause of this last explosion was continuous overheating of the magazine. . . . The watchman con-

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> [29] During the severe winter of 1867 and 1868, the Deerfield dam became obstructed with ice, and it was important that it should be cleared out without delay. W. P. Granger, Esq., engineer in charge, determined to attempt its removal by a blast of nitroglycerine. In order to appreciate the following details, it must be borne in mind that the current literature of this explosive distinctly asserted that, when congealed, the slightest touch or jar was sufficient to explode nitroglycerine. Mr. Granger desired me to prepare for him ten cartridges, and, as he had to carry them in his sleigh from the west end of the tunnel to the east end or Deerfield dam, a distance of nine miles over the mountain, he requested them to be packed in such a way that they would not be affected by the inclement weather. I therefore caused the nitroglycerine to be warmed up to ninety degrees, warmed the cartridges, and, after charging them, packed them in a box with sawdust that had been heated to the same temperature; the box was tied to the back of the sleigh, with a buffalo robe thrown over it. In floundering across the divide where banks, road, hedge and water courses were indistinguishable beneath the drifted snow, horse, sleigh and rider were upset, the box of cartridges got loose, and were spread indiscriminately over the snow. After rectifying this mishap, picking up the various contents of the sleigh, and getting ready to start again, it occurred to Mr. Granger to examine his cartridges; his feelings may be imagined when he discovered the nitroglycerine frozen solid. To have left them behind and proceeded to the dam, where miners, engineers and laborers were waiting to see this then much dreaded explosive, would never do; so accepting the situation, he replaced them in the case, and, laying it between his feet, proceeded on his way, thinking a heap but saying nothing. Arrived, he forthwith attached fuse, exploder, powder and some guncotton, and inserted the cartridge in the ice. Lighting the fuse, he retired to a proper distance to watch the explosion. Presently a sharp crack indicated that the fuse had done its work, and, on proceeding to the hole drilled in the ice, it was found that fragments of the copper cap were imbedded in the solid cylinder of congealed nitroglycerine, which was driven through and out of the tin cartridge into the anchor ice beneath, but not exploded. A second attempt was attended with like results. Foiled in attempting to explode the frozen nitroglycerine, Mr. Granger thawed the contents of another cartridge, attached the fuse and exploder as before; this time the explosion was entirely successful. From that day I have never transported nitroglycerine except in a frozen condition, and to that lesson are we indebted for the safe transmission of more than two hundred and fifty thousand pounds of this explosive, over the roughest roads of New Hampshire, Vermont, Massachusetts, New York, and the coal and oil regions of Pennsylvania, in spring wagons with our own teams.

Mowbray, *op. cit.,* pp. 45–46.

> fessed he had neglected to examine the thermometer, made his fire under the boiler, and gone to bed. . . . Fortunately, this accident involved no damage to life or limb, whilst a very instructive lesson was taught in the following circumstance: Within twelve feet of the magazine was a shed, sixteen feet by eight, containing twelve fifty-pound cans of congealed nitroglycerine ready for shipment. This shed was utterly destroyed, the floor blasted to splinters, the joists rent to fragments, the cans of congealed nitroglycerine driven into the ground, the tin of which they were composed perforated, contorted, battered, and portions of tin and nitroglycerine sliced off but not exploded. Now, this fact proves one of two things: Either that the tri-nitroglycerine made by the Mowbray process, differs from the German nitroglycerine in its properties, or the statements printed in the foreign journals, as quoted again and again, that nitroglycerine, when congealed, is more dangerous than when in the fluid state, are erroneous.[30]

Mowbray used his nitroglycerin in the liquid state, either loaded in cylindrical tin cannisters or cartridges, or poured directly into the bore hole, and exploded it by means of electric detonators. The electric detonators were operated by means of a static electric machine which caused a spark to pass between points of insulated wire; the spark set fire to a priming mixture made from copper sulfide, copper phosphide, and potassium chlorate; and this fired the detonating charge of 20 grains of mercury fulminate contained in a copper capsule, the whole being waterproofed with asphaltum varnish and insulated electrically with gutta-percha. The devices were so sensitive that they could be exploded by the static electricity which accumulated on the body of a miner operating a compressed air drill, and they required corresponding precautions in their use.

Liquid nitroglycerin is still used as an explosive to a limited extent, particularly in the blasting of oil wells, but its principal use is in the manufacture of dynamite and of the propellants, ballistite and cordite.

Dinitroglycerin (Glyceryl dinitrate)

Dinitroglycerin does not differ greatly from nitroglycerin in its explosive properties. It is appreciably soluble in water, and more expensive and more difficult to manufacture than nitrogly-

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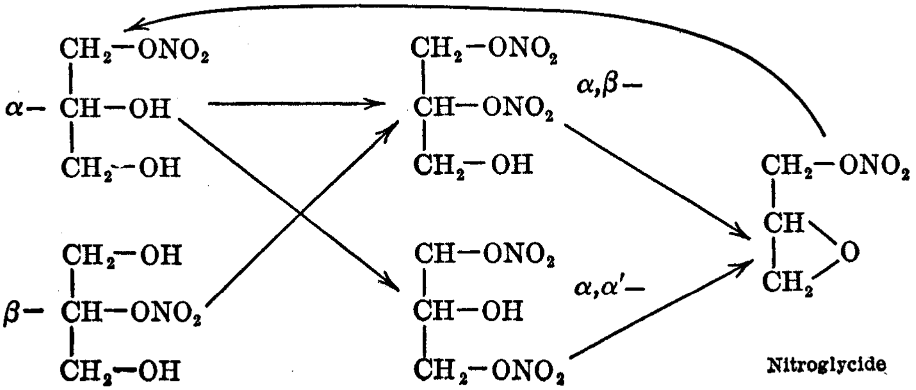
[30] *Ibid.*, pp. 44–45.

cerin. It mixes with the latter substance in all proportions and lowers its freezing point, and was formerly used in Germany in such mixtures in non-freezing dynamites. It has now been superseded entirely for that purpose by dinitrochlorohydrin which is insoluble in water, and cheaper and more convenient to manufacture.

Dinitroglycerin is never formed alone by the nitration of glycerin but is always accompanied by the trinitrate or the mononitrate or both. If the nitration is carried out in a manner to give the best yields of the dinitrate, then considerable trinitrate is formed: if the process is modified to reduce the yield of trinitrate, then the yield of dinitrate is also reduced and some mononitrate is formed. If 3 or 4 parts by weight of nitric acid is added slowly to 1 part of glycerin, so that the glycerin or its nitrated product is always in excess, then the dinitrate is the principal product. If the order of mixing is reversed, so that the glycerin dissolves first in the strong nitric acid, then the yield of trinitrate is more considerable. Dinitroglycerin is formed if glycerin is added to mixed acid which is low in nitric acid or high in water, or which contains insufficient sulfuric acid for the necessary dehydrating action. It is also one of the products of the hydrolysis of nitroglycerin by cold concentrated (95%) sulfuric acid, the trinitrate by this reagent being in part dissolved and in part converted to the dinitrate, the mononitrate, and to glyceryl sulfate according to the relative amount of sulfuric acid which is used. Dinitroglycerin is separated from its mixture with nitroglycerin and obtained pure by treating the oil with about 15 volumes of water, separating the insoluble trinitrate, extracting the aqueous solution with ether, washing the ether with dilute sodium carbonate solution, and evaporating. The resulting dinitroglycerin gives a poor heat test because of the peroxide which it contains from the ether. Material which gives an excellent heat test may be procured by evaporating the aqueous solution in vacuum.

The dinitroglycerin obtained by the nitration of glycerin is a colorless, odorless oil, more viscous and more volatile than nitroglycerin. It causes the same kind of a headache. It has a specific gravity of 1.51 at 15°, boils at 146–148° at 15 mm. with only slight decomposition, and solidifies at −40° to a glassy solid which melts if the temperature is raised to −30°. It is readily soluble in alcohol, ether, acetone, and chloroform, somewhat less soluble than nitroglycerin in benzene, and insoluble in carbon tetrachloride and ligroin. It consists of a mixture of the two possible structural isomers, the 1,2- or α,β-dinitrate, known also as "dinitroglycerin F," and the 1,3- or α,α′-dinitrate or "dinitroglycerin K." Both are uncrystallizable oils, and both are hygroscopic and take up about 3% of their weight of moisture from the air. They are separated by virtue of the fact that the α,α′-dinitrate forms a hydrate[31] with one-third of a molecule of water, $C_3H_6O_7N_2 + \frac{1}{3} H_2O$, water-clear prisms, m.p. 26°. No hydrate of the α,β-dinitrate has ever been isolated in the state of a crystalline solid. If a test portion of the moist mixture of the isomers is mixed with fuller's earth and chilled strongly, it deposits crystals; and if these are used for seeding the principal quantity of the moist dinitroglycerin, then the hydrate of the α,α′-dinitrate crystallizes out. It may be recrystallized from water, or from alcohol, ether, or benzene without losing its water of crystallization, but it yields the anhydrous α,α′-dinitrate if it is dried over sulfuric acid or warmed in the air at 40°.

The chemical relationships between the mononitroglycerins and dinitroglycerins supply all the evidence which is needed for inferring the identities of the isomers. Of the two mononitrates, the β-compound obviously cannot yield any α,α′-dinitrate by nitration; it can yield only the α,β-. That one of the two isomers which yields only one dinitrate is therefore the β-mononitrate, and the dinitrate which it yields is the α,β-dinitrate. The α-mononitrate on the other hand yields both the α,β- and the α,α′-dinitrates.



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[31] Will, *Ber.*, 41, 1113 (1908).

Both of the dinitroglycerins on treatment with 30% sodium hydroxide solution at room temperature yield nitroglycide, and this substance on boiling with water gives α-mononitroglycerin, a series of reactions which demonstrates the identity of the last-named compound.

Dinitroglycerin is a feeble acid and gives a wine-red color with blue litmus, but none of its salts appear to have been isolated and characterized. It does not decompose carbonates, but dissolves in caustic alkali solutions more readily than in water. One hundred parts of water alone dissolves about 8 parts at 15° and about 10 parts at 50°.

Dinitroglycerin gelatinizes collodion nitrocotton rapidly at ordinary temperature. The gel is sticky, less elastic, and more easily deformed than a nitroglycerin gel. Unlike the latter it is hygroscopic, and becomes softer and greasier from the absorption of moisture from the air. Water dissolves out the dinitroglycerin and leaves the nitrocellulose as a tough, stiff mass.

Dinitroglycerin has about the same sensitivity to initiation as nitroglycerin, only slightly less sensitivity to shock, and offers no marked advantages from the point of view of safety. It shows a greater stability in the heat test, and a small amount can be evaporated by heat without explosion or deflagration. It gives off red fumes above 150°, and at 170° decomposes rapidly with volatilization and some deflagration, or in larger quantities shows a tendency to explode.

Naoúm[32] reports that a 10-gram sample of dinitroglycerin in the Trauzl test with water tamping gave a net expansion of about 500 cc., or 83.3% as much as the expansion (600 cc.) produced by 10 grams of nitroglycerin under the same conditions. He points out that the ratio here is almost the same as the ratio between the heats of explosion, and that in this case the Trauzl test has supplied a fairly accurate measure of the relative energy contents of the two explosives. In the small lead block test the effect of the greater brisance and higher velocity of detonation of nitroglycerin becomes apparent; 100 grams of dinitroglycerin gave a compression of 21 mm. while the same amount of nitroglycerin gave one of 30 mm.

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[32] *Op. cit.*, p. 170.

Mononitroglycerin (Glyceryl mononitrate)

Mononitroglycerin is a by-product in the preparation of dinitroglycerin and is separated from the latter substance by its greater solubility in water. It is usually obtained as a colorless oil, density 1.417 at 15°, more viscous than dinitroglycerin and less viscous than nitroglycerin. This oil is a mixture of the two isomers which are crystalline when separate but show little tendency to crystallize when they are mixed. α-Mononitroglycerin when pure consists of colorless prisms, m.p. 58–59°, specific gravity 1.53 at 15°; it yields both of the dinitrates on nitration. The β-compound crystallizes in dendrites and leaflets, m.p. 54°, and is more readily soluble in ether than the α-compound; it yields only the α,β-dinitrate on nitration. Both isomers boil at 155–160° at 15 mm.

Mononitroglycerin resembles glycerin in being very hygroscopic and miscible in all proportions with water and alcohol, and in being only slightly soluble in ether, but it differs from glycerin in being freely soluble in nitroglycerin. It does not form a satisfactory gel with collodion cotton. Its aqueous solution reacts neutral. It appears to be perfectly stable on moderate heating, but decomposes to some extent at 170°, gives off gas, and turns yellow.

Mononitroglycerin is insensitive to shock. In the form of oil it is not detonated by a No. 8 blasting cap in the Trauzl test. If the oil is absorbed in fuller's earth, 10 grams gives a net expansion of 75 cc. The crystalline material, however, detonates easily; 10 grams gives an expansion of 245 cc. It is interesting to compare these results, reported by Naoúm,[33] with the results which the same author reports for nitroglycide which is the anhydride of mononitroglycerin. Ten grams of liquid nitroglycide with water tamping and a No. 8 detonator gave a net expansion of 430 cc.; 10 grams absorbed in fuller's earth, with sand tamping, gave 310 cc.; and 10 grams gelatinized with 5% collodion nitrocotton, with sand tamping, gave 395 cc.

Nitroglycide

This substance cannot be prepared by the nitration of glycide, for the action of acids upon that substance opens the ethylene

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[33] *Ibid.*, pp. 174, 177.

oxide ring, and mononitroglycerin is formed. Nitroglycide was first prepared by Naoúm[34] in 1907 by shaking dinitroglycerin at room temperature with a 30% aqueous solution of sodium hydroxide. The clear solution presently deposited a colorless oil, and this, washed with water and dried in a desiccator, constituted a practically quantitative yield of nitroglycide.

Nitroglycide is a very mobile liquid with a faint but pleasant aromatic odor, specific gravity 1.332 at 20°. It does not freeze at −20°. It boils at 94° at 20 mm., and with some decomposition at 174–175° at atmospheric pressure. It is not hygroscopic but is distinctly soluble in water, 5 grams in 100 cc. at 20°. Ether will extract nitroglycide from the cool aqueous solution; if the solution is boiled, however, the nitroglycide is hydrated to mononitroglycerin. Nitroglycide is miscible in all proportions with alcohol, ether, acetone, ethyl acetate, and nitroglycerin. It gelatinizes collodion nitrocotton and even guncotton rapidly at ordinary temperature. It explodes in contact with concentrated sulfuric acid. If dissolved in dilute sulfuric acid and then treated with strong sulfuric acid, it gives off nitric acid. It is converted into dinitroglycerin and nitroglycerin by the action of nitric acid. It dissolves in concentrated hydrochloric acid with the evolution of considerable heat, and the solution on dilution with water gives a precipitate of monochlorohydrin mononitrate. Nitroglycide reduces ammoniacal silver nitrate slowly on gentle warming; glycide reduces the same reagent in the cold.

When heated rapidly in a test tube nitroglycide explodes with a sharp report at 195–200°. It is more easily detonated than liquid nitroglycerin. Naoúm believes that its great sensitivity results mainly from the easy propagation of the wave of detonation by a liquid of low viscosity.[35] He points out further that mononitroglycerin has 69.5% of the energy content (i.e., heat of explosion) of nitroglycide, but as a crystal powder in the Trauzl test it gives only about 62% as much net expansion, whence it is to be inferred that nitroglycide has the higher velocity of detonation. Nitroglycide has only 52% of the energy content of nitroglycerin, but produces 72% as much effect in the Trauzl test. It is therefore "relatively more brisant than nitroglycerin."

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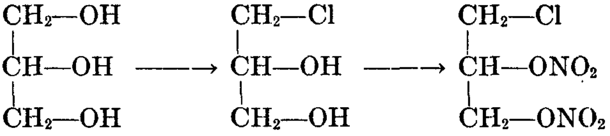
[34] *Ibid.*, p. 176.

[35] *Ibid.*, p. 178.

Dinitrochlorohydrin (Glycerin chlorohydrin dinitrate)

Among the various substances which may be used in admixture with nitroglycerin for the purpose of lowering its freezing point, dinitrochlorohydrin is preferred in Germany but has not found favor in the United States. Since dinitrochlorohydrin is distinctly safer to prepare than nitroglycerin, it is most commonly prepared by itself, that is, by the nitration of chlorohydrin which is substantially pure and contains not more than a small amount of glycerin. The product is used directly for the preparation of certain explosives, or it is mixed with nitroglycerin for the manufacture of non-freezing dynamites.

Chlorohydrin is prepared by autoclaving glycerin with concentrated hydrochloric acid or by treating it at moderate temperature with sulfur chloride. In the former process, in order to avoid the formation of dichlorohydrin, only enough hydrochloric acid is used to convert about 75% of the glycerin. The product is procured by a vacuum distillation. The monochlorohydrin, which consists almost entirely of the α-compound, comes over between 130° and 150° at 12–15 mm. and the unchanged glycerin between 165° and 180°. It is nitrated with the same mixed acid as is used for the preparation of nitroglycerin; less acid is needed of course, less heat is produced, and the process is safer and more rapid.



$$\begin{array}{l} CH_2\text{—}OH \\ | \\ CH\text{—}OH \\ | \\ CH_2\text{—}OH \end{array} \longrightarrow \begin{array}{l} CH_2\text{—}Cl \\ | \\ CH\text{—}OH \\ | \\ CH_2\text{—}OH \end{array} \longrightarrow \begin{array}{l} CH_2\text{—}Cl \\ | \\ CH\text{—}ONO_2 \\ | \\ CH_2\text{—}ONO_2 \end{array}$$

If a mixture of chlorohydrin and glycerin is nitrated, the resulting mixture of nitrates contains relatively more nitroglycerin than the original mixture contained of glycerin, for the relative increase of molecular weight during the nitration of glycerin is greater.

Commercial dinitrochlorohydrin is usually yellowish or brownish in color, specific gravity about 1.541 at 15°. It boils at atmospheric pressure with decomposition at about 190°. It may be distilled at 13 mm. at 121.5°, or at 10 mm. at 117.5°, but some decomposition occurs for the distillate is acid to litmus.

Dinitrochlorohydrin is non-hygroscopic, distinctly more volatile than nitroglycerin, and it has similar physiological effects. It can be frozen only with great difficulty, shows a strong tendency to supercool, and can be kept for a long time at −20° without depositing crystals. The solubility of dinitrochlorohydrin and nitroglycerin in each other is so great that only small quantities of nitroglycerin can be frozen out from the mixtures, even after seeding, at winter temperatures. A mixture of 75 parts of nitroglycerin and 25 parts of dinitrochlorohydrin is practically nonfreezing, and yields a dynamite which is not significantly less strong than one made from straight nitroglycerin.

Dinitrochlorohydrin does not take fire readily, and, if ignited, burns rather slowly without detonating and with but little of the sputtering which is characteristic of nitroglycerin mixtures. "Even larger quantities of pure dinitrochlorohydrin in tin cans burn without explosion when in a fire, so that liquid dinitrochlorohydrin is permitted on German railroads in tin cans holding 25 kg., as a safe explosive for limited freight service in the 200 kg. class, while liquid nitroglycerin is absolutely excluded."[36] Dinitrochlorohydrin is more stable toward shock than nitroglycerin. Naoúm, working with a pure sample, was not able to secure a first-rate explosion in the drop test.[37] A 2-kilogram weight dropped from a height of 40 cm. or more gave a very slight partial decomposition and a slight report, from a height of 75 cm. or more, a somewhat more violent partial deflagration but in no case a sharp report, and even a 10-kilogram weight dropped from a height of 10 or 15 cm. gave a very weak partial decomposition. The substance, however, is detonated readily by fulminate. It gives in the Trauzl test a net expansion of 475 cc., or 79% of the 600-cc. expansion given by nitroglycerin, although its heat of explosion is only about 71% of the heat of explosion of nitroglycerin.

Dinitrochlorohydrin produces hydrogen chloride when it explodes. This would tend to make it unsuitable for use in mining explosives were it not for the fact that the incorporation into the explosives of potassium or sodium nitrate sufficient to form chloride with the chlorine of the dinitrochlorohydrin prevents it altogether—and this amount of the nitrate is usually present anyway for other reasons.

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[36] Naoúm, *ibid.*, p. 187.

[37] *Ibid.*, p. 188.

Acetyldinitroglycerin (monoacetin dinitrate) and formyldinitroglycerin (monoformin dinitrate) have been proposed by Vender[38] for admixture with nitroglycerin in non-freezing dynamite. The former substance may be prepared[39] by nitrating monoacetin or by acetylating dinitroglycerin. The latter substance may be procured already mixed with nitroglycerin by warming glycerin with oxalic acid, whereby monoformin (glyceryl monoformate) is formed, and nitrating the resulting mixture of monoformin and glycerin. Formyldinitroglycerin has apparently not yet been isolated in the pure state. These substances are satisfactory explosives but are more expensive to manufacture than dinitrochlorohydrin over which they possess no distinct advantage, and they have not come into general use.

Tetranitrodiglycerin (Diglycerin tetranitrate)

If glycerin is heated with a small amount of concentrated sulfuric acid, ether formation occurs, water splits out, and diglycerin and polyglycerin are formed. If the heating is carried out in the absence of acids, and in such a way that the water which is formed is allowed to escape while the higher-boiling materials are condensed and returned, especially if a small amount of alkali, say 0.5%, or of sodium sulfite is present as a catalyst, then the principal product is diglycerin and not more than a few per cent of polyglycerin is formed. It is feasible for example to convert glycerin into a mixture which consists of 50–60% diglycerin, 4–6% polyglycerin, and the remainder, 34–46%, unchanged glycerin. The diglycerin is ordinarily not isolated in the pure state. The mixture, either with or without the addition of glycerin, is nitrated directly to form a mixture of tetranitrodiglycerin and nitroglycerin which is used for the manufacture of non-freezing dynamite.

Diglycerin when obtained pure by a vacuum distillation is a water-white liquid, more viscous and more dense than glycerin, sweet-tasting, very hygroscopic, b.p. 245–250° at 8 mm. It is nitrated with the same mixed acid as glycerin, although a smaller

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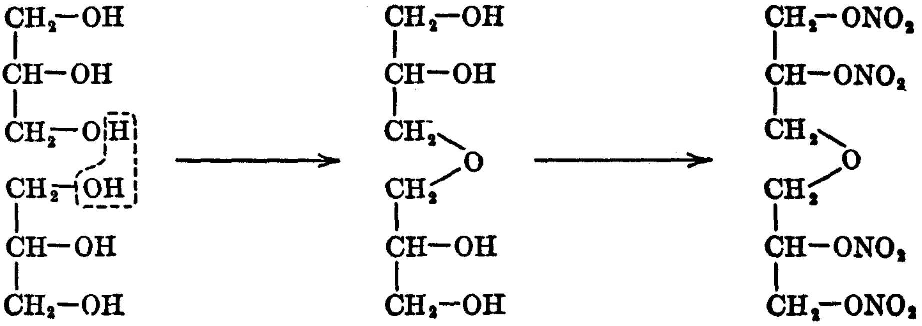
[38] *Z. ges. Schiess- u. Sprengstoffw.*, 2, 21 (1907). *Fourth Internat. Congr.* 2, 582 (1906).

[39] Ger. Pat. 209,943 (1906); Brit. Pat. 9791 (1906); French Pat. 372,267 (1906); Swiss Pat. 50,836 (1910); U. S. Pat. 1,029,519 (1912).

amount is necessary. Salt solutions are always used for washing the nitrated product, otherwise the separation of the phases is extremely slow.



Tetranitrodiglycerin is a very viscous oil, non-hygroscopic, insoluble in water, and readily soluble in alcohol and in ether. It has not been obtained in the crystalline state. It is not a good gelatinizing agent for collodion cotton when used alone. Its mixture with nitroglycerin gelatinizes collodion cotton more slowly than nitroglycerin alone but gives a satisfactory gel. It is less sensitive to mechanical shock than nitroglycerin, about the same as dinitroglycerin, but is readily exploded by fulminate. According to Naoúm[40] 75% tetranitrodiglycerin guhr dynamite gave in the Trauzl test a net expansion of 274 cc. or 85.6% of the expansion (320 cc.) produced by 75% nitroglycerin guhr dynamite.

Nitroglycol (Ethylene glycol dinitrate, ethylene dinitrate)

Nitroglycol first found favor in France as an ingredient of non-freezing dynamites. It has many of the advantages of nitroglycerin and is safer to manufacture and handle. Its principal disadvantage is its greater volatility. Formerly the greater cost of procuring glycol, which is not as directly accessible as glycerin but has to be produced by synthesis from ethylene, was an impediment to its use, but new sources of ethylene and new methods of synthesis have reduced its cost and increased its accessibility.

Ethylene was formerly procured from alcohol (itself produced from raw material which was actually or potentially a foodstuff) by warming with sulfuric acid, by passing the vapors over heated coke impregnated with phosphoric acid, or by comparable methods. Ethylene combines with bromine to give ethylene dibromide,

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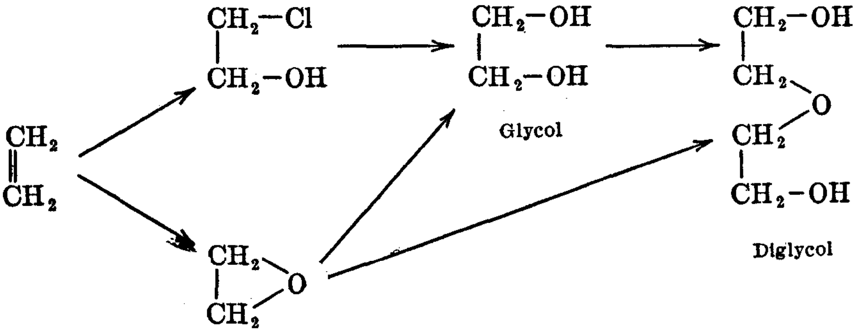
[40] *Op. cit.*, p. 201.

which yields glycol by hydrolysis, but bromine is expensive. Ethylene also combines readily with chlorine, but, even if care is exercised always to have the ethylene present in excess, substitution occurs, and tri- and tetrachloroethane are formed along with the ethylene dichloride, and these do not yield glycol by hydrolysis. Ethylene is now produced in large quantities during the cracking of petroleum. Its comportment with chlorine water has been found to be much more satisfactory for purposes of synthesis than its comportment with chlorine gas. Chlorine water contains an equilibrium mixture of hydrogen chloride and hypochlorous acid.

$$Cl_2 + H_2O \leftrightarrows HCl + HOCl$$

Ethylene adds hypochlorous acid more readily than it adds either moist chlorine or hydrogen chloride. Bubbled into chlorine water, it is converted completely into ethylene chlorohydrin, and by the hydrolysis of this substance glycol is obtained. Ethylene chlorohydrin is important also because of its reaction with ammonia whereby mono-, di-, and triethanolamine are formed, substances which are used in the arts and are not without interest for the explosives chemist. Ethylene may be oxidized catalytically in the gas phase to ethylene oxide which reacts with water to form glycol and with glycol to form diglycol which also is of interest to the dynamite maker.



Glycol is a colorless liquid (bluer than water in thick layers), syrupy, sweet tasting, less viscous than glycerin, specific gravity 1.1270 at 0°, 1.12015 at 10°, and 1.11320 at 20°.[41] It shows a tendency to supercool but freezes at temperatures between −13° and −25°, and melts again at −11.5°. It boils at 197.2° at atmospheric pressure. It is very hygroscopic, miscible in all pro-

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[41] C. A. Taylor and W. H. Rinkenbach, *Ind. Eng. Chem.*, **18**, 676 (1926).

portions with water, alcohol, glycerin, acetone, and acetic acid, and not miscible with benzene, chloroform, carbon disulfide, and ether.

Nitroglycol is manufactured with the same mixed acid and with the same apparatus as nitroglycerin. Somewhat more heat is produced by the nitration reaction, and, as glycol is less viscous than glycerin, it is feasible to conduct the operation at a lower temperature. The washing is done with cold water and with less agitation by compressed air, and smaller amounts of wash water are used than are used with nitroglycerin, for nitroglycol is appreciably more volatile and more soluble in water. The tendency of the partially washed product to undergo an acid-catalyzed decomposition is less in the case of nitroglycol than in the case of nitroglycerin.

Nitroglycol is a colorless liquid, only slightly more viscous than water, specific gravity ($x°/15°$) 1.5176 at 0°, 1.5033 at 10°, and 1.4890 at 20°.[42] It freezes at about $-22.3°$. Rinkenbach reports the index of refraction of nitroglycol for white light to be 1.4452 at 22.3°, and that of a commercial sample of nitroglycerin under the same conditions to be 1.4713. The same author reports the vapor pressure of nitroglycol to be 0.007 mm. of mercury at 0° and 0.0565 mm. at 22°, and points out that its vapor pressure at 22° is approximately 150 times as great as the vapor pressure, 0.00037 mm., reported by Peace and Marshall[43] for nitroglycerin at 22°. Nitroglycol produces a headache similar to that produced by nitroglycerin, but, corresponding to its greater volatility, the headache is more violent and does not last so long. Nitroglycol is non-hygroscopic. Its comportment with organic solvents is similar to that of nitroglycerin, but it is distinctly more soluble in water than that substance. Naoúm[44] reports that 1 liter of water at 15° dissolves 6.2 grams of nitroglycol, at 20° 6.8 grams of nitroglycol or 1.8 grams of nitroglycerin, and at 50° 9.2 grams of nitroglycol.

Nitroglycol has a slightly larger energy content than nitroglycerin. In the Trauzl test with 10-gram samples and water tamping, Naoúm[45] found that nitroglycol gave a net expansion

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[42] Rinkenbach, *Ind. Eng. Chem.*, **18**, **1195** **(1926)**.

[43] *Loc. cit.*

[44] Naoúm, *op. cit.*, p. 224.

[45] *Ibid.*, p. 227.

of 650 cc. and nitroglycerin one of 590 cc. Nitroglycol, like nitroglycerin, burns with sputtering and explodes if local overheating occurs, but nitroglycol and nitroglycol explosives in general burn more quietly and show less tendency to explode from heat than the corresponding nitroglycerin preparations. Nitroglycol explodes with a sharp report if heated rapidly to 215°. It is less sensitive to mechanical shock than nitroglycerin. Naoúm[46] reports the height of drop necessary to cause explosion, with a 2-kilogram weight, as follows.

	HEIGHT OF DROP, CENTIMETERS	
	Nitroglycol	Nitroglycerin
Drop absorbed on filter paper	20–25	8–10
Blasting gelatin	25–30	12
Guhr dynamite	15	5

Rinkenbach[47] reports tests with a small drop machine having a weight of 500 grams, nitroglycol 110 cm., nitroglycerin 70 cm., and a commercial mixture of nitroglycerin and nitropolyglycerin 90 cm.

Nitroglycol gelatinizes collodion cotton much faster than nitroglycerin and acts at ordinary temperatures, while nitroglycerin requires to be warmed. The greater volatility of nitroglycol does not affect its usefulness in gelatin dynamite, especially in temperate climates, but renders it unsuitable for use during the warm season of the year in ammonium nitrate explosives which contain only a few per cent of the oily nitric ester. It is too volatile for use in double-base smokeless powder, for its escape by evaporation affects the ballistic properties.

Dinitrodiglycol (Diethylene glycol dinitrate)

A study of the preparation and properties of dinitrodiglycol was reported by Rinkenbach[48] in 1927 and a further study of the nitration of diethylene glycol by Rinkenbach and Aaronson[49] in 1931. Dinitrodiglycol is a viscous, colorless, and odorless liquid, specific gravity ($x°/15°$) 1.4092 at 0°, 1.3969 at 10°, and 1.3846 at 20°, freezing point −11.5°. It is completely miscible at ordinary temperatures with nitroglycerin, nitroglycol, ether, acetone,

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[46] *Op. cit.*, p. 225.

[47] *Loc. cit.*

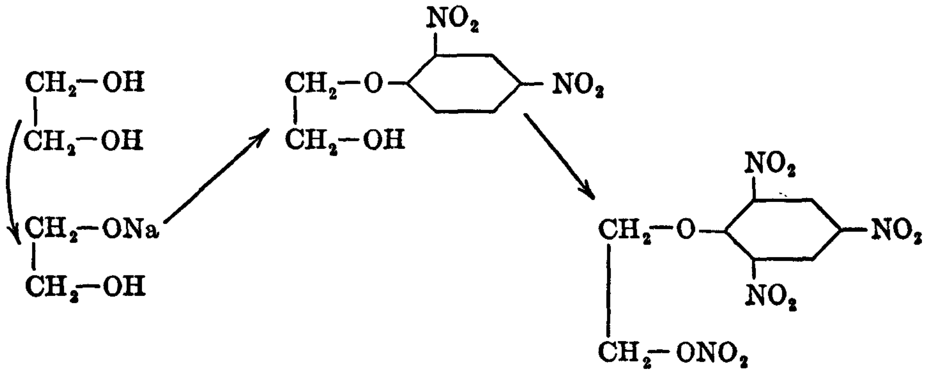
[48] *Ind. Eng. Chem.*, 19, 925 (1927).

[49] *Ind. Eng. Chem.*, 23, 160 (1931).

methyl alcohol, chloroform, benzene, and glacial acetic acid. It is immiscible, or only slightly soluble, in ethyl alcohol, carbon tetrachloride, and carbon disulfide. It is slightly hygroscopic and is soluble in water to the extent of about 4.1 grams per liter of water at 24°. It can be ignited only with difficulty, and in small quantity is not readily exploded by heat. It is less sensitive than nitroglycol in the drop test. It is so insensitive to initiation that it will not propagate its own detonation under conditions where nitroglycol and nitroglycerin will do it. In 50/50 mixture however with either of these substances it detonates satisfactorily "and shows an explosive effect but little less than that of either of these compounds." It has a vapor pressure of about 0.007 mm. of mercury at 22.4°, and produces headaches similar to those produced by nitroglycerin.

Trinitrophenoxyethyl Nitrate

Another explosive which is preparable from glycol and which may perhaps be of interest for special purposes in the future is the β-2,4,6-trinitrophenoxyethyl nitrate described by Wasmer[50] in 1938. Glycol is converted into its monosodium derivative, and this is made to react with dinitrochlorobenzene at 130° for the production of β-dinitrophenoxyethyl alcohol which gives the explosive by nitration with mixed acid.



Trinitrophenoxyethyl nitrate is procured as a white powder, m.p. 104.5°, insoluble in water and readily soluble in acetone. It gelatinizes collodion nitrocotton, and is intermediate between picric acid and tetryl in its sensitivity to mechanical shock.

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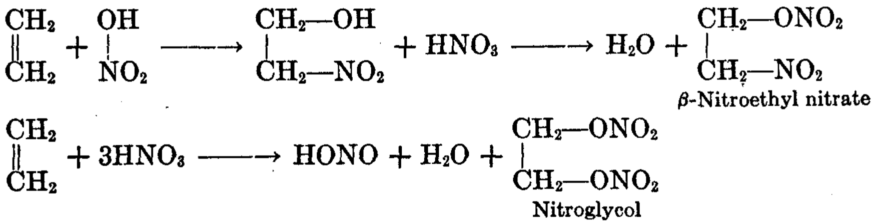
[50] *Mém. poudres,* **28,** 171 (1938).

Nitration of Ethylene

By passing ethylene into a mixture of concentrated nitric and sulfuric acids Kekulé[51] obtained an oil, specific gravity 1.47, which broke down when distilled with steam to give glycollic acid, oxalic acid, nitric oxide, and nitric acid. On reduction with sodium amalgam it yielded glycol and ammonia among other products. Wieland and Sakellarios[52] distilled the Kekulé oil in steam and then in vacuum, and obtained nitroglycol, b.p. 105° at 19 mm., and β-nitroethyl nitrate, b.p. 120–122° at 17 mm. These two substances are evidently formed from ethylene by the reactions indicated below.



$$\begin{array}{l}CH_2\\ \Vert\\ CH_2\end{array} + \begin{array}{l}OH\\ |\\ NO_2\end{array} \longrightarrow \begin{array}{l}CH_2{-}OH\\ |\\ CH_2{-}NO_2\end{array} + HNO_3 \longrightarrow H_2O + \underset{\beta\text{-Nitroethyl nitrate}}{\begin{array}{l}CH_2{-}ONO_2\\ |\\ CH_2{-}NO_2\end{array}}$$

$$\begin{array}{l}CH_2\\ \Vert\\ CH_2\end{array} + 3HNO_3 \longrightarrow HONO + H_2O + \underset{\text{Nitroglycol}}{\begin{array}{l}CH_2{-}ONO_2\\ |\\ CH_2{-}ONO_2\end{array}}$$

A considerable amount of nitrous acid is present in the spent acid. β-Nitroethyl nitrate is feebly acidic and dissolves in dilute alkali solutions with a yellow color. It is not sufficiently stable for use in commercial explosives. On digestion with warm water or on slow distillation with steam it undergoes a decomposition or sort of hydrolysis whereby nitrous acid and other materials are produced. Numerous patents have been issued for processes of procuring pure nitroglycol from the Kekulé oil. One hundred parts of the last-named material yield about 40 parts of nitroglycol, and the economic success of the process depends upon the recovery of valuable by-products from the β-nitroethyl nitrate which is destroyed.

Öhman[53] in Sweden has developed an ingenious electrolytic process for the production of nitric esters direct from ethylene. The discharge of the nitrate ion (NO_3^-) at the anode liberates the free nitrate radical (NO_3) which in part combines directly with ethylene to form nitroglycol.

$$\begin{array}{l}CH_2\\ \Vert\\ CH_2\end{array} + 2NO_3 \longrightarrow \begin{array}{l}CH_2{-}ONO_2\\ |\\ CH_2{-}ONO_2\end{array}$$

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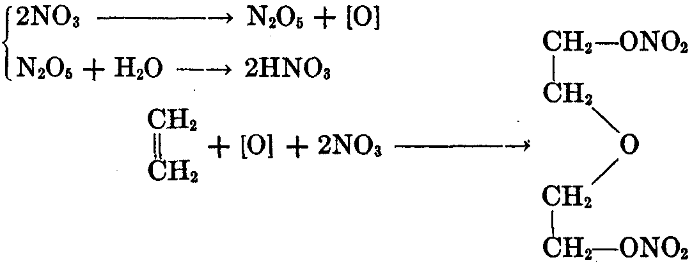
[51] *Ber.*, **2**, 329 (1869).

[52] *Ber.*, **53**, 201 (1920).

[53] *Z. Elektrochem.*, **42**, 862 (1936); *Svensk Kemisk Tid.*, **50**, 84 (1938).

Another portion of the free nitrate radical apparently reacts with itself and with water as indicated below, and the oxygen which becomes available enters into the reaction with the consequent formation of dinitrodiglycol.



$$\begin{cases} 2NO_3 \longrightarrow N_2O_5 + [O] \\ N_2O_5 + H_2O \longrightarrow 2HNO_3 \end{cases}$$

A platinum gauze anode is used. It is immersed in an acetone solution of calcium nitrate which is kept continuously saturated with ethylene which is bubbled through in such manner that it sweeps over the surface of the platinum gauze. An aluminum cathode is used, in a catholyte consisting of a nitric acid solution of calcium nitrate, and the cathode compartment is filled to a higher level since the liquid moves into the anode compartment as the electrolysis progresses. After the electrolysis, the cathode liquid is fortified with nitric acid for use again. The anode liquid is neutralized with slaked lime, and distilled in vacuum for the recovery of the acetone, and the residue, after the removal of calcium nitrate, washing, and drying, consists of a mixture of nitroglycol and dinitrodiglycol and is known as *Oxinite*. Dynamites made from Oxinite differ but little from those made from nitroglycerin.

Pentryl

Pentryl, or 2,4,6-trinitrophenylnitraminoethyl nitrate, is another explosive which is derived from ethylene. It is a nitric ester, an aromatic nitro compound, and a nitroamine. The substance was described in 1925 by Moran [54] who prepared it by the action of mixed acid on 2,4-dinitrophenylethanolamine (large orange-yellow crystals from alcohol, m.p. 92°) procured by the interaction of dinitrochlorobenzene with ethanolamine. von Herz later prepared pentryl by the nitration of β-hydroxyethylaniline, a material which is more commonly called phenylethanolamine and is now available commercially in this country, and was granted

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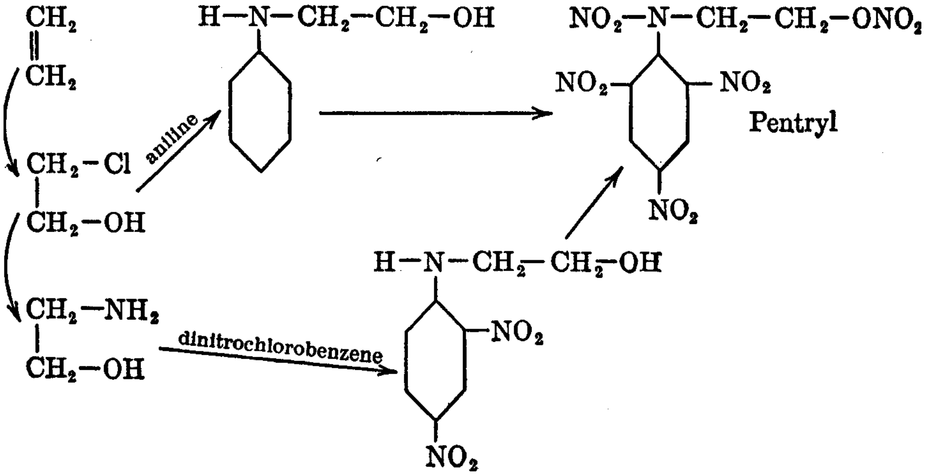
[54] U. S. Pat. 1,560,427 (1925).

British and German patents[55] for its use for certain military purposes. The genesis of pentryl from ethylene, through the intermediacy both of ethanolamine and of phenylethanolamine, is indicated below. The preparation and properties of pentryl have



been studied extensively by LeRoy V. Clark[56] at the U. S. Bureau of Mines. By the reaction of dinitrochlorobenzene in the presence of sodium hydroxide with ethanolamine in alcohol solution at 70–80° he procured dinitrophenylethanolamine in 70% yield. The alcohol solution was filtered for the removal of sodium chloride, which was found to be mixed with a certain quantity of the by-product tetranitrodiphenylethanolamine (lemon-yellow fine powder, m.p. 222°); it was then concentrated to about one-third its volume, and deposited crystals of the product on cooling. This material, dissolved in concentrated sulfuric acid and nitrated by adding the solution to nitric acid and heating, gave pentryl in yields of about 90%, minute cream-colored crystals from benzene, m.p. 128°.

Clark reports that pentryl has an absolute density of 1.82 and an apparent density of only 0.45. When compressed in a detonator shell at a pressure of 3400 pounds per square inch, it has an apparent density of 0.74. It is soluble to some extent in most of the common organic solvents, and is very readily soluble in nitroglycerin. In the drop test with a 2-kilogram weight, 0.02 gram of pentryl was exploded by a drop of 30 cm., a similar sample of

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[55] Brit. Pat. 367,713 (1930); Ger. Pat. 530,701 (1931).

[56] *Ind. Eng. Chem.*, 25, 1385 (1933).

tetryl by one of 27.5 cm., and one of picric acid by a drop of 42.5 cm., while TNT was not exploded by a drop of 100 cm. It is somewhat more sensitive to friction than tetryl, and much more sensitive than picric acid and TNT. Pentryl explodes in 3 seconds at 235°.

The results of Clark's experiments to determine the minimum amounts of primary explosive necessary to initiate the explosion of pentryl and of other high explosives are tabulated below. For the purpose of these experiments a half-gram portion of the high explosive was weighed into a No. 8 detonator shell, a weighed amount of primary explosive was introduced on top of it, and both were compressed under a reenforcing capsule at a pressure of 3400 pounds per square inch. Without the reenforcing capsule diazodinitrophenol did not cause detonation, and pentryl required 0.035 gram of lead azide and more than 0.4 gram of fulminate. The results show that pentryl has about the same sensitivity to initiation as tetryl and hexanitrodiphenylamine.

	MINIMUM INITIATING CHARGE (GRAMS) OF		
	Diazodinitrophenol	Mercury Fulminate	Lead Azide
Pentryl	0.095	0.150	0.025
Picric acid	0.115	0.225	0.12
TNT	0.163	0.240	0.16
Tetryl	0.075	0.165	0.03
Trinitroresorcinol	0.110	0.225	0.075
Trinitrobenzaldehyde	0.075	0.165	0.05
Tetranitroaniline	0.085	0.175	0.05
Hexanitrodiphenylamine	0.075	0.165	0.05

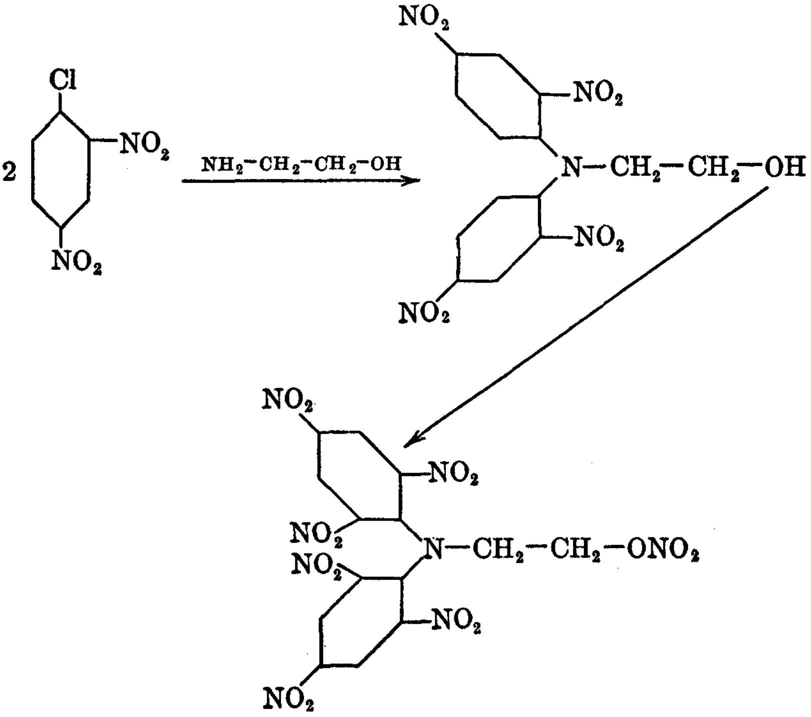
In the small Trauzl test pentryl caused an expansion of 15.8 cc., while the same weight of tetryl caused one of 13.8 cc., TNT 12.2 cc., and picric acid 12.4 cc. In the small lead block compression test, in which 50 grams of the explosive was exploded by means of a detonator on top of a lead cylinder 64 mm. long, it was found that pentryl produced a shortening of the block of 18.5 mm., tetryl 16.6 mm., picric acid 16.4 mm., TNT 14.8 mm., and diazodinitrophenol 10.5 mm. Determinations of velocity of detonation made with half-meter lengths, the explosives being contained in extra light lead tubing ½ inch internal diameter and weighing 12 ounces to the foot, gave the following figures.

	Density	Velocity of Detonation (Meters per second)
Pentryl	0.80	5000
Tetryl	0.90	5400
Picric acid	0.98	4970
TNT	0.90	4450

These are not however the maximum velocities of detonation of the substances.

Hexanitrodiphenylaminoethyl Nitrate

This substance also has been studied by LeRoy V. Clark[57] who prepared it by the nitration with mixed acid of tetranitrodiphenylethanolamine, a by-product from the preparation of pentryl.



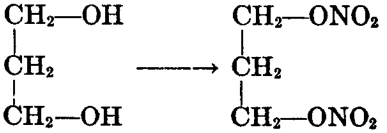
He procured the pure substance in the form of pale yellow glistening plates, m.p. 184° (corr.), precipitated from acetone solution by the addition of alcohol. Its explosive properties are not widely different from those of pentryl. Its response to initiation

[57] *Ibid.,* **26, 554 (1934).**

is about the same; it is slightly less sensitive to impact, about 7% less effective in the sand test, and about 3% more effective in the small Trauzl test. In compound detonators it is somewhat better than TNT and somewhat poorer than pentryl, tetryl, and picric acid, as indicated by the lead plate test. When heated rapidly, it ignites at 390–400°.

Trimethylene Glycol Dinitrate

Trimethylene glycol occurs in the glycerin which is produced by fermentation. There is no harm in leaving it in glycerin which is to be used for the manufacture of explosives. It may however be separated by fractional distillation. When pure it is a colorless, odorless, syrupy liquid, specific gravity ($x°/4°$) 1.0526 at 18°. It mixes with water in all proportions and boils at atmospheric pressure at 211° without decomposition. At temperatures above 15° or so, it is oxidized rapidly by nitric acid or by mixed acid. It is accordingly nitrated at 0–10° under conditions similar to those which are used in the preparation of ethyl nitrate and other simple aliphatic nitric esters (except methyl nitrate).



$$\begin{array}{l} CH_2{-}OH \\ | \\ CH_2 \\ | \\ CH_2{-}OH \end{array} \longrightarrow \begin{array}{l} CH_2{-}ONO_2 \\ | \\ CH_2 \\ | \\ CH_2{-}ONO_2 \end{array}$$

Trimethylene glycol dinitrate is a water-white liquid, very mobile, and scarcely more viscous than nitroglycol, specific gravity (20°/4°) 1.393 at 20°. It boils at 108° at 10 mm. without decomposition. It is less volatile than nitroglycol and more volatile than nitroglycerin. It has about the same solubility relationships as nitroglycerin, and forms a good gelatin with collodion nitrocotton. It causes headache by contact with the skin. When heated slowly it takes fire with a puff and burns tranquilly or decomposes at about 185° and deflagrates at about 225°. It is much less sensitive to shock than nitroglycerin and is much more stable in storage. Naoúm [58] reports that a 10-gram sample in the Trauzl test with water tamping gave an expansion of 540 cc. or about 90% of the expansion produced by nitroglycerin. The calculated energy content of trimethylene glycol dinitrate is only

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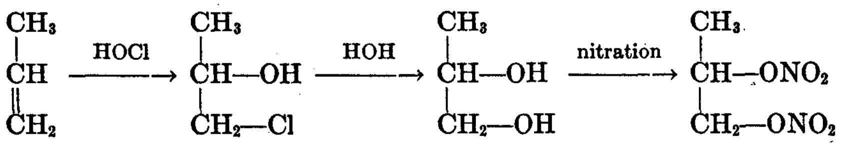
[58] *Op. cit.,* p. 235.

about 77% of that of nitroglycerin, but the relatively greater brisance results from the low viscosity of the substance which gives it a higher velocity of detonation. Naoúm also reports that a 93% trimethylene glycol dinitrate gelatin with 7% collodion cotton gave an expansion of 470 cc. or about 80% as much as a similar nitroglycerin gelatin.

Propylene Glycol Dinitrate (Methylglycol dinitrate, methylnitroglycol)

Propylene occurs along with ethylene in cracking gas. Its use as a raw material for the synthesis of glycerin has already been mentioned in the section on nitroglycerin. It yields propylene glycol when subjected to the same chemical processes as those which are used for the preparation of glycol from ethylene.[59] Propylene glycol shows the same tendency toward oxidation during nitration that trimethylene glycol does, but to a less extent; noticeable decomposition occurs only above 30°.



$$\begin{array}{l} \mathrm{CH_3} \\ | \\ \mathrm{CH} \\ \| \\ \mathrm{CH_2} \end{array} \xrightarrow{\mathrm{HOCl}} \begin{array}{l} \mathrm{CH_3} \\ | \\ \mathrm{CH{-}OH} \\ | \\ \mathrm{CH_2{-}Cl} \end{array} \xrightarrow{\mathrm{HOH}} \begin{array}{l} \mathrm{CH_3} \\ | \\ \mathrm{CH{-}OH} \\ | \\ \mathrm{CH_2{-}OH} \end{array} \xrightarrow{\text{nitration}} \begin{array}{l} \mathrm{CH_3} \\ | \\ \mathrm{CH{-}ONO_2} \\ | \\ \mathrm{CH_2{-}ONO_2} \end{array}$$

Propylene glycol dinitrate is a colorless liquid of characteristic aromatic odor, more volatile and less viscous than trimethylene glycol dinitrate with which it is isomeric. Its specific gravity (20°/4°) is 1.368 at 20°. It boils at 92° at 10 mm., and does not freeze at −20°. Its solubilities, gelatinizing power, and explosive properties are substantially the same as those of its isomer. Indeed, Naoúm [60] reports that it gave exactly the same expansion as trimethylene glycol dinitrate in the Trauzl lead block test, namely, 540 cc.

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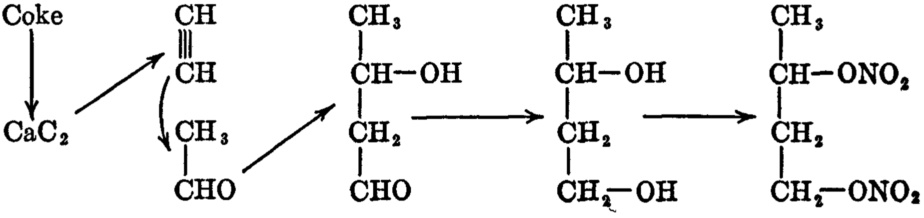
[59] Symmes, in a footnote, p. 375, in his English translation of Naoúm's book, *op. cit.*, cites U. S. patents 1,307,032, 1,307,033, 1,307,034, and 1,371,215 which describe a method for the manufacture of mixed ethylene and propylene glycols from cracking gas, satisfactory methods for the nitration of the mixture and for the stabilization of the mixed nitric esters, and explosives made from the products "which practical tests in actual use showed could not be frozen even at temperatures prevailing in winter along the Canadian border, or −10° to −30° F."

[60] *Op. cit.*, p. 237.

Butylene Glycol Dinitrate

Of the four isomeric butylene glycols, the 1,3-compound appears to be the only one which has attracted any interest as a raw material for the preparation of explosives. Its dinitrate, either alone or in admixture with nitroglycerin, has been proposed for use in non-freezing dynamites.[61] The preparation of the glycol from acetaldehyde has been suggested,[62] the acetaldehyde being condensed to aldol and the aldol reduced to glycol. Since acetaldehyde is produced commercially by the catalyzed hydration of acetylene, then butylene glycol-1,3 can be procured by synthesis from coke.



Butylene glycol shows a strong tendency to oxidize during nitration, and ought to be nitrated at a temperature of −5° or lower. Butylene glycol dinitrate is a colorless liquid, intermediate in volatility between nitroglycol and nitroglycerin, possessing a specific gravity of 1.32 at 15°. It does not freeze at temperatures as low as −20°. It yields a good gelatin with collodion nitrocotton. It deflagrates feebly if heated suddenly. It is very insensitive to mechanical shock but detonates easily by initiation. Naoúm[63] reports that a mixture of 75% butylene glycol dinitrate and 25% kieselguhr gave about 240 cc. expansion in the Trauzl test, and that a gelatin containing 90% butylene glycol dinitrate and 10% collodion nitrocotton gave about 370 cc.

Nitroerythrite (Erythritol tetranitrate)

$$NO_2\text{—}O\text{—}CH_2\text{—}(CH\text{—}ONO_2)_2\text{—}CH_2\text{—}ONO_2$$

i-Erythrite occurs in algae and in lichens. It is a white, crystalline, sweet-tasting substance, very readily soluble in water, m.p. 120°, b.p. 330°, specific gravity 1.59. The tetranitrate is prepared

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[61] U. S. Pats. 994,841 and 994,842 (1911).

[62] U. S. Pat. 1,008,333 (1911).

[63] *Op. cit.*, p. 239.

by dissolving erythrite in strong nitric acid with cooling, and then precipitating by the addition of concentrated sulfuric acid.[64] It crystallizes from alcohol in colorless plates, m.p. 61°. Its use as an addition to smokeless powder has been suggested,[65] but it is as powerful as nitroglycerin, and has the advantage over it that it is a solid, and it would be suitable, if it were cheaper, for the same uses as nitromannite.

Nitromannite (Mannitol hexanitrate)

$$NO_2—O—CH_2—(CH—ONO_2)_4—CH_2—ONO_2$$

d-Mannitol occurs fairly widely distributed in nature, particularly in the *Fraxinus ornus*, the sap of which is *manna*. It may also be procured by the reduction of *d*-mannose either electrolytically or by means of sodium amalgam, or along with *d*-sorbite by the reduction of *d*-fructose. It may be nitrated satisfactorily with the same mixed acid as is used for the nitration of glycerin, or more conveniently, because the mass of crystals is so voluminous, by dissolving in strong nitric acid and precipitating by the addition of concentrated sulfuric acid.

Preparation of Nitromannite. Fifty grams of nitric acid (specific gravity 1.51) is cooled thoroughly in a 300-cc. Erlenmeyer pyrex flask immersed in a freezing mixture of ice and salt. Ten grams of mannite is then introduced in small portions at a time while the flask is tilted from side to side and the contents is stirred gently with a thermometer, care being taken that the temperature does not rise above 0°. After all is dissolved, 100 grams of sulfuric acid (specific gravity 1.84) is added slowly from a dropping funnel while the liquid is stirred and the temperature is maintained below 0°. The porridge-like mass is filtered on a sinter-glass filter, or on a Büchner funnel with a hardened filter paper, washed with water, then with dilute sodium bicarbonate solution, then finally again with water. The crude product is dissolved in boiling alcohol; the solution is filtered if need be, and on cooling deposits white needle crystals of nitromannite, m.p. 112-113°. A second crop of crystals may be obtained by warming the alcoholic mother liquors to boiling, adding water while still boiling until a turbidity appears, and allowing to cool. Total yield about 23 grams.

Nitromannite is readily soluble in ether and in hot alcohol, only slightly soluble in cold alcohol, and insoluble in water.

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[64] Stenhouse, *Ann.*, **70**, 226 (1849); **130**, 302 (1864).

[65] Ger. Pat. 110,289 (1898); Brit. Pat. 27,397 (1898).

While its stability at ordinary temperatures is such that it can be used commercially, at slightly elevated temperatures it is distinctly less stable than nitroglycerin. Nitroglycerin will tolerate heating in a covered glass vessel for several days at 75° before it begins to give off acid fumes; nitroglycol, methylglycol dinitrate, and trimethylene glycol dinitrate are more stable yet, but nitromannite decomposes after a few hours and evolves red fumes. If a small quantity is heated, it decomposes at once at about 150° with copious evolution of nitrous fumes but ordinarily does not deflagrate. With larger samples deflagration occurs at 160–170°.

FIGURE 57. Nitromannite, Crystals from Alcohol (5×). (Courtesy Atlas Powder Company.)

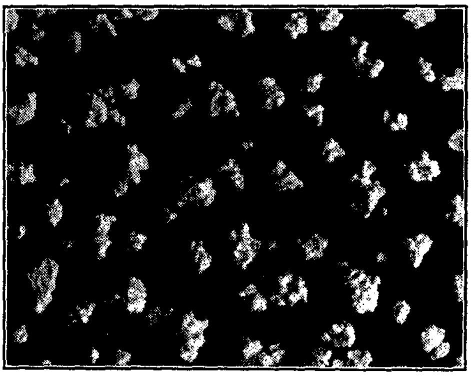

FIGURE 58. Nitromannite, in Grained Form for Charging Detonators (5×). (Courtesy Atlas Powder Company.)

Kast[66] has reported a velocity of detonation of 8260 meters per second for nitromannite compressed to a density of 1.73 in a column 12.8 mm. in diameter.

Nitromannite is about as sensitive as nitroglycerin to shock and to friction. It detonates under a 4-cm. drop of a 2-kilogram weight, and may be exploded readily on a concrete surface by a blow of a carpenter's hammer. It is not fired by the spit of a fuse, but is made to detonate by the flame of a match which causes local overheating. It is almost, but not quite, a primary explosive. It is used as the high-explosive charge in compound detonators which contain the relatively safe diazodinitrophenol as the primary explosive. A mixture of nitromannite and tetracene is a powerful and brisant primary explosive which detonates from moderate heat.

Nitrodulcite (Dulcitol hexanitrate)

Dulcite is obtained from Madagascar manna by extraction with water and recrystallizing, large monoclinic prisms, m.p. 188°, less soluble than mannite. It may also be procured by the action of sodium amalgam on aqueous solutions of lactose and of *d*-galactose. Nitrodulcite, isomeric with nitromannite, crystallizes from alcohol in needles which melt at 94–95°.

Nitrosorbite (Sorbitol hexanitrate)

d-Sorbite occurs in the berries of the mountain ash, but is more readily procured by the electrolytic reduction of *d*-glucose. It crystallizes with one molecule of water in small crystals which lose their water when heated and melt at about 110°. Nitrosorbite, isomeric with nitromannite, exists as a viscous liquid and has never been obtained in the crystalline state. It is used in nonfreezing dynamites.

Nitrated Sugar Mixtures

The sugars are polyhydric alcohols which contain an aldehyde or a ketone group or a cyclic acetal or ketal arrangement within the molecule. They yield nitric esters which are perhaps less stable than the nitric esters of the simple polyhydric alcohols but which probably owe part of their reputation for instability to the

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[66] *Z. angew. Chem.*, **36**, 74 (1923).

fact that they are difficult to purify. The nitrosugars resemble the sugars from which they are derived in the respect that often they do not crystallize rapidly and easily. When warmed gently, they frequently soften and become sticky and resinous. In this condition they retain within their masses traces of decomposition products by which further decomposition is provoked; they cannot be washed free from acid, and in the solid or semi-solid state are impossible to stabilize. The stabilization however may be accomplished easily if the nitrosugar is in solution.

A mixture of nitrosucrose and nitroglycerin, prepared by nitrating a solution of 20 parts of cane sugar in 80 parts of glycerin, or of 25 parts in 75, has been used in this country under the name of *nitrohydrene.* It is suitable for use in non-freezing dynamites, and is cheaper than nitroglycerin to the extent that sugar is cheaper than glycerin. The nitrated product is much more viscous than nitroglycerin and forms emulsions readily. It requires repeated washings with soda solution to insure a satisfactory heat test, and then washings with concentrated salt solutions to facilitate the separation of the phases. Nitrohydrene 80/20 (from 80 parts of glycerin and 20 parts of cane sugar) consists of about 86% nitroglycerin and 14% nitrosucrose, and nitrohydrene 75/25 of about 82% nitroglycerin and 18% nitrosucrose. Naoúm[67] reports the following data. The stability of nitrohydrene is distinctly poorer than that of nitroglycerin and appears to depend upon the proportion of nitrosucrose which it contains, for nitrohydrene 75/25 gives a poorer heat test than nitrohydrene 80/20 which contains less nitrosucrose. Naoúm[68] points out that the wood meal, etc., which is contained in dynamite made from nitrohydrene apparently acts as a stabilizer and

		LEAD BLOCK EXPANSION, 10-GRAM SAMPLE IN GLASS TUBE	
	SPECIFIC GRAVITY AT 20°	Sand Tamping, cc.	Water Tamping, cc.
Nitroglycerin	1.596	550	595
Nitrohydrene 80/20	1.605	533	560
Nitrohydrene 75/25	1.612	514	535

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[67] *Op. cit.,* p. 253.

[68] *Ibid.,* p. 255.

absorbs or reacts chemically with the first decomposition products and destroys them. He says:

> Better still, are very small additions of diphenylamine, which is admirably suited for the stabilization of smokeless powder, since it readily takes up the nitrous acid. Nitrohydrene 80/20 or 75/25, containing only 0.1 to 0.2 per cent of diphenylamine, was stored for seventy-five days at 55°C. without undergoing decomposition. The samples merely showed a coloration and became dark green, a phenomenon which also occurred but to a less extent with a check sample of nitroglycerin containing the same quantity of diphenylamine. After seventy-five days the nitroglycerin still had a slight odor of diphenylamine, but the nitrohydrene smelled slightly acid, somewhat like sour milk, but not like nitrous or nitric acid.
>
> Similar samples of 100 grams each of the above nitrohydrene containing 0.1 per cent diphenylamine have been stored by the author for more than eight years in diffuse daylight at room temperatures, about 20°C. So far they have remained unchanged, have no acid odor, and show no signs of decomposition. . . . From this it is evident that nitrosugar dissolved in nitroglycerin, although its stability does not reach that of the latter, is sufficiently stable for practical purposes, particularly in the presence of stabilizers.

The individual nitrosugars are stabilized similarly by diphenylamine, and certain ones of them, specifically nitromaltose, nitrolactose, and nitrosucrose, have been able by means of that substance to find a limited industrial application.

Solutions of cane sugar in glycol, and of glucose and lactose in glycerin, have been nitrated to produce mixtures of nitric esters comparable to nitrohydrene.

Nitroarabinose (*l*-Arabinose tetranitrate), $C_5H_6O(ONO_2)_4$

Nitroarabinose is prepared,[69] as indeed the highly nitrated sugars in general may be prepared, by adding concentrated sulfuric acid drop by drop to a solution of the corresponding sugar in concentrated nitric acid at 0°. It consists of colorless monoclinic crystals which melt at 85° and decompose at 120°. It is readily soluble in alcohol, acetone, and acetic acid, and insoluble in water and ligroin. It reduces Fehling's solution on warming. It is but little stable above 50°, and is easily exploded by shock.

[69] Will and Lenze, *Ber.*, 31, 68 (1898).

Nitroglucose (*d*-Glucose pentanitrate), $C_6H_7O(ONO_2)_5$

d-Glucose pentanitrate[69] is a colorless viscous syrup, insoluble in water and in ligroin, readily soluble in alcohol. It becomes hard at 0°. It is unstable above 50°, and if heated slowly to a higher temperature decomposes rapidly at about 135°. It reduces Fehling's solution on warming. *Glucosan trinitrate,* $C_6H_7O_2(ONO_2)_3$, is produced by the nitration of α-glucosan and by the action for several days of mixed acid on *d*-glucose. It is readily soluble in alcohol and insoluble in water. It has been obtained in the form of aggregates or crusts of crystals which melted not sharply at about 80° and which were probably not entirely free from glucose pentanitrate.

Nitromannose (*d*-Mannose pentanitrate), $C_6H_7O(ONO_2)_5$

d-Mannose pentanitrate,[69] transparent rhombic needles from alcohol, melts at 81–82° and decomposes at about 124°. It is soluble in alcohol and insoluble in water and reduces Fehling's solution slowly on warming. It undergoes a rapid decomposition if stored at 50°.

Nitromaltose (Maltose octonitrate), $C_{12}H_{14}O_3(ONO_2)_8$

Maltose octonitrate,[69, 70] glistening needles from methyl alcohol, melts with decomposition at 164–165°. If heated quickly, it puffs off at 170–180°. It decomposes slowly at 50°. If fused and allowed to solidify, it has a specific gravity of 1.62. It is readily soluble in methyl alcohol, acetone, and acetic acid, difficultly soluble in ethyl alcohol, and insoluble in water. It reduces warm Fehling's solution more rapidly than nitrosucrose.

Nitrolactose (Lactose octonitrate), $C_{12}H_{14}O_3(ONO_2)_8$

Lactose octonitrate,[69, 71] monoclinic needles from methyl or ethyl alcohol, melts at 145–146° with decomposition. Its specific gravity is 1.684. It is readily soluble in methyl alcohol, hot ethyl alcohol, acetone, and acetic acid, difficultly soluble in cold ethyl alcohol, and insoluble in water. It reduces Fehling's solution on warming.

[70] Pictet and Vogel, *Helv. Chim. Acta,* **10,** 588 (1927).
[71] Gé, *Ber.,* **15,** 2238 (1882).

Lactose hexanitrate, $C_{12}H_{16}O_5(ONO_2)_6$, has been found in the alcoholic mother liquors from the crystallization of the octonitrate, white, amorphous material melting not sharply at about 70°.

Crater[72] in 1934 described explosives containing nitrolactose, one consisting, say, of nitrolactose 25%, ammonium nitrate 65%, sodium nitrate 6%, and vegetable absorbent material 4%, another made by treating wood pulp with an acetone solution of nitrolactose and dinitrotoluene and containing about 78% nitrolactose, about 9% DNT, and about 13% wood pulp. For this use the nitrolactose ought to be stabilized with diphenylamine.

Nitrosucrose (Sucrose octonitrate), $C_{12}H_{14}O_3(ONO_2)_8$

The nitration of cane sugar[69, 73] yields sucrose octonitrate, white glistening needles, which melt at 85.5°. If heated slowly, nitrosucrose decomposes at about 135° and if heated rapidly deflagrates at about 170°. The fused and solidified material has a specific gravity of 1.67. It is readily soluble in methyl alcohol, ether, and nitrobenzene, difficultly soluble in ethyl alcohol and benzene, and insoluble in water and in petroleum ether. It reduces Fehling's solution on warming. It is relatively stable when pure. Monasterski reports that it gives a feeble puff under a 20-cm. drop of a 2-kilogram weight, a puff with one of 25 cm., and a detonation with one of 30 cm. He states that samples of 10 grams in the Trauzl test gave average net expansions of 296 cc.

Other Nitrosugars

The nitration of *d*-xylose[69] yields *d-xylose tetranitrate,* $C_5H_6O(ONO_2)_4$, an oily substance insoluble in water, and a crystalline by-product, m.p. 141°, insoluble in water, which is evidently the *trinitrate,* $C_5H_7O_2(ONO_2)_3$. *Xylosan dinitrate,* $C_5H_6O_2(ONO_2)_2$, has been prepared by the action of mixed acid on *d*-xylose. It consists of little spherical crystal aggregates, soluble in alcohol and melting at 75–80°.

l-Rhamnose tetranitrate,[69] $C_6H_8O(ONO_2)_4$, crystallizes in compact short rhombs which melt with decomposition at 135°. It is

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[72] U. S. Pat. 1,945,344 (1934).

[73] Hoffman and Hawse, *J. Am. Chem. Soc.*, 41, 235 (1919). Monasterski, *Z. ges. Schiess- u. Sprengstoffw.*, 28, 349 (1933). Wyler, U. S. Pats. 2,081,161 (1938), 2,105,390 (1938), 2,165,435 (1939).

readily soluble in acetone, acetic acid, and in methyl and ethyl alcohol, and is relatively stable. It reduces Fehling's solution on warming. *l-Rhamnose trinitrate,*[74] $C_6H_9O_2(ONO_2)_3$, results from the action of mixed acid on *l*-rhamnose. It is a white amorphous material, melting below 100°, readily soluble in alcohol and insoluble in water. It explodes feebly under a hammer blow.

α-Methylglucoside tetranitrate,[69] $C_7H_{10}O_2(ONO_2)_4$, crystallizes from alcohol in quadrilateral plates which melt at 49–50° and decompose at 135°. It is more stable than the nitrate of the free sugar. It reduces Fehling's solution slowly on warming.

α-Methylmannoside tetranitrate,[69] $C_7H_{10}O_2(ONO_2)_4$, from the nitration of *d*-*α*-methylmannoside, crystallizes in fine asbestos-like needles which melt at 36°. It is relatively stable at 50°.

d-Galactose pentanitrate α, $C_6H_7O(ONO_2)_5$, from the nitration of *d*-galactose[69] crystallizes in bundles of transparent needles which melt at 115–116° and decompose at 126°. It is sparingly soluble in alcohol. It decomposes slowly at 50°, and reduces Fehling's solution slowly on warming. The alcoholic mother liquors from the *α*-form yield *d-galactose pentanitrate β,* transparent monoclinic needles which melt at 72–73° and decompose at 125°. This substance is readily soluble in alcohol, decomposes rapidly at 50°, and reduces hot Fehling's solution. *Galactosan trinitrate,* $C_6H_7O_2(ONO_2)_3$, results from the action during several days of mixed acid on *d*-galactose. It is deposited from alcohol in crusts of small crystals.

Fructosan trinitrate α, $C_6H_7O_2(ONO_2)_3$, is produced by the action of mixed acid at 0–15° on *d*-fructose or on laevulosan,[75] colorless, quickly effluorescing needles from alcohol, which melt at 139–140° and decompose at about 145°. It is readily soluble in methyl and ethyl alcohol, acetic acid, and acetone, and insoluble in water. It is relatively stable at 50°. It reduces hot Fehling's solution. The alcoholic mother liquors from the *α*-form yield *fructosan trinitrate β,* crusts of white crystals which melt at 48–52° and decompose at 135°. The material decomposes slowly at 50°. It reduces Fehling's solution rapidly on warming.

The action of mixed acid on *d*-sorbose at 15° yields *sorbosan trinitrate,* $C_6H_7O_2(ONO_2)_3$, a crystalline substance which melts not sharply at 40–45°.

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[74] Hlasiewetz and Pfaundler, *Ann.,* **127,** 362 (1863).

[75] Pictet and Reilly, *Helv. Chim. Acta,* **4,** 613 (1921).

d-α-Glucoheptose hexanitrate, $C_7H_8O(ONO_2)_6$, from the nitration of *d*-α-glucoheptose,[69] crystallizes from alcohol in transparent needles which melt at 100°. It reduces Fehling's solution on warming.

Trehalose octonitrate, $C_{12}H_{14}O_3(ONO_2)_8$, from the nitration of trehalose,[69] crystallizes from alcohol in birefringent pearly leaflets which melt at 124° and decompose at 136°. It reduces Fehling's solution on warming.

Raffinose hendecanitrate, $C_{18}H_{21}O_5(ONO_2)_{11}$, from the nitration of raffinose,[69] exists in the form of amorphous aggregates which melt at 55–65° and decompose at 136°. It reduces Fehling's solution on warming. It decomposes rapidly when kept at 50°.

α-Tetraamylose octonitrate, $[C_6H_8O_3(ONO_2)_2]_4$, from α-tetraamylose,[76] crystallizes from acetic acid in fine glistening needles which decompose at 204°. It is readily soluble in ethyl acetate, amyl acetate, pyridine, and nitrobenzene, and sparingly soluble or insoluble in alcohol, ether, benzene, and water. *α-Diamylose hexanitrate,*[76] $[C_6H_7O_2(ONO_2)_3]_2$, prepared from α-diamylose or as the final product of the nitration of tetraamylose, crystallizes from acetone in plates which puff off at 206–207°. It is difficultly soluble in acetic acid, and is reported to be but little stable. The alcohol extract of the crude hexanitrate yields a certain amount of the amorphous *tetranitrate.*[76] *β-Triamylose hexanitrate,*[76] $[C_6H_8O_3(ONO_2)_2]_3$, is procured by dissolving either β-triamylose or β-hexaamylose in strong nitric acid at 0° and adding concentrated sulfuric acid drop by drop, and extracting the crude product with alcohol. It crystallizes from the alcoholic extract in aggregates of microscopic cubes, m.p. 203°. The residue which is insoluble in hot alcohol is recrystallized from acetic acid and yields crystalline crusts of *β-triamylose enneanitrate,*[76] $[C_6H_7O_2(ONO_2)_3]_3$, m.p. 198°.

Early History of Nitrated Carbohydrates

The history of modern explosives commenced with the discoveries of nitroglycerin and of nitrocellulose. At about the time that Sobrero first prepared nitroglycerin, Schönbein at Basel and Böttger at Frankfort-on-the-Main independently of each other nitrated cotton, perceived the possibilities in the product, and

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[76] Leibowitz and Silmann, *Ber.*, **58**, 1889 (1925).

soon cooperated with each other to exploit its use in artillery. Pelouze had nitrated paper at an earlier time, and the question may indeed be raised whether he was not the first discoverer of nitrocellulose. Before that, Braconnot, professor of chemistry at Nancy, had prepared a nitric ester from starch. The principal events in the early history of these substances are summarized below.[77]

1833. Braconnot[78] found that starch dissolved in concentrated nitric acid and that the liquid on dilution with water gave a curdy precipitate of material which, after washing, dried out to a white, pulverulent, tasteless, and neutral mass. The product gave a brown color with a solution of iodine. It was not affected by bromine. It did not dissolve in boiling water but softened to a sticky mass. Dilute sulfuric acid did not affect it. Concentrated sulfuric acid dissolved it, and the solution gave no precipitate if it was diluted with water. The material, to which Braconnot gave the name of *xyloïdine,* dissolved in acetic acid very readily on heating, and the solution, if evaporated slowly, gave a transparent film which retained its transparency when placed in water. Applied to paper or cloth it yielded a brilliant, varnish-like coating which was impervious to water. Xyloïdine took fire very readily. It carbonized and liquefied if heated upon a piece of cardboard or heavy paper while the cardboard or paper, though exposed directly to the heat, was not appreciably damaged. Sawdust, cotton, and linen yielded products which Braconnot considered to be identical with the xyloïdine from starch.

1838. Pelouze[79] studied xyloïdine further. He found that if starch was dissolved in concentrated nitric acid and if the solution was diluted immediately with water, xyloïdine precipitated and the acid filtrate on evaporation yielded practically no residue. If the solution of starch in nitric acid was allowed to stand before being precipitated with water, then the amount of xyloïdine was less. If it was allowed to stand for 2 days, or perhaps only for some hours, the xyloïdine was entirely destroyed, a new acid was formed, no precipitate appeared when the solution was diluted,

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[77] The papers which are cited in this connection have been published in English in the book by George W. MacDonald, "Historical Papers on Modern Explosives," Whittaker & Co., London and New York, 1912.

[78] *Ann. chim. phys.,* [2] 52, 290 (1833).

[79] *Compt. rend.,* 7, 713 (1838).

and the liquid on evaporation gave the new acid in the form of a solid, white, non-crystalline, deliquescent mass of considerably greater weight than the starch which was taken for the experiment. Neither carbon dioxide nor oxalic acid was produced during the reaction, but the new acid on long standing, or on boiling, with nitric acid was converted to oxalic acid without the formation of carbon dioxide. Pelouze considered xyloïdine to be a nitrate of starch. He observed that it was readily combustible, that it ignited at a temperature of 180° and burned with very considerable violence leaving practically no residue. The observation, he says, led him to make certain experiments which, he believed, might have practical application in artillery. Paper, dipped into nitric acid of specific gravity 1.5 and left there long enough for the acid to penetrate into it (generally 2 or 3 minutes), removed, and washed thoroughly, gave a parchment-like material which was impervious to moisture and was extremely combustible. Pelouze had nitrocellulose in his hands, but evidently did not recognize that the material, which had not changed greatly in its physical form, was nevertheless nitrated through-

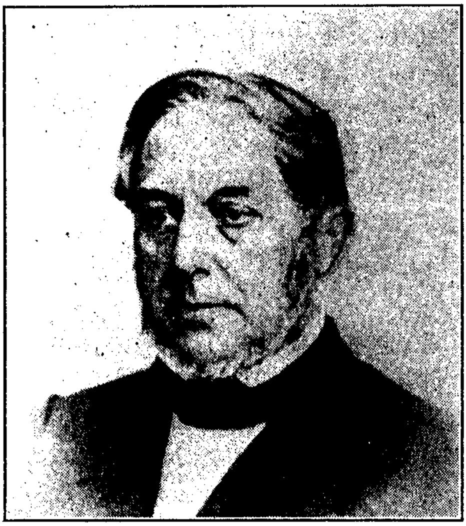

FIGURE 59. Théophile-Jules Pelouze (1807-1867). (Courtesy E. Berl.) Made many important contributions to organic and inorganic chemistry—ethereal salts, the first nitrile, borneol, glyceryl tributyrate, pyroxylin, improvements in the manufacture of plate glass. He nitrated paper in 1838 and was thus probably the first to prepare nitrocellulose. Reproduced from original in Kekulé's portrait album.

out its mass, for he believed that the products which he obtained from paper and from cotton and linen fabrics owed their new properties to the xyloïdine which covered them.

1846. Schönbein announced his discovery of guncotton at a meeting of the Society of Scientific Research at Basel on May 27, 1846. In an article, probably written in 1847 but published in the *Archives des sciences physiques et naturelles* of 1846, he described some of his experiences with the material and his efforts to put it to practical use and discussed the controversial question of priority of discovery; he described the nitration of cane sugar but deliberately refrained from telling how he had prepared his nitrocellulose. He was led to perform the experiments by certain theoretical speculations relative to ozone which he had discovered a few years before. One volume of nitric acid (1.5) and 2 volumes of sulfuric acid (1.85) were mixed and cooled to 0°, finely powdered sugar was stirred in so as to form a paste, the stirring was continued, and after a few minutes a viscous mass separated from the acid liquid without the disengagement of gas. The pasty mass was washed with boiling water until free from acid, and was

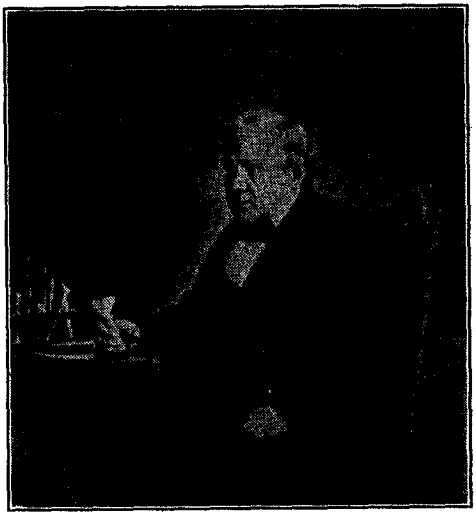

FIGURE 60. Christian Friedrich Schönbein (1799-1868). (Courtesy E. Berl.) Discovered guncotton, 1846. Discovered ozone, worked on hydrogen peroxide, auto-oxidation, the passivity of iron, hydrosulfites, catalysts, and prussic acid. Professor of Chemistry at Basel from 1829 until the time of his death. He published more than 300 papers on chemical subjects. Reproduced from original in Kekulé's portrait album.

dried at a low temperature. The product was brittle at low temperatures, could be molded like jalap resin at slightly elevated ones, was semi-fluid at 100°, and at high temperatures gave off red fumes. When heated more strongly, it deflagrated suddenly and with violence. Schönbein also experimented with other organic substances, and states that in experiments carried out during December, 1845, and the first few months of 1846 he discovered, one after another, all those substances about which so much had lately been said in the French Academy. In March he sent specimens of the new compounds, among them guncotton, to several of his friends, notably, Faraday, Herschel, and Grove.

About the middle of April, 1846, Schönbein went to Württemberg where he carried out experiments with guncotton at the arsenal at Ludwigsburg in the presence of artillery officers and at Stuttgart in the presence of the king. During May, June, and July he experimented at Basel with small arms, mortars, and cannon. On July 28 he fired for the first time a cannon which was loaded with guncotton and with a projectile. Shortly afterward he used guncotton to blast rocks at Istein in the Grand Duchy of Baden and to blow up some old walls in Basel.

In the middle of August Schönbein received news from Professor Böttger of Frankfort-on-the-Main that he too had succeeded in preparing guncotton, and the names of the two men soon became associated in connection with the discovery and utilization of the material. There were, moreover, several other chemists who at about the same time, or within a few months, also worked out methods of preparing it. In a letter[80] to Schönbein dated November 18, 1846, Berzelius congratulated him on the discovery as interesting as it was important, and wrote, "Since Professor Otto of Brunswick made known a method of preparing the guncotton, this discovery has perhaps occupied a greater number of inquisitive persons than any other chemical discovery ever did. I have likewise engaged in experiments upon it."

In August Schönbein went to England where, with the help of the engineer Richard Taylor of Falmouth, he carried out experiments with guncotton in the mines of Cornwall. He also demonstrated his material successfully with small arms and with artillery at Woolwich, at Portsmouth, and before the British

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[80] MacDonald, *op. cit.*, pp. 47, 48.

Association. He did not apply for an English patent in his own name but communicated his process to John Taylor of Adelphi, Middlesex, who was granted English patent 11,407, dated October 8, 1846, for "Improvements in the Manufacture of Explosive Compounds, communicated to me from a certain foreigner residing abroad."[81] He entered into an agreement for three years with Messrs. John Hall & Sons of Faversham that they should have the sole right in England to manufacture guncotton by his process and in return should pay him one-third of the net profit with a minimum of £1000 down and the same each year. The first factory for the manufacture of guncotton was erected at Faversham. On July 14, 1847, within less than a year, the factory was destroyed by an explosion with the loss of twenty-one lives. After this, Messrs. John Hall & Sons refused to continue the manu-

FIGURE 61. Rudolf Böttger (1806-1887). (Courtesy E. Berl.) Professor at Frankfort-on-the-Main. Discovered guncotton independently of Schönbein but somewhat later, in the same year, 1846. He also invented matches, and made important studies on the poisoning of platinum catalysts. Reproduced from original in Kekulé's portrait album.

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[81] *Ibid.*, pp. 42–44.

facture. About the same time disastrous guncotton explosions occurred at Vincennes and at Le Bouchet, and these produced such an unfavorable effect that no more guncotton was manufactured in England or in France for about sixteen years.

Schönbein offered his process to the Deutscher Bund for 100,000 thalers, and a committee was formed to consider the matter, Liebig representing the state of Hesse and Baron von Lenk, who was secretary, representing Austria. The committee continued to sit until 1852 when it finally decided to take no action. At the suggestion of von Lenk, Austria then acquired the process for 30,000 gulden.

1846. The *Comptes rendus* of 1846 contains several papers on the nitration of cellulose, which papers were presented to the French Academy before the details of Schönbein's process were yet known. Among these, the papers by Dumas and Pelouze are especially interesting. Dumas [82] stated that certain details of the manufacture of guncotton had already been published in Germany. Professor Otto of Brunswick dipped the cotton for half a minute in concentrated fuming nitric acid, pressed between two pieces of glass, washed until free from acid, and afterwards dried.

> The explosive property can be considerably increased by several dippings, and I have found that a product of extreme force is obtained after an immersion of 12 hours. A point of extreme importance is the care which ought to be exercised in washing the cotton. The last traces of acid are very difficult to remove, and should any remain it will be found that, on drying, the substance smells strongly of oxides of nitrogen, and when ignited also produces a strong acid smell. The best test of a sample of guncotton is to ignite it upon a porcelain plate. Should it burn slowly, leaving a residue upon the plate, it must be considered as unsatisfactory. A good guncotton burns very violently without leaving any residue. It is also of very great importance that when the guncotton is withdrawn from the acid, it should be washed immediately in a large quantity of water. Should small quantities of water be used it will be found that the guncotton becomes very hot, and that spots of a blue or green color are produced, which are very difficult to remove, and the guncotton is very impure.

Dr. Knopp of the University of Leipzig used a mixture of equal parts of concentrated sulfuric and nitric acids, and immersed the

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[82] *Compt. rend.*, 806 (1846); MacDonald, *op. cit.*, pp. 15-17.

cotton in it for several minutes at ordinary temperature. Dumas stated that satisfactory guncotton could be obtained without observing any great exactitude in the proportion of the two acids or in the duration of the immersion. Dr. Bley of Bernberg had discovered that sawdust, treated in the same way as cotton, yielded an explosive which, he believed, might replace gunpowder in firearms and in blasting.

1846. Pelouze [83] made clear distinction between xyloïdine and guncotton. "I shall call *pyroxyline* or *pyroxyle* the product of the action of monohydrated nitric acid on cotton, paper, and ligneous substances, when this action has taken place without having caused the solution of the cellulose." Braconnot in 1833 had prepared xyloïdine from starch; Pelouze had prepared pyroxylin in 1838. He pointed out that xyloïdine dissolves readily in strong nitric acid and, in the course of a day, is destroyed by it and converted to a deliquescent acid. Pyroxylin does not dissolve in concentrated nitric acid. Xyloïdine is very inflammable and explodes when struck, but it leaves a considerable residue of carbon when heated in a retort and may be analyzed like an ordinary organic substance by heating with copper oxide. Pyroxylin explodes when heated to 175° or 180° and cannot be distilled destructively. Pelouze found that 100 parts of starch, dissolved in nitric acid and precipitated immediately, yielded at most 128 to 130 parts of xyloïdine. One hundred parts of cotton or paper, after a few minutes' or after several days' immersion in concentrated nitric acid, yielded 168 to 170 parts of washed and dried pyroxylin. The acid mother liquors, both from the nitration of the starch and from the nitration of the cotton, contained not more than mere traces of organic matter.

1846. Schönbein's process soon became known through the publication of the English patent to John Taylor (cited above). He carried out the nitration by means of a mixture of 1 volume of strong nitric acid (1.45 to 1.5) and 3 volumes of strong sulfuric acid (1.85). The cotton was immersed in this acid at 50–60°F. for 1 hour, and was then washed in a stream of running water until free from acid. It was pressed to remove as much water as possible, dipped in a very dilute solution of potassium carbonate (1 ounce to the gallon), and again pressed as dry as possible.

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[83] *Ibid.*, 809, 892 (1846); MacDonald, *op. cit.*, pp. 17–20.

It was then rinsed with a very dilute solution of potassium nitrate (1 ounce to the gallon). The patent states that "the use of this solution appears to add strength to the compound, but the use of this solution and also potassium carbonate are not essential and may be dispensed with." The product is pressed, opened out, and dried at 150°F., and when dried it is fit for use. The patent also covers the possibility of using instead of cotton "other matters of vegetable origin and the possibility of carrying out the nitration with nitric acid alone or with mixed acids of inferior strength."

1846. Teschemacher[84] studied the preparation of guncotton and demonstrated that no sulfuric acid is consumed by the reaction.

1847. Gladstone[85] by exercising special precautions was able to carry out combustion analyses of xyloïdine and of pyroxylin prepared according to the directions of Schönbein. Nitrogen was determined by the differential method. The pyroxylin was found to contain 12.75% nitrogen and was thought to correspond to a pentanitrate while the xyloïdine corresponded more nearly to a trinitrate.

1847. Crum[86] nitrated cotton until he could introduce no further nitrogen into the molecule, and analyzed the product for nitric acid by the method which is used in the nitrometer. His result calculated as nitrogen gives a figure of 13.69%. It is interesting to note that Crum's cotton was "bleached by boiling in caustic soda and put in a solution of bleaching powder; then caustic soda again, and afterwards weak nitric acid. It was well washed and beaten in a bag with water after each operation. . . . The cotton, dried and carded after bleaching, was exposed in parcels of 10 grains each for several hours to the heat of a steam bath, and each parcel was immersed, while hot, into a 1 oz. measure of the following mixture: Sulphuric acid (1.84) 1 measure, and 3 measures of pale lemon-colored nitric acid (1.517). After one hour it was washed in successive portions of water until no trace of acid remained, and was then dried in the open air"—or, for analysis, was dried completely in a vacuum desiccator over sulfuric acid.

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[84] *Mem. of the Chem. Soc.*, 253 (1846); MacDonald, *op. cit.*, pp. 28–31.

[85] *Ibid.*, 412 (1847); MacDonald, *op. cit.*, pp. 31–41.

[86] *Proc. Phil. Soc. Glasgow*, 163 (1847); MacDonald, *op. cit.*, pp. 21–27.

1852. The Austrian government acquired the use of Schönbein's process (as mentioned above) and the Emperor of Austria appointed a committee to investigate the use of guncotton for military purposes. This committee, of which von Lenk was the leading spirit, continued to function with some interruptions until 1865. In 1853 a factory was erected at Hirtenberg for the manufacture of guncotton by the method of von Lenk which involved a more elaborate purification than Schönbein's original process. The product was washed for 3 weeks, then boiled with dilute potassium carbonate solution for 15 minutes, washed again for several days, impregnated with water glass, and finally dried. Von Lenk constructed 12-pounder guns which were shot with guncotton cartridges, but they were much damaged by the firing. About 1860 he tried bronze guns, which were less likely to burst than iron ones, and with propelling charges of guncotton fired from them shells which were filled with bursting charges of guncotton. The shells often burst within the barrel, for the acceleration produced by the propelling charge of guncotton was much too sudden and shocking. They could be shot out without exploding when a propelling charge of black gunpowder was used. On July 20, 1863, the magazine at Hirtenberg exploded, and the Austrian government thereupon decided to abandon the use of guncotton as a propellent explosive. Von Lenk was permitted to communicate his process to other nations. In 1862 and 1863, under the name of Révy, he took out English patents to protect his method of purification.[87] In 1863 he visited England and described his process to a committee of the British Association. In the same year Messrs. Prentice and Co. commenced the manufacture of guncotton at Stowmarket by von Lenk's process, but an explosion soon occurred at their establishment. In 1865 a guncotton magazine at Steinfelder Heath, near Vienna, exploded, and on October 11 of that year the manufacture of guncotton in Austria was officially forbidden.

1862. Tonkin's English patent [88] deserves our notice because it mentions the pulping of guncotton—and it was the pulping of guncotton, introduced later by Abel, which remedied in large measure the difficulties of stability which had given guncotton a bad repute and brought it back again to the favorable con-

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[87] Brit. Pats. 1090 (1862), 2720 (1863).

[88] Brit. Pat. 320 (1862); MacDonald, *op. cit.*, p. 44.

sideration of the users of explosives. The patent describes the nitration of the cotton with mixed acid, the washing with running water, the pressing, and the dipping in a very dilute solution of potassium carbonate. "The fibre is then taken in the wet state and converted into pulp in the same manner as is practiced by paper-makers, by putting the fibre into a cylinder, having knives revolving rapidly, working close to fixed knives." The patent makes no claim to the pulping of guncotton, but only claims the use of pulped guncotton in an explosive consisting of sodium nitrate 65%, charcoal 16%, sulfur 16%, and guncotton pulp 3%.

1865. Abel's patent[89] for "Improvements in the Preparation and Treatment of Guncotton" claims the pulping and the pressing of it into sheets, discs, cylinders, and other forms and was probably designed to cover the process of getting it into a state where it would burn less violently in the gun. The compressed blocks were an improvement over the yarn of von Lenk, but they were still much too fast; they damaged the guns and were not ballistically uniform in performance. The blocks of compressed guncotton, however, have continued to find use in blasting. And the outstanding advantage of Abel's pulping was that it converted the guncotton into a state where the impurities were more easily washed out of it, and resulted thereby in a great improvement in stability.

1866–1867. Abel's "Researches on Guncotton"[90] demonstrated that guncotton, after proper purification, is far more stable than it had been thought to be. Moisture does not harm it, or exposure to sunlight, and it decomposes only slowly at elevated temperatures; the principal cause of its decomposition is acid, and this is removed by the pulping. Abel wrote:

> In reducing the material to a very fine state of division by means of the ordinary beating and pulping machines, the capillary power of the fibre is nearly destroyed, and the guncotton is, for a considerable period, very violently agitated in a large volume of water. It would be very difficult to devise a more perfect cleansing process than that to which the guncotton is submitted; and the natural result of its application is that the material thus additionally purified acquires considerably increased powers of resisting the de-

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[89] Brit. Pat. 1102 (1865); MacDonald, *op. cit.*, pp. 45-46.

[90] *Loc. cit.*

> structive effects of heat. Samples of the pulped guncotton, even in the most porous conditions, have been found to resist change perfectly upon long-continued exposure to temperatures which developed marked symptoms of decomposition in the guncotton purified only as usual. The pulping process applied to guncotton affords, therefore, important additional means of purifying the material, the value of which may be further enhanced by employing a slightly alkaline water in the pulping machine. The slightest change sustained by guncotton is attended by the development of free acid, which, if it accumulates in the material, even to a very trifling extent, greatly promotes decomposition.
>
> Numerous experimental data have been collected with respect to the establishment and acceleration of decomposition in guncotton by free acid whilst exposed to light or elevated temperature. This acid is present either in the imperfectly purified material or has been developed by decomposition of guncotton or its organic impurities. Samples of guncotton which, by exposure to elevated temperatures or for considerable periods to strong daylight, had sustained changes resulting in a considerable development of acid, have afterwards been thoroughly purified by washing. When exposed to light for months, and in some instances for two or three years (up to the present time), they have undergone no further change, while corresponding samples confined in close vessels without being purified, have continued, in some instances, to undergo decomposition, and the original substance has been completely transformed into the products repeatedly spoken of.

Abel found that the guncotton regularly produced at Waltham Abbey contained a small amount of material soluble in ether-alcohol, an average amount of 1.62% in the guncotton which was made by treating cotton with 18 times its weight of mixed acid, and an average of 2.13% in the guncotton which was made by the use of 10 parts of acid. "The employment of the higher proportion of acid furnished results more nearly approaching perfection than those obtained when the guncotton was left in contact with a smaller proportion of the acid mixture. As far as can be judged at present, however, from the general properties of the products, the difference observed when the larger or the smaller proportion of acid is used, is not of sufficient importance to render necessary the consumption of the larger quantity of acid in the manufacture." Abel was able to carry out satisfactory combustion analyses, with the following average results:

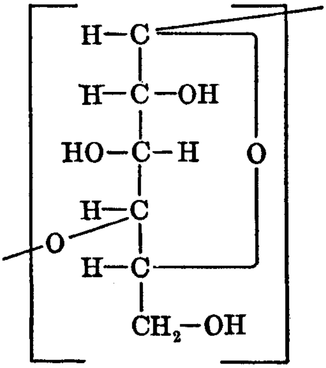
Material soluble in ether-alcohol, C 30.50%; H 2.91%; N 11.85%;
Material insoluble in ether-alcohol, C 24.15%; H 2.46%; N 13.83%.

He concluded that the different analytical results which had been procured with different samples of guncotton resulted from the samples containing different amounts of the ether-alcohol soluble material, and judged that completely nitrated guncotton is the trinitrate of cellulose, $[C_6H_7O_2(ONO_2)_3]_n$, as had been first suggested by Crum. This substance contains theoretically 14.14% nitrogen.

1868. E. A. Brown, assistant to Abel, discovered[91] that dry compressed guncotton could be made to detonate very violently by the explosion of a fulminate detonator such as Nobel had already used for exploding nitroglycerin. Shortly afterwards he made the further important discovery that wet guncotton could be exploded by the explosion of a small quantity of dry guncotton (the principle of the booster). This made it possible to use large blocks of wet guncotton in naval mines with comparative safety.

Nitrocellulose (NC)

Cellulose occurs everywhere in the vegetable kingdom; it is wood fiber and cell wall, the structural material of all plants. Cotton fiber is practically pure cellulose, but cellulose of equal purity, satisfactory in all respects for the manufacture of explosives and smokeless powder, may be produced from wood. Cellulose and starch both yield glucose on hydrolysis, and the molecules of both these substances are made up of anhydroglucose units linked together.



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[91] Brit. Pat. 3115 (1868).

The two substances differ in the configuration of the number 1 carbon atom. In cellulose this atom has the β-configuration; 2000 or 3000 anhydroglucose units are linked together in long, straight, threadlike masses which are essentially one dimensional. In starch the number 1 carbon atom has the α-configuration which leads to spiral arrangements essentially three dimensional, and the molecule contains not more than 25 or 30 anhydroglucose units.

Cellulose contains 3 hydroxyl groups per anhydroglucose unit, and yields a trinitrate on complete nitration (14.14% N). An absolutely complete nitration is difficult to secure, but a product containing 13.75% nitrogen may be produced commercially. If the conditions of nitration, concentration of acid, temperature, and duration of the reaction, are less severe, less nitrogen is introduced, and products ranging all the way from a few per cent of nitrogen upward, and differing widely in solubilities and viscosities, may be secured. In the cellulose nitrates which contain less than enough nitrogen to correspond to the trinitrate, the nitrate groups are believed to be distributed at random among the three possible positions, and no definite structural formulas can be assigned to the materials. Nor is it to be supposed that a sample which may correspond in empirical composition to cellulose mononitrate or dinitrate really represents a single chemical individual.

Collodion is a nitrocellulose which is soluble in ether-alcohol and contains, according to the use for which it is destined, from 8%, more or less, of nitrogen to 12% or thereabouts. The name of *pyroxylin* is now generally applied to collodion of low nitrogen content intended for use in pharmacy, in the making of lacquers or of photographic film, or intended in general for industrial uses outside of the explosives industry. In 1847 Maynard discovered that nitrocellulose existed which was soluble in a mixture of ether and alcohol although it would not dissolve in either of these solvents taken singly.[92] The discovery soon led to the invention of collodion photography by Archer in 1851. Chardonnet's first patent [93] for artificial silk was granted in 1884. *Celluloid,* made by dissolving collodion nitrocellulose in camphor with the use of

[92] After the material is dissolved, the solution may be diluted either with alcohol or with ether without precipitating.

[93] French Pat. 165,345 (1884).

heat and pressure, was patented by J. W. and I. S. Hyatt[94] in 1870. Worden[95] states that collodion for the manufacture of celluloid is made by nitrating tissue paper with a mixed acid which contains nitric acid 35.4%, sulfuric acid 44.7%, and water 19.9%. Twenty-two pounds of acid are used per pound of paper. The nitration is carried out at 55° for 30 minutes, and the product contains 11.0–11.2% nitrogen. Ether-alcohol solutions of collodion, to which camphor and castor oil have been added in order that they may yield tough and flexible films on evaporation, are used in pharmacy for the application of medicaments to the skin in cases where prolonged action is desired. Two per cent of salicylic acid, for example, in such a mixture makes a "corn remover." Collodion for use with nitroglycerin to make blasting gelatin is generally of higher nitrogen content. Here the desideratum is that the jelly should be stiff, and the higher nitrogen content tends in that direction, but the collodion dissolves in the nitroglycerin more slowly, and the product becomes stiffer on prolonged storage, and less sensitive, and may cause misfires. The nitrogen content of collodion for use in the manufacture of blasting explosives is generally between 11.5 and 12.0%. The official definition in England of collodion for this purpose gives an upper limit of 12.3% nitrogen.

Two kinds of nitrocellulose were used in France at the time of the first World War, *coton-poudre No. 1* (CP_1), insoluble in ether-alcohol and containing about 13% nitrogen, and *coton-poudre No. 2* (CP_2), soluble in ether-alcohol and containing about 12% nitrogen.[96] CP_1 thus contained a little less nitrogen than the material which we are accustomed to call guncotton, and CP_2 contained a little more than the material which we are accustomed to call collodion. CP_1 and CP_2 were not respectively wholly insoluble and wholly soluble in ether-alcohol; their compositions were approximate, and CP_2 always contained a certain amount of material soluble in alcohol alone. A mixture of CP_1 and CP_2 colloided with ether-alcohol was used for making *pou-*

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[94] U. S. Pat. 105,338 (1870).

[95] *J. Soc. Chem. Ind.*, 29, 540 (1910).

[96] The French are accustomed to report their analyses of nitrocellulose, not as per cent nitrogen, but as cubic centimeters of NO (produced in the nitrometer and measured under standard conditions) per gram of sample. Per cent nitrogen times 15.96 equals number of cubic centimeters of NO per gram of nitrocellulose.

dre B. Either CP_1 with nitroglycerin and an acetone solvent or both with nitroglycerin and an ether-alcohol solvent were used for making ballistite, and both of them with nitroglycerin and with non-volatile solvents were used in attenuated ballistite. CP_2 was also used in France for the manufacture of blasting gelatin.

Mendeleev studied the nitration of cellulose during the years 1891 to 1895 in an effort to prepare a nitrocellulose which should have the largest content of nitrogen (and hence the greatest explosive power) compatible with complete solubility in ether-alcohol. He produced *pyrocellulose* containing 12.60% nitrogen. Russia adopted a military smokeless powder made from pyrocellulose by colloiding with ether-alcohol, and the United States in 1898 was using a similar powder in the Spanish-American War.

The word *guncotton* has about the same meaning in English and in American usage, namely, nitrocellulose containing 13% or more of nitrogen, usually 13.2–13.4%, insoluble in ether-alcohol and soluble in acetone and in ethyl acetate. One American manufacturer prefers to call guncotton *high-grade nitrocellulose.*

Preparation of Pyrocellulose. Equal volumes of sulfuric acid (1.84) and nitric acid (1.42) are mixed by pouring the sulfuric acid with stirring into the nitric acid, and the mixture is allowed to cool to room temperature. Five grams of absorbent cotton, previously dried at 100° for 2 hours, is thrust quickly into 150 cc. of this mixed acid and allowed to remain there for 30 minutes while it is stirred occasionally with a glass rod. The cotton is removed, freed as much as possible from acid by pressing against the side of the vessel, and introduced quickly into a large beaker of cold water where it is stirred about in such manner as to accomplish the prompt dilution of the acid with which it is saturated. The product is washed thoroughly in running water, and boiled for an hour with distilled water in a large beaker, then boiled three times with fresh portions of distilled water for a half hour each time. If the water from the last boiling shows the slightest trace of acidity to litmus paper, the pyrocellulose ought to be rinsed and boiled once more with distilled water. Finally, the excess of water is wrung out, and the pyrocellulose is dried in a paper tray for 48 hours at room temperature.

Pyrocellulose is made commercially from purified cotton *linters* or *hull shavings* or wood cellulose, most commonly by the mechanical dipper process. The thoroughly dry cellulose is introduced into the mixed acid contained in an iron or stainless steel nitrator which is equipped with two paddles revolving vertically in opposite directions and designed to thrust the cotton quickly under the surface of the acid. For 32 pounds of cellulose a charge of about 1500 pounds of mixed acid is used. This contains approximately 21% nitric acid, 63% sulfuric acid, and 16% water. It may contain also a small amount, say 0.5%, of nitrous acid, NO_2 or N_2O_4, which, however, is calculated as being equivalent to a like amount of water and is not reckoned as any part of the *nitrating total* of actual nitric and sulfuric acids. The sulfuric acid content of the nitrating acid is kept as constant as possible in practice; the nitric acid content may vary somewhat, less than 1%, however, for slightly more nitric acid is necessary in warm weather to offset the tendency toward denitration which exists at that time. At the start the acid has a temperature of about 30°, the introduction of the cellulose requires about 4 minutes, and the nitration is continued for 20 minutes longer while the mixture is stirred mechanically with the paddles and the temperature is kept between 30° and 34°. When the nitration is complete, a valve in the bottom of the nitrator is opened and the slurry is allowed to run into a centrifuge on the floor below. Here the crude nitrocellulose is separated quickly from the spent acid which is fortified for use again or, in part, goes to the acid recovery plant. Wringer fires are by no means uncommon, especially on damp days, for the air which is sucked through the acid-soaked material in the centrifuge gives up its moisture to the strong acid and dilutes it with the development of considerable heat. The nitrated product is forked through an orifice in the bottom of the wringer and falls into an immersion basin below, where it is *drowned* by being mixed rapidly with a swiftly moving stream of water. Thence it proceeds on its way down the *guncotton line* where it is *stabilized* or purified and then prepared for shipment or for use.

The crude nitrocellulose contains certain amounts of cellulose sulfate, of nitrate of oxycellulose, and possibly of some cellulose nitrate which is less stable than the ordinary, all of which are capable of being hydrolyzed by long-continued boiling with slightly acidified water. Guncotton requires a longer stabilizing boil than pyrocellulose. After the boiling the acid is washed off and removed from the nitrocellulose, yielding a product which is now stabilized because it contains neither free acid nor component materials which are prone to decompose with the formation of acid.

The *preliminary boiling* or *sour boiling* is carried out in large wooden tubs heated by means of steam. At the beginning the nitrocellulose is boiled with water which contains 0.25% to 0.50% of acidity calculated as sulfuric acid. The first boil lasts usually for 16 hours during which time the acidity of the solution increases. The increase is due largely to actual sulfuric acid. After 16 hours the steam is shut off, the solution is decanted from the nitrocellulose, the tub is filled with fresh water, and the material is boiled again for 8 hours. The boiling is repeated until each tubful has been boiled for 40 hours with at least 4 changes of water.

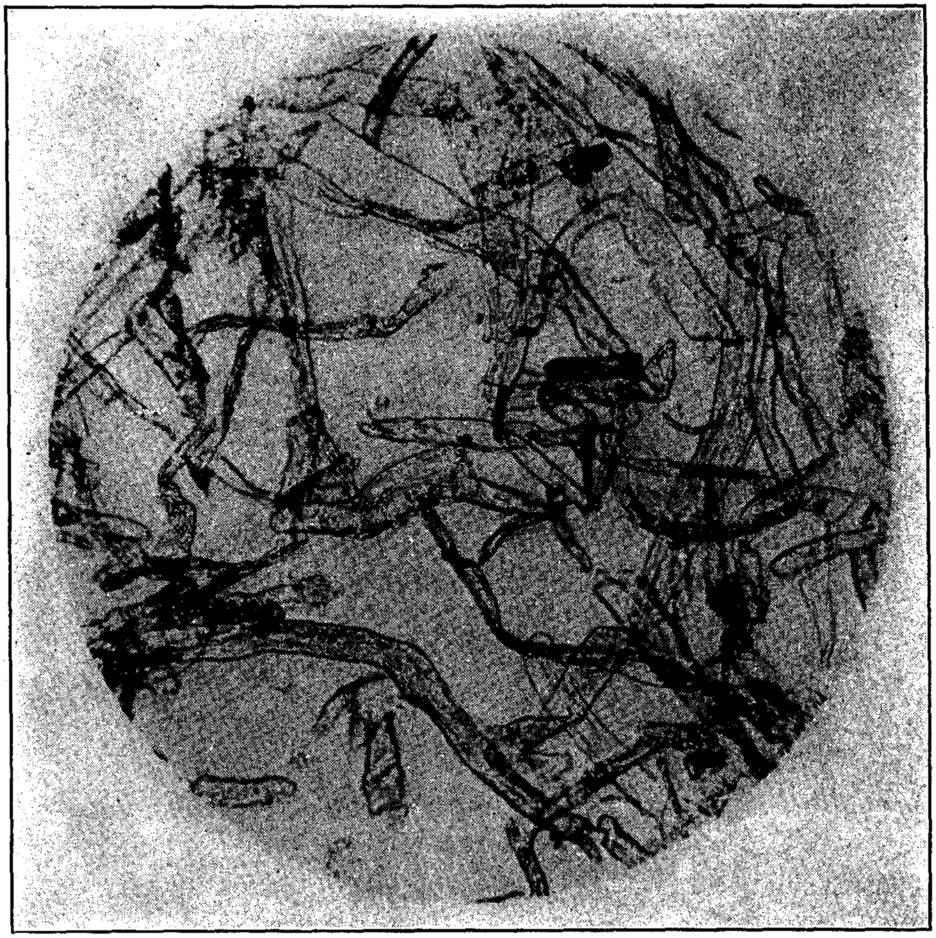

FIGURE 62. Nitrocellulose Fibers before Beating (132×). (Courtesy Western Cartridge Company.)

The hollow fibers still contain an acid solution within them. In order that this acid may be washed out, they are *pulped* or broken up into short lengths by means of apparatus like that which is used in the manufacture of paper. A Jordan mill cuts the fibers off rather sharply, leaving square ends, but a beater tears them, leaving ends which appear rough and shredded under the microscope and which result on the whole in the better opening up of the tubular fibers. The two machines are usually used in series. A weak solution of sodium carbonate is added during the pulping to neutralize the acid which is liberated. The pulping is continued until the desired fineness has been attained as shown by laboratory test.

FIGURE 63. Nitrocellulose Fibers after Beating (132×). (Courtesy Western Cartridge Company.)

The pulped fibers still retain acid adsorbed or occluded on their surface. This is removed by *poaching* the nitrocellulose, by boiling it again, first for 4 hours with fresh water with or without the addition of dilute sodium carbonate solution,[97] then for 2 hours with water without addition of soda, then twice with water for 1 hour each time. The material is then washed at least 8 times by thorough agitation with cold water, and by decantation each time of at least 40% of the liquid. After the washing, the material undergoes *screening,* where it passes through apertures 0.022 inch in width, *wringing,* whereby its moisture content is reduced to 26–28%, and finally *packing* for shipment or for storage in containers which are hermetically sealed.

Guncotton is made in substantially the same way as pyrocellulose except that a stronger mixed acid containing approximately 24% nitric acid, 67% sulfuric acid, and 9% water is used. Long-fiber high-grade guncotton is usually manufactured by the pot process and with the use of mixed acid which is nearly anhydrous. Iron pots are generally used. For the nitration of 4 pounds of dry cotton, 140 pounds of acid is introduced into the pot and the cotton is immersed in it, pressed down, and allowed to digest for 20 or 30 minutes. The contents of several pots are centrifuged at once, and the product is stabilized in the same way as pyrocellulose except that it is not pulped.

There can be no doubt that, in the standard method of stabilizing nitrocellulose, there are, among the results which the poaching accomplishes, at least some which would have been accomplished much earlier during the boiling if the material at that time had been pulped. This seems especially evident with respect to the hydrolysis of easily hydrolyzed material adjacent to the inner wall of the tubular fibers. Olsen,[98] discussing the standard method, has written, "The preliminary boiling tub treatment reduced the acidity of the fibers and of the interstitial material, but the pulping process, by macerating these fibers, has set free an additional amount of acid. It is, therefore, necessary to repurify the pyrocotton by boiling." He discovered that a marked reduction in time and in cost could be secured by carrying out the pulping operation prior to the hydrolyzing boils. If the pulping is done at

[97] Not more than 10 gallons of sodium carbonate solution (1 pound per gallon) for every 2000 pounds of nitrocellulose (dry weight).

[98] U. S. Pat. 1,798,270 (1931).

the outset, "less than half of the 16 hours sour boiling usually employed will suffice for obtaining the desired degree of purity when followed by alternating boils in fresh water and washes with cold fresh water, again less than half of the amount of boiling being sufficient." With less than 20 hours total time of purification, he obtained results as good as are ordinarily procured by the 52 hours of the standard method.

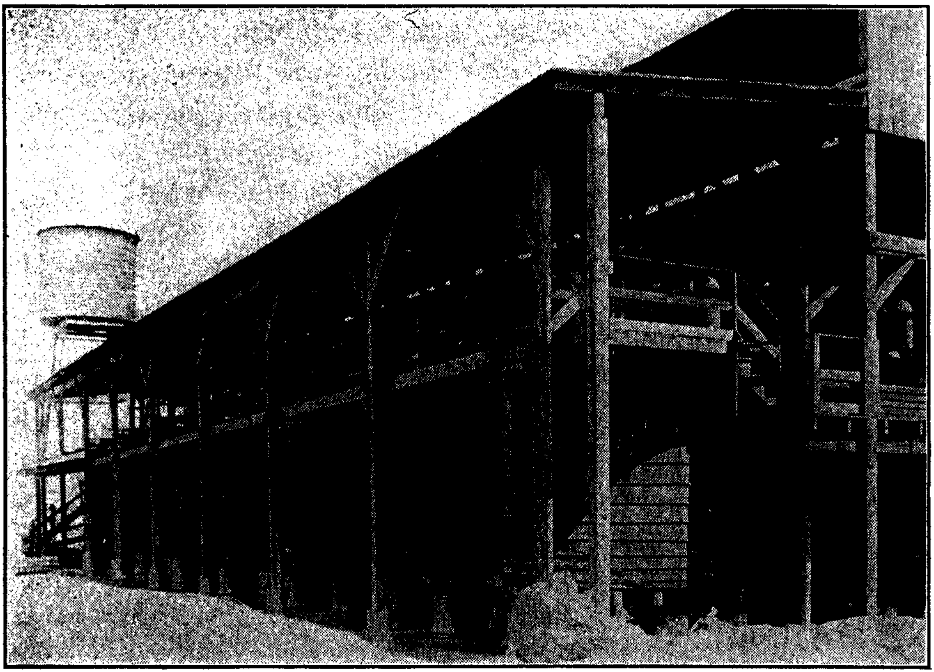

FIGURE 64. Boiling Tubs for Purification of Nitrocellulose.

Olsen's quick stabilization process[99] is the result of further thinking along this same line and represents an ingenious application of a simple principle of colloid chemistry. After the nitrocellulose has been thoroughly pulped, and after the easily decomposed cellulose sulfate, etc., have been hydrolyzed, there remains only the necessity for removing the acid which clings to the fiber. The acid, however, is adsorbed on the nitrocellulose, or bound to it, in such manner that it is not easily washed away by water or even by dilute soda solution; many boilings and washings are necessary to remove it. Olsen has found that the acid is removed rapidly and completely if the nitrocellulose is digested or washed with a solution of some substance which is adsorbed by nitro-

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[99] U. S. Pat. 1,893,677 (1933).

cellulose with greater avidity than the acid is adsorbed, that is, with a solution of some substance which has, as he says, a greater *adhesion tension* for nitrocellulose than the acid has. Such substances are aniline red, Bismarck brown, methyl orange, *m*-phenylenediamine, urea, substituted ureas such as diethyldiphenylurea, and diphenylamine. A 0.5% solution of urea in water may be used. A half-hour washing with a 0.5% solution of diphenylamine in alcohol was more effective in producing stability

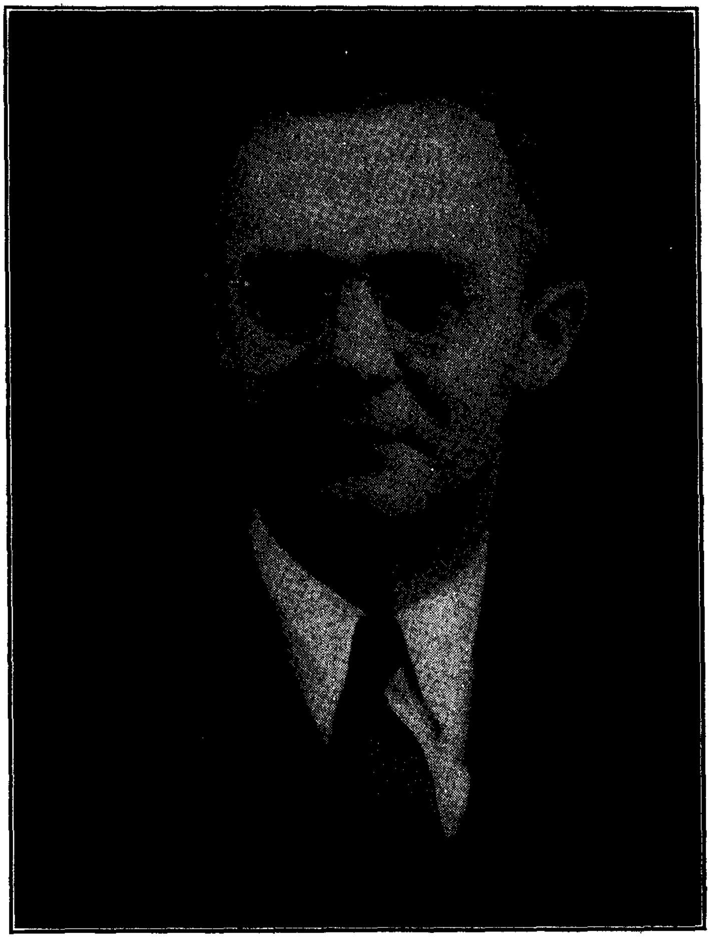

FIGURE 65. Fred Olsen. Has done important work on cellulose and has made many improvements in detonating explosives, high explosives, and smokeless powder; in particular, has invented processes for the quick stabilization of nitrocellulose and for the production of ball-grain powder. Chief of Chemical Research, Aetna Explosives Company, 1917-1919; Chemical Adviser, Picatinny Arsenal, 1919-1928; Technical Director, Western Cartridge Company, 1929—.

than 20 hours of boiling with water. A solution of 0.1 gram of Bismarck brown in 300 cc. of water gave better stabilization of 30 grams of nitrocellulose in 1 hour than 10 boilings of 1 hour each with separate 300-cc. portions of water.

Nitrocellulose, like all other nitric esters with the possible exception of PETN, is intrinsically unstable, even at ordinary temperatures. Yet the decomposition of a thoroughly purified sample is remarkably slow. Koehler and Marqueyrol[100] have made a careful study of the decomposition of nitrocellulose at various temperatures in the vacuum of a mercury pump. They found that it evolved gas at the rate of about 0.7 cc. per gram per day at 100°, 0.01 cc. per gram per day at 75°, and 0.0001 cc. per gram per day at 40°.

A sample of CP_1 was freed from carbonate by digestion with carbonated water and subsequent washing; it was dried thoroughly, and 35.152 grams of the material (analyzing 211.2 cc. NO per gram) was heated in vacuum at 75°. The results are summarized in the following table, where all gas volumes have been reduced to 0° and 760 mm. The residual gas, insoluble both in ferrous sulfate and in caustic soda solution, was analyzed and was found to consist approximately of 46% carbon monoxide, 18% nitrous oxide, 35% nitrogen, and a trace of hydrocarbons. After 309 days of heating at 75°, the temperature of the oven was reduced, and the same sample of nitrocellulose was heated in vacuum at 40° for 221 days. During this time it evolved a total of 0.697 cc. of gas or 0.0001154 cc. per gram per day. The same sample was then heated in vacuum at 100°, as follows.

DURATION OF HEATING AT 75°	TOTAL VOLUME, CUBIC CENTIMETERS	CUBIC CENTIMETERS PER GRAM PER DAY	COMPOSITION OF GAS, %		
			NO	CO_2	Residue
1st period (5 days)	2.25	0.0128	62.5	16.7	20.8
2nd period (56 days)	17.29	0.0088	63.2	19.5	17.3
3rd period (56 days)	18.25	0.00927	60.8	21.5	17.6
4th period (56 days)	18.34	0.0080	65.5	18.0	16.5
5th period (56 days)	18.19	0.0079	60.0	20.7	19.6
6th period (56 days)	18.3	0.0084	61.2	20.4	18.3

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[100] *Mém. poudres,* 18, 101, 106 (1921).

Duration of Heating at 100°	Total Volume, Cubic Centimeters	Cubic Centimeters per Gram per Day	Composition of Gas, %		
			NO	CO_2	Residue
1st period (30 hrs.)	29.09	0.662	51.9	24.1	24.0
2nd period (8.5 hrs.)	8.57	0.689	68.1	17.6	14.3
3rd period (9 hrs.)	8.09	0.614			

The residual gas, neither NO nor CO_2, was found to contain about 64% of carbon monoxide, the remainder being nitrous oxide and nitrogen with a trace of hydrocarbons. The nitrocellulose left at the end of the experiment weighed 34.716 grams corresponding to a loss of 1.24% of the weight of the original material. It gave on analysis 209.9 cc. NO per gram corresponding to a denitration per gram of 2.2 cc.

The gases from the decomposition of nitrocellulose in vacuum contain nothing which attacks nitrocellulose. If the decomposition occurs in air, the nitric oxide which is first produced combines with oxygen to form nitrogen dioxide, and the red fumes, which are acidic in the presence of moisture, attack the nitrocellulose and promote its further decomposition. The decomposition then, if it occurs in the presence of air or oxygen, is self-catalyzed. The amount of nitric oxide which is produced if the decomposition occurs in the absence of air, or the amount of nitrogen dioxide which is produced in the first instance if the decomposition occurs in the presence of air, is a function solely of the mass of the sample. The extent to which the red fumes attack the nitrocellulose depends, on the other hand, upon the concentration of the gases and upon the area of the surface of the sample which is accessible to their attack. The greater the density of loading of the sample, the greater will be the concentration of the red fumes. For the same density of loading, the finer the state of subdivision of the sample, the greater will be the surface. Pellets of compressed nitrocellulose, heated in the air, decompose more rapidly than the same nitrocellulose in a fluffier condition. The pellets give a poorer heat test (see below) but obviously consist of material which has the same stability. Likewise, nitrocellulose which has been dissolved in ether-alcohol and precipitated by the addition of water, decomposes in the air more rapidly than the original, bulkier material. Straight nitrocellulose powder always gives a better heat test than the nitrocellulose from which it was made. If small grains and large grains of smokeless powder are made from the same nitrocellulose, the large grains will give the better heat test.

In this country the most common heat tests which are made regularly upon nitrocellulose and smokeless powder are the 65.5° KI starch test and the 134.5° methyl violet test. In the former of these, five several portions of the material under test, differing in their moisture content from nearly dry to thoroughly dry, are heated in test tubes in a bath warmed by the vapors of boiling methyl alcohol. Within each tube, a strip of potassium iodide starch paper, spotted with a 50% aqueous solution of glycerin, hangs from a hook of platinum wire a short distance above the sample, the hook itself being supported from a glass rod through a cork stopper. The tubes are examined constantly, and the time needed for the first appearance of any color on the test paper in any one of the tubes is reported.

In the 134.5° methyl violet test, heavy glass test tubes about a foot long are used. They are closed loosely at their upper ends with perforated or notched cork stoppers, and are heated for almost their whole length in a bath which is warmed by the vapors of boiling xylene. Two tubes are used. The samples occupy the lower 2 inches of the tubes, strips of methyl violet paper are inserted and pushed down until their lower ends are about 1 inch above the samples, the tubes are heated and examined every 5 minutes, and the times are noted which are necessary for the test papers to be turned completely to a salmon-pink color, for the first appearance of red fumes, and for explosion. The explosion usually manifests itself by the audible popping of the cork from the tube, but causes no other damage. A test similar to this one, but operated at 120°, using blue litmus paper and reporting the time necessary for the paper to be reddened completely, is sometimes used.

In the Bergmann-Junk test the number of cubic centimeters of nitrogen dioxide produced by heating a 5-gram sample for 5 hours at 132° is reported. The determination was originally made by absorbing the gas in ferrous sulfate solution, liberating the nitric oxide by warming, and measuring its volume. A method based upon the absorption of the gas in caustic soda solution and the titration of its acidity is now often used instead.

There are many other variations of the heat test.[101] They are sometimes called *stability tests,* but most of them, it will be noted, involve the self-catalyzed decomposition of the sample in an atmosphere of air or of red fumes. They indicate the comparative stability only of materials which are physically alike. True indications of the stability of nitric esters are to be secured only by studying the decomposition of the substances in vacuum. For this purpose the 120° vacuum stability test is most generally preferred.

Ash in nitrocellulose is determined by gelatinizing the sample with acetone which contains 5% of castor oil, setting fire to the colloid, allowing it to burn tranquilly, and igniting the charred residue to constancy of weight. It is sometimes determined as sulfate by dissolving the sample in pure concentrated sulfuric acid and igniting to constant weight.

Nitrogen in nitrocellulose is determined by means of the *nitrometer,* an instrument of great usefulness to the chemist who is working with nitric esters or with nitroamines.

Determination of Nitrogen

Nitric acid and organic and inorganic nitrates, and in general all substances which contain free nitric acid or yield nitric acid when they are treated with concentrated sulfuric acid, are analyzed by means of the nitrometer. The method depends upon the measurement of the volume of the nitric oxide which is produced when concentrated sulfuric acid acts upon the sample in the presence of mercury. It is satisfactory also for the determination of nitro group nitrogen in certain nitroamines, in nitroguanidine and in tetryl but not in methylnitramine. It is not satisfactory in the presence of mononitro aromatic compounds or of other substances which are nitrated readily by a solution of nitric acid in concentrated sulfuric acid.

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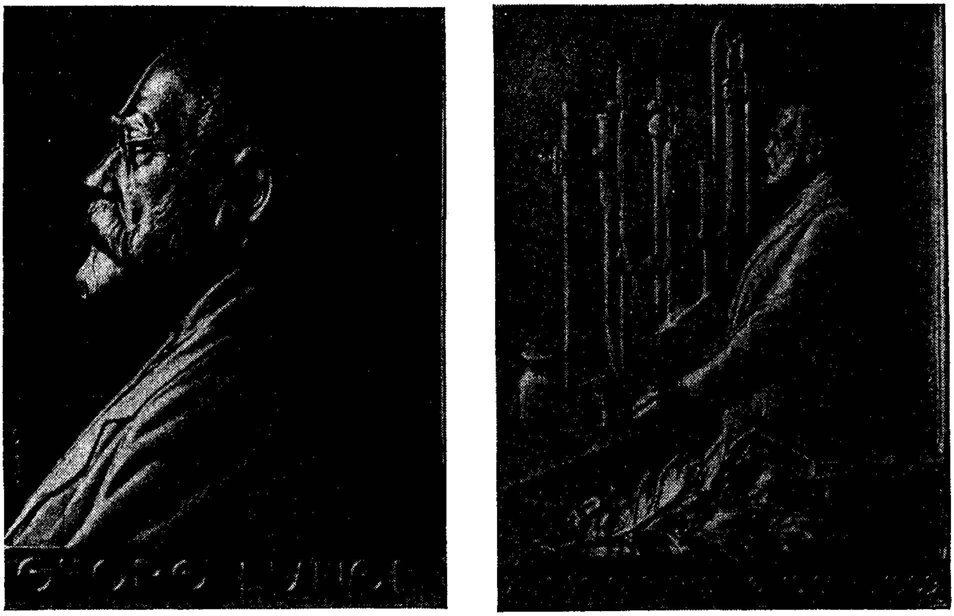
[101] U. S. War Department Technical Manual TM 9-2900 and the U. S. Bureau of Mines *Bulletins* on the analysis of explosives describe the standard heat tests in detail. "Explosives, Matches, and Fireworks" by Joseph Reilly, New York, D. Van Nostrand Company, Inc., 1938, pp. 71-83, describes about 40 different heat tests.

Cold concentrated sulfuric acid does not attack mercury. Cold nitric acid acts upon mercury to form mercurous nitrate with the evolution of nitric oxide. If concentrated sulfuric acid is present, mercurous nitrate cannot form, and the nitric acid is converted by the mercury quantitatively into nitric oxide. The method appears to have been used for the first time by Walter Crum[102] who applied it at an early date to the analysis of guncotton. He introduced the sample of guncotton into a eudiometer filled with mercury and inverted in that liquid, and carried out the reaction and measured the gas volume in the same eudiometer. Since he was unable to separate the guncotton from the air entangled with it, the measured gas volume was too large. The true volume of nitric oxide was determined by admitting a solution of ferrous sulfate to the eudiometer and noting the volume of gas which was absorbed.



FIGURES 66 and 67. Georg Lunge and His Nitrometer. Obverse and reverse of commemorative bronze plaquette by Hans Frei in celebration of Lunge's seventieth birthday.

The Lunge nitrometer is so designed that the nitrate or nitric ester is dissolved first in concentrated sulfuric acid and the solution, without entrained gas, is afterwards admitted to the re-

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[102] *Loc. cit.*

action vessel. In the usual form of the instrument as used in Europe, the gas from the reaction is measured in cubic centimeters at atmospheric pressure, the barometer and the thermometer are read, and the weight of the nitrogen in the nitric oxide and the percentage of nitrogen in the sample are calculated.

In the extremely ingenious DuPont nitrometer, a 1-gram sample is used for the analysis, and the gas is collected in a measuring tube which has been graduated to read, at a certain temperature and pressure, the correct percentage of nitrogen in the 1-gram sample. By means of a compensating bulb and leveling device, the gas in the measuring tube is brought to the volume which it would occupy if it were confined at the temperature and pressure at which the graduations are correct, and the percentage of nitrogen is then read off directly. The DuPont nitrometer[103] was invented by Francis I. DuPont about 1896. It quickly came into general use in the United States, and represents the form of the nitrometer which is preferred and generally used in this country. Lunge in 1901 claimed that it differs in no significant respect from the "gasvolumeter" or "five-part nitrometer"[104] which he had described in 1890.

Calibration and Use of the DuPont Nitrometer. The five essential parts of the DuPont nitrometer are illustrated in Figure 68. The graduations on the measuring bulb correspond to dry nitric oxide measured at 20° and 760 mm., which nitric oxide contains the indicated number of centigrams of nitrogen. Thus, the point marked 10 indicates the volume which would be occupied under the standard conditions of temperature and pressure by the quantity of dry nitric oxide which contains 0.10 gram of nitrogen, that is, by the nitric oxide produced in the nitrometer reaction from a 1-gram sample of nitrate containing 10% nitrogen. The point marked 12 corresponds to 12/10 of this volume, that marked 14 to 14/10, and so on. And the tube reads correctly the per cent of nitrogen in a 1-gram sample provided the gas is measured at 20° and 760 mm.

In setting up the instrument, dry air is introduced into the compensating bulb and the outlet at the upper end of the bulb is sealed. Dry air is introduced into the measuring bulb, the outlet is connected to a sulfuric acid manometer, and the mercury reservoir and the compensating bulb are raised or lowered until the portions of air confined

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[103] Pitman, *J. Soc. Chem. Ind.*, **19**, 982 (1900).

[104] *Ibid.*, **9**, 547 (1890); **20**, 100 (1901).

in both bulbs are at atmospheric pressure. The stopcock is closed, the volume in the measuring bulb is read, thermometer and barometer are noted, the volume which the air in the measuring bulb would occupy at 20° and 760 mm. is calculated, and the mercury reservoir and the bulbs are adjusted until the air in the measuring bulb occupies this calculated volume and until the air in the compensating bulb is at exactly the same pressure as that in the measuring bulb. A glass tube bent twice at right angles and containing some water is used for leveling the mercury in the two bulbs. The position of the mercury in the compensating bulb is now marked by means of a strip of paper glued to the glass. Whenever in the future the gas in the compensating bulb is again confined in this same volume, and whenever the nitric oxide in the measuring bulb is confined at the same pressure as the gas in the compensating bulb, then the nitric oxide will occupy the volume which it would occupy if confined at 20° and 760 mm., and, if a 1-gram sample was taken for the analysis, the reading will indicate correctly the nitrogen content. If a sample larger or smaller than 1 gram was taken, then the reading is to be corrected accordingly.

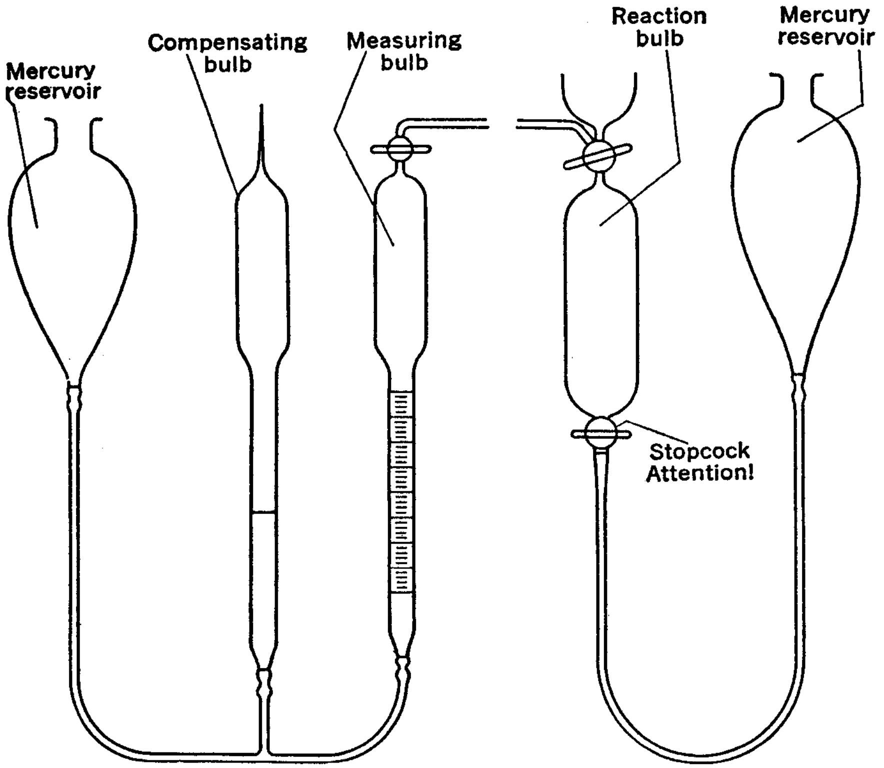

FIGURE 68. Du Pont Nitrometer.

At the beginning of an analysis, the reaction bulb and the measuring bulb and the capillary tubes at the tops of the bulbs are completely filled with mercury. A sample of about 1 gram of nitrocellulose is weighed in a small weighing bottle, dried for an hour and a half at 100°, cooled in a desiccator, and weighed accurately. A little 95% sulfuric acid is poured onto the nitrocellulose and the whole is washed into the reaction bulb. The weighing bottle is rinsed out with several small portions of sulfuric acid, the same acid is used for rinsing the cup and is finally introduced into the reaction bulb, until altogether about 20 cc. of acid has been used, care being taken that no air is introduced. The mercury reservoir is lowered to give a reduced pressure in the reaction bulb and the bulb is shaken gently, *the stopcock at its bottom being open,* until the generation of gas has practically ceased. The bulb is then raised until the level of the mercury drops nearly to its lower shoulder, the stopcock is closed, and the bulb is shaken vigorously for 3 minutes. The cock is opened and the apparatus is allowed to stand for several minutes. The mercury level is then adjusted as before, the cock is closed, and the shaking is repeated for another 3 minutes. Finally the gas is transferred to the measuring bulb and allowed to stand for about 20 minutes. The measuring bulb and the compensating bulb are then adjusted in such fashion that the mercury in both stands at the same level and that the mercury in the compensating bulb stands at the point indicated by the paper strip. The volume in the measuring bulb is then read. After each determination the reaction bulb is rinsed out twice with concentrated sulfuric acid.

In practice it is convenient to standardize the nitrometer from time to time by means of a sample of pure potassium nitrate (13.85% N) or of nitrocellulose of known nitrogen content.

The nitrometer is dangerous to one who does not understand it fully. The closing at the wrong time of the stopcock at the bottom of the reaction bulb may result in the explosion of that vessel and the throwing about of glass and of acid.

Nitrostarch

Nitrostarch[105] is manufactured and used in the United States, but has not found favor in other countries. In all the early attempts to manufacture nitrostarch, the starch was dissolved in strong nitric acid and the nitric ester was precipitated by mixing the solution with sulfuric acid or with the spent acid from some

[105] The article by Urbanski and Häckel in *Z. ges. Schiess- u. Sprengstoffw.,* **30,** 98 (1935), is accompanied by an extensive bibliography.

other nitration, as from the nitration of glycerin. The product resembled the xyloïdine of Braconnot, showed a very poor stability, and could not be stored or handled safely in the dry condition. The pulverulent, dusty form of the dry material probably also contributed to the disrepute into which it fell in Europe. In this country starch is nitrated with mixed acid in which it does not dissolve, and the product retains the appearance of ordinary starch, as guncotton retains the appearance of cotton.

Cassava or tapioca starch was preferred at first, for it was claimed that it contained less fat than corn starch and that the granules, being smaller than those of corn and potato starch, permitted a more uniform nitration and a more efficient purification. Since 1917 corn starch has been used in this country. The starch is first freed from fats and from pectic acid by washing with dilute caustic soda or ammonia solution and then with water, and it is dried until it contains less than 0.5% of moisture. In one process which produced a nitrostarch containing 12.75% nitrogen, a mixed acid containing 38% of nitric acid and 62% of sulfuric acid was used, 800 pounds of the acid in a single nitrator for 200 pounds of starch. The initial temperature of the acid was 32°, the mixture was agitated by a mechanical stirrer having a downward pitch, and the temperature during the nitration was kept between 38° and 40°. At the end of the nitration

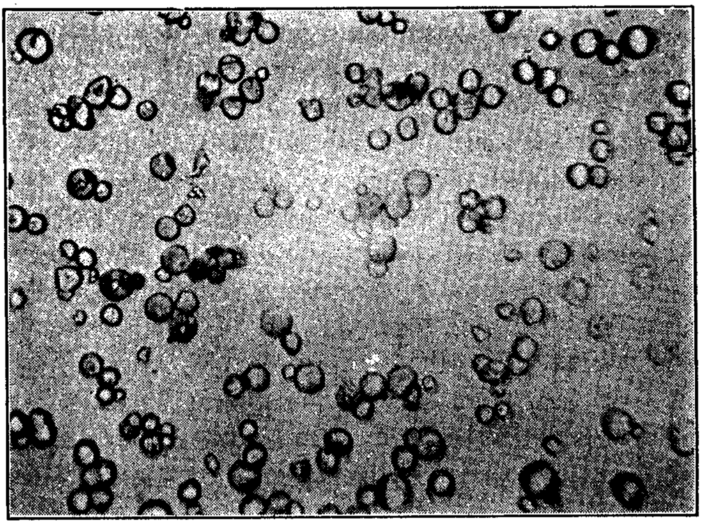

FIGURE 69. Nitrostarch Granules (about 30×). (Courtesy Trojan Powder Company.)

the contents of the nitrator was drowned in a small tub of water. The product was purified entirely by cold-water washings, without boiling. Ammonia was used to neutralize the acidity during the preliminary washing, and it is probable that this use of ammonia determined the stability of the product, perhaps because ammonia was preferentially adsorbed, instead of acid, by the material of the nitrostarch granules. The product was dried at 35–40°.

Nitrostarch gives no color with iodine. It is insoluble in water and does not gelatinize to form a paste as starch does when it is boiled with water. It is not notably hygroscopic, but may take up 1 or 2% of moisture from a damp atmosphere. It is soluble in acetone. The varieties of nitrostarch which are soluble in ether-alcohol contain about the same amounts of nitrogen as the varieties of nitrocellulose which dissolve in that mixed solvent. Nitrostarch does not form a good film or tough colloid as nitrocellulose does.

During the first World War a *Trojan explosive* which contained nitrostarch was used in trench mortar shells and in hand and rifle grenades.[106] Its composition was as follows.

	NOT LESS THAN	NOT MORE THAN
Nitrostarch	23.0%	27.0%
Ammonium nitrate	31.0	35.0
Sodium nitrate	36.0	40.0
Charcoal	1.5	2.5
Heavy hydrocarbons	0.5	1.5
Anti-acid	0.5	1.5
Diphenylamine	0.2	0.4
Moisture	....	1.2

All the *dope materials* were first ground to the desired fineness and dried, and then turned over in a large mixing barrel while the dry nitrostarch was added. Trench mortar shells were loaded by *stemming*, but the explosive was *jarred* into the grenades through small funnel-shaped openings. Another nitrostarch explosive, which was used only in grenades, was called *Grenite* and consisted almost entirely of nitrostarch (about 97%) with small amounts (about 1.5% each) of petroleum oil and of gum arabic. It was made by spraying the dry materials with a solution of the

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[106] U. S. War Department Technical Manual TM 9-2900, p. 109.

binder while the mixture was stirred in a rotary mixer. The resulting granules were dried and screened, and yielded a free-running explosive which could be loaded easily by machine.

Three United States patents[107] granted in 1916 to Bronstein and Waller describe several nitrostarch blasting explosives, of which the following table reports typical examples. In actual use, these explosives would also contain a small amount of some stabilizer, say 0.2% of diphenylamine or of urea.

	I	II	III	IV	V	VI
Nitrostarch	30.0%	39.0%	30.0%	40.0%	40.0%	40.0%
Ammonium nitrate TNT mixture	15.0	20.0	...	...	...	20.0
Sodium nitrate	46.8	37.25	58.0	37.7	34.7	17.7
Barium nitrate	...	...	...	20.0	20.0	20.0
Carbonaceous material	3.0	...	5.0	...	...	...
Paraffin oil	0.7	0.75	0.5	0.8	0.8	0.8
Sulfur	3.0	2.0	5.0	...	3.0	...
Calcium carbonate	1.5	1.0	1.5	1.5	1.5	1.5

Utilization of Formaldehyde

At the time of the first World War the methyl alcohol which was needed for the preparation of tetryl was procured from the distillation of wood. It was expensive and limited in amount. Formaldehyde was produced then, as it is now, by the oxidation of methyl alcohol, and a demand for it was a demand upon the wood-distillation industry. Formaldehyde was the raw material from which methylamine was produced commercially, and the resulting methylamine could be used for the preparation of tetryl by the alternative method from dinitrochlorobenzene. It was also the raw material from which certain useful explosives could be prepared, but its high price and its origin in the wood-distillation industry deprived the explosives in question of all but an academic interest. With the commercial production of synthetic methyl alcohol, the same explosives are now procurable from a raw material which is available in an amount limited only by the will of the manufacturers to produce it.

Carbon monoxide and hydrogen, heated under pressure in the presence of a suitable catalyst, combine to form methyl alcohol. A mixture of zinc oxide and chromium oxide has been used as a

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[107] U. S. Pats. 1,188,244, 1,188,245, 1,188,246 (1916).

catalyst for the purpose. Carbon monoxide and hydrogen (equimolecular amounts of each) are produced as *water gas* when steam is passed over hot coke.

$$C + H_2O \longrightarrow CO + H_2$$

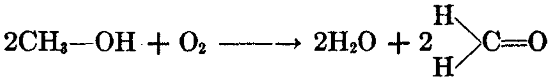
Additional hydrogen, from the action of iron on steam or from the electrolysis of water, is added to the water gas to provide the mixture which is needed for the synthesis of methyl alcohol.

$$CO + 2H_2 \longrightarrow CH_3{-}OH$$

It is evident that carbon dioxide may be used instead of the monoxide if a correspondingly larger amount of hydrogen is also used.

$$CO_2 + 3H_2 \longrightarrow CH_3{-}OH + H_2O$$

Methyl alcohol in fact is made in this manner from the carbon dioxide which results from certain industrial fermentations. When methyl alcohol vapor is mixed with air and passed over an initially heated catalyst of metallic copper or silver gauze, oxidation occurs, sufficient heat is evolved to maintain the catalyst at a bright red, and formaldehyde is formed.



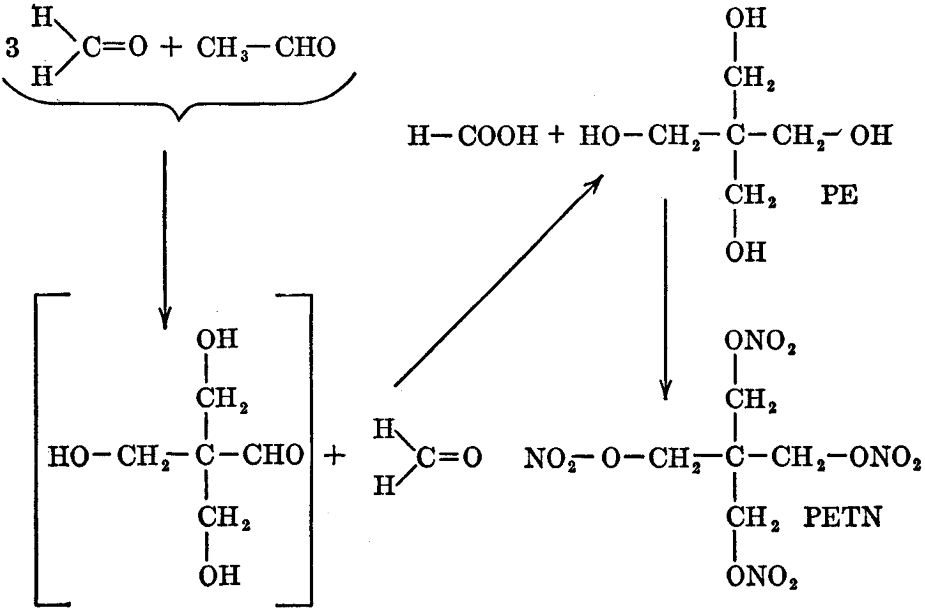
$$2CH_3{-}OH + O_2 \longrightarrow 2H_2O + 2\,{}^{H}_{H}\!>\!C{=}O$$

Of the several explosives which are preparable from formaldehyde, two are the most powerful and brisant of the solid high explosives which are suitable for military use. One of these, *cyclotrimethylenetrinitramine* or *cyclonite,* is a nitroamine and is discussed in the chapter which is devoted to those substances. The other, *pentaerythrite tetranitrate* or PETN, is a nitric ester. Both may be prepared from coke and air.

Formaldehyde enters readily into combination with substances which add to its unsaturated carbonyl group. If a substance containing an active hydrogen adds to formaldehyde or condenses with it, the active hydrogen attaching itself to the oxygen of the formaldehyde and the rest of the molecule attaching itself to the carbon, the result is that the position originally occupied by the active hydrogen is now occupied by a $-CH_2-OH$ or methylol group. Hydrogens which are active in condensation reactions are those which are α- to a carbonyl, a nitro, or a cyano group, etc., that is, they are attached to a carbon atom to which a carbonyl, a nitro, or a cyano group is also attached and are in general the hydrogen atoms which are involved in the phenomena of tautomerism. The condensation of formaldehyde with acetaldehyde, with nitromethane, with cyclopentanone, and with cyclohexanone thus leads to polyhydric primary alcohols the nitric esters of which are useful explosives.

Pentaerythrite Tetranitrate (PETN, penta, niperyth, penthrit)

Four equivalents of formaldehyde in warm aqueous solution in the presence of calcium hydroxide react with one equivalent of acetaldehyde to form pentaerythrite. Three of the four react with the three α-hydrogens of the acetaldehyde, the fourth acts as a reducing agent, converts the —CHO group to —CH_2—OH, and is itself oxidized to formic acid.



The name, pentaerythrite, indicates that the substance contains five carbon atoms and (like erythrite) four hydroxyl groups. In commercial practice [108] the reaction is carried out at 65–70°. After 2 hours at this temperature, the calcium is precipitated by means of sulfuric acid, the mixture is filtered, and the filtrate is concentrated and crystallized by evaporation in vacuum. Penta-

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[108] For the laboratory preparation see *Org. Syntheses,* **4,** 53 (1912), John Wiley & Sons, New York. Also Tollens and Wigand, *Ann.,* **265,** 316 (1891); Rave and Tollens, *ibid.,* **276,** 58 (1893); Stettbacher, *Z. ges. Schiess- u. Sprengstoffw.,* **11,** 182 (1916).

erythrite crystallizes from water in white tetragonal crystals, m.p. 253°. One part requires 18 parts of water at 15° for its solution.

PETN may be prepared, according to Naoúm,[109] by adding 100 grams of finely powdered pentaerythrite to 400 cc. of nitric acid (1.52) while the temperature is maintained between 25° and 30° by efficient cooling. Toward the end of the nitration a certain amount of the tetranitrate crystallizes out. The separation of the product is completed by the gradual addition of 400 cc. of concentrated sulfuric acid (1.84) while the stirring and cooling are continued. The mixture is not drowned, but the crude PETN (85–90% of the theory) is filtered off directly, and washed first with 50% sulfuric acid and then with water. It still contains some occluded acid and is purified, according to Naoúm, by dissolving in hot acetone to which a little ammonium carbonate is added, and filtering the hot solution into twice its volume of 90% alcohol by which the PETN is precipitated in fine needles.

Pentaerythrite may also be nitrated satisfactorily, and probably in better yield, without the use of sulfuric acid and with the use of nitric acid from which the nitrous acid has been removed.

Preparation of Pentaerythrite Tetranitrate. Four hundred cc. of strong *white* nitric acid—prepared by adding a little urea to fuming nitric acid, warming, and blowing dry air through it until it is completely decolorized—is cooled in a 600-cc. beaker in a freezing mixture of ice and salt. One hundred grams of pentaerythrite, ground to pass a 50-mesh sieve, is added to the acid a little at a time with efficient stirring while the temperature is kept below 5°. After all has been added, the stirring and the cooling are continued for 15 minutes longer. The mixture is then drowned in about 3 liters of cracked ice and water. The crude product, amounting to about 221 grams or 95% of the theory, is filtered off, washed free from acid, digested for an hour with a liter of hot 0.5% sodium carbonate solution, again filtered off and washed, dried, and finally recrystallized from acetone. A good commercial sample of PETN melts at 138.0–138.5°. The pure material melts at 140.5–141.0°, short prismatic needles, insoluble in water, difficultly soluble in alcohol and ether.

Pentaerythrite tetranitrate is the most stable and the least reactive of the explosive nitric esters. It shows no trace of decomposition if stored for a very long time at 100°. While nitrocellulose

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[109] *Op. cit.*, p. 244.

is destroyed within a few minutes by boiling with a 2.5% solution of caustic soda, PETN requires several hours for its complete decomposition. Ammonium sulfide solution attacks PETN slowly at 50°, and a boiling solution of ferrous chloride decomposes it fairly rapidly. It does not reduce Fehling's solution even on boiling, and differs in this respect from erythrite tetranitrate.

PETN does not take fire from the spit of a fuse. If a small quantity is submitted to the action of a flame, it melts and takes fire and burns quietly with a slightly luminous flame without smoke. Above 100° it begins to show appreciable volatility, and at 140–145°, or at temperatures slightly above its melting point, it shows red fumes within half an hour. It inflames spontaneously at about 210°. It is relatively insensitive to friction but makes a loud crackling when rubbed in a rough porcelain mortar. It may be exploded readily by pounding with a carpenter's hammer on a concrete floor. In the drop test it is detonated by a 20-cm. drop of a 2-kilogram weight, sometimes by a drop of 10 or 15 cm.

Naoúm[110] reports that 10 grams of PETN in the Trauzl test with sand tamping gave a net expansion of about 500 cc., with water tamping one of 560 cc. The same investigator[111] found a velocity of detonation of 5330 meters per second for the material, only slightly compressed, at a density of loading of 0.85 in an iron pipe 25 mm. in internal diameter. For PETN compressed to a density of 1.62 Kast[112] found a velocity of detonation of 8000 meters per second.

PETN is extraordinarily sensitive to initiation. It is detonated by 0.01 gram of lead azide, whereas tetryl requires 0.025 gram of lead azide for its certain detonation. This sensitivity and its great brisance combine to make PETN exceptionally serviceable in compound detonators.

Under high pressure powdered PETN agglomerates to a mass which has the appearance of porcelain, but which, when broken up into grains, is a very powerful smokeless powder functioning satisfactorily with the primers which are commonly used in small arms ammunition. The powder is hot and unduly erosive, but cooler powders have been prepared by incorporating and compressing PETN in binary or in ternary mixtures with TNT,

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[110] *Ibid.*, p. 246.

[111] *Ibid.*, p. 247.

[112] *Z. angew. Chem.*, **36**, 74 (1923).

nitroguanidine, and guanidine picrate. A mixture of PETN with guanidine picrate is less sensitive to heat and to shock than ordinary colloided smokeless powder, and is stable at all temperatures which are likely to be encountered. PETN does not colloid with nitrocellulose. It dissolves readily in warm trinitrotoluene, and mixtures may be prepared which contain 65% or more of PETN. The richer mixtures may be used as propellent powders. The less-rich mixtures are brisant and powerful high explosives comparable in their behavior and effects to TNB.

Stettbacher[113] in 1931 described several dynamite-like explosives which contained both PETN and nitroglycerin. He called them by the general name of *Penthrinit,* and described simple penthrinit, *gelatin penthrinit,* and *ammonpenthrinit.* Naoúm[114] later in the same year reported comparative tests of ammonpenthrinit and gelatin dynamite, as follows.

	AMMONPENTHRINIT	GELATIN DYNAMITE
Composition		
PETN	37%	....
Nitroglycerin	10%	63%
Collodion nitrocotton	....	2%
Dinitrotoluene	5%	....
Wood meal	....	5%
Ammonium nitrate	48%	30%
Trauzl test (average)	430 cc.	465 cc.
Velocity of detonation (average)	6600 meters per sec.	7025 meters per sec.
At density of loading	1.36	1.47

A Swiss patent of 1932 to Stettbacher[115] covers the conversion of PETN into a plastic mass by means of 10–30% of a fluid nitric ester such as nitroglycerin or nitroglycol. It states that a mixture of 80% PETN and 20% nitroglycerin is a plastic mass, density 1.65, which does not separate into its components and which is suitable for loading shells and detonators. For the latter purpose it is initiated with 0.04 gram of lead azide.

Dipentaerythrite Hexanitrate (Dipenta)

The formation of a certain amount of dipentaerythrite is unavoidable during the preparation of pentaerythrite. It is nitrated

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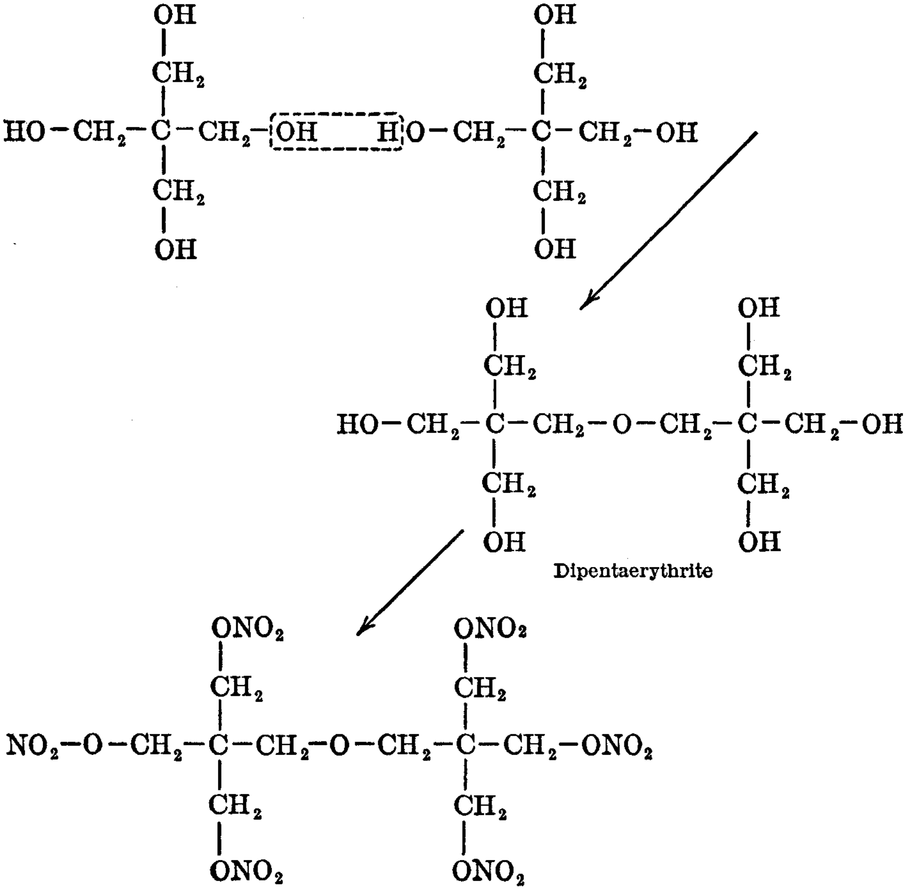
[113] *Z. ges. Schiess- u. Sprengstoffw.,* **26,** 8, 39 (1931).

[114] *Ibid.,* **26,** 42 (1931).

[115] Swiss Pat. 137,476 (1932).

along with the latter substance, and, unless a special purification is made, remains in the PETN where its presence is undesirable because of its lower stability.



Dipentaerythrite

Dipentaerythrite hexanitrate

Dipentaerythrite hexanitrate[116] is procured in the pure state by the fractional crystallization from moist acetone of the crude PETN which precipitates when the nitration mixture is drowned in water, white crystals, m.p. 72°. The crystals have a specific gravity of 1.630 at 15°, after being fused and solidified 1.613 at 15°. The substance is less sensitive to friction, less sensitive to the mechanical shock of the drop test, and less sensitive to temperature than PETN, but it is less stable and decomposes much more rapidly at 100°.

Brün[117] reports measurements by the Dautriche method of the

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[116] Friederich and Brün, *Ber.,* 63, 2861 (1930); Brün, *Z. ges. Schiess- u. Sprengstoffw.,* 27, 71, 125, 156 (1932).

[117] *Ibid.,* 27, 126 (1932).

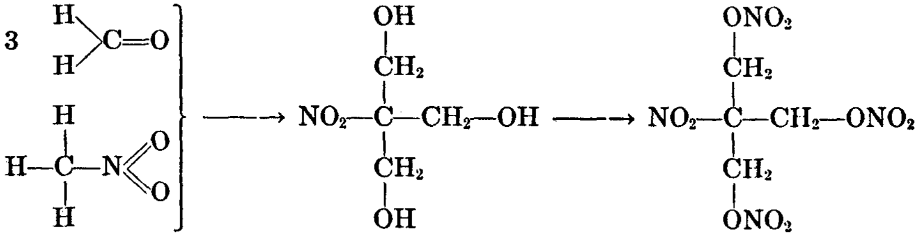
velocities of detonation of several explosives loaded in copper tubes 10 mm. in diameter and compressed under a pressure of

Explosive	Density	Velocity of Detonation, Meters per Second
Dipentaerythrite hexanitrate	1.589	7370
	1.589	7450
Pentaerythrite tetranitrate	1.712	8340
	1.712	8340
Tetryl	1.682	7530
	1.682	7440
Trinitrotoluene	1.615	7000
	1.615	7000

2500 kilograms per square centimeter. He also reports that a 10-gram sample of dipentaerythrite hexanitrate in the Trauzl test gave a net expansion of 283 cc. (average of 2), and PETN under the same conditions gave a net expansion of 378 cc. (average of 3).

Trimethylolnitromethane Trinitrate (Nitroisobutanetriol trinitrate, nitroisobutylglycerin trinitrate, nib-glycerin trinitrate)[118]

This explosive was first described in 1912 by Hofwimmer[119] who prepared it by the condensation of three molecules of formaldehyde with one of nitromethane in the presence of potassium bicarbonate, and by the subsequent nitration of the product.



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[118] The first two of these names are scientifically correct. The third is not correct but is used widely. The trihydric alcohol from which the nitric ester is derived is not an isobutylglycerin. In the abbreviated form of this name, the syllable, nib, stands for nitro-iso-butyl and is to be pronounced, not spelled out like TNT and PETN.

[119] *Z. ges. Schiess- u. Sprengstoffw.*, 7, 43 (1912). Brit. Pat. 6447 (1924). Stettbacher, *Nitrocellulose*, 5, 159, 181, 203 (1935).

At a time when the only practicable methods for the preparation of nitromethane were the interaction of methyl iodide with silver nitrite and the Kolbe reaction from chloracetic acid, the explosive was far too expensive to merit consideration. The present cheap and large scale production of nitromethane by the vapor-phase nitration of methane and of ethane has altered the situation profoundly. Trimethylolnitromethane trinitrate is an explosive which can now be produced from coke, air, and natural gas. Nitromethane too has other interest for the manufacturer of explosives. It may be used as a component of liquid explosives, and it yields on reduction methylamine which is needed for the preparation of tetryl.

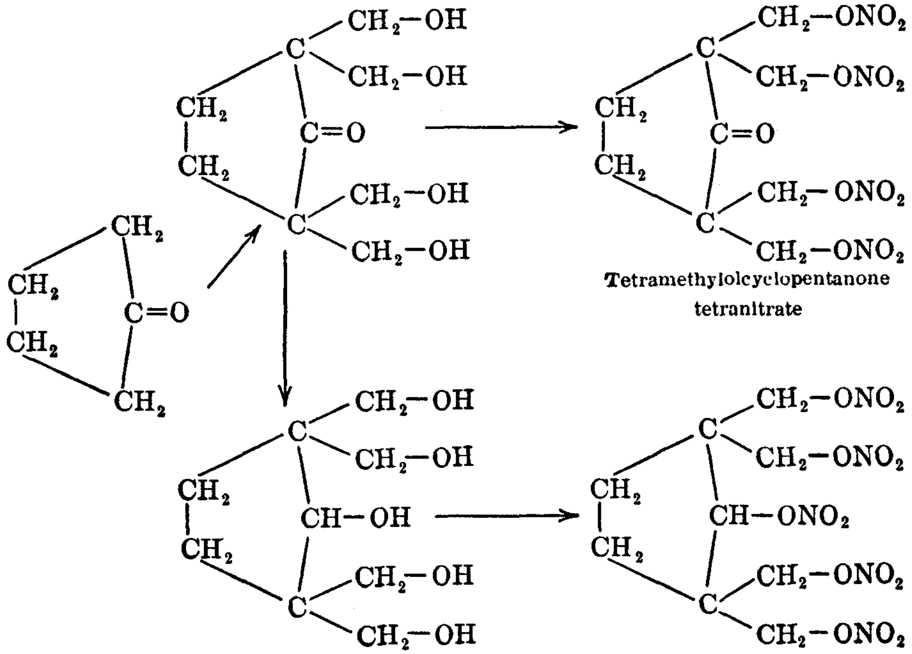
The crude trimethylolnitromethane from the condensation commonly contains a small amount of mono- and dimethylolnitromethane from reactions involving one and two molecules of formaldehyde respectively. It is recrystallized from water to a melting point of 150°, and is then nitrated. Stettbacher reports that the pure substance after many recrystallizations melts at 164–165°. The nitration is carried out either with the same mixed acid as is used for the nitration of glycerin (40% nitric acid, 60% sulfuric acid) or with very strong nitric acid, specific gravity 1.52. If the trihydric alcohol has been purified before nitration, there is but little tendency for the nitrate to form emulsions during the washing, and the operation is carried out in the same way as with nitroglycerin. In the laboratory preparation, the nitric ester is taken up in ether, neutralized with ammonium carbonate, dried with anhydrous sodium sulfate, and freed from solvent in a vacuum desiccator.

The explosive is procured as a yellow oil, more viscous than nitroglycerin, density 1.68 at ordinary temperature. It has but little tendency to crystallize at low temperatures. A freezing point of −35° has been reported. It is very readily soluble in ether and in acetone, readily soluble in alcohol, in benzene, and in chloroform, and insoluble in ligroin. It is less soluble in water and less volatile than nitroglycerin. Because it is less volatile, it is slower to cause headaches, and for the same reason the headaches are slower to go away. It is distinctly inferior to nitroglycerin as a gelatinizing agent for collodion nitrocotton. The nitro group attached directly to an aliphatic carbon atom appears to have an unfavorable effect on stability, for trimethylolnitromethane trinitrate gives a poorer potassium iodide 65.5° heat test than nitroglycerin. Naoúm[120] reports the data which are tabulated below.

	TRIMETHYLOL-NITROMETHANE TRINITRATE	NITRO-GLYCERIN
Trauzl test: 75% kieselguhr dynamite	325 cc.	305 cc.
93% blasting gelatin	580 cc.	600 cc.
Drop test, 2-kilogram weight	6 cm.	2 cm.

Nitropentanone and Related Substances

Cyclopentanone and cyclohexanone contain four active hydrogen atoms and condense with formaldehyde to form substances which contain four —CH_2—OH groups. The latter may be converted directly into explosive tetranitrates or they may be reduced, the carbonyl groups yielding secondary alcohol groups, and the products then may be nitrated to pentanitrates.



Tetramethylolcyclopentanone tetranitrate

Tetramethylolcyclopentanol pentanitrate

The explosives derived in this way from cyclopentanone and cyclohexanone were patented in 1929 by Friederich and Flick.[121] They

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[120] *Op. cit.*, p. 241.

[121] Ger. Pat. 509,118 (1929).

are less sensitive to mechanical shock than PETN, and three out of four of them have conveniently low melting points which permit them to be loaded by pouring. *Tetramethylolcyclopentanone tetranitrate,* called *nitropentanone* for short, melts at 74°. *Tetramethylolcyclopentanol pentanitrate* is called *nitropentanol* and melts at 92°. *Tetramethylolcyclohexanone tetranitrate,* m.p. 66°, is called *nitrohexanone,* and *tetramethylolcyclohexanol pentanitrate,* m.p. 122.5°, *nitrohexanol.* They are less brisant than PETN. Wöhler and Roth [122] have measured their velocities of detonation at various densities of loading, as follows.

Explosive	Density of Loading	Velocity of Detonation, Meters per Second
Nitropentanone	1.59	7940
	1.44	7170
	1.30	6020
	1.13	4630
Nitropentanol	1.57	7360
	1.51	7050
	1.29	6100
	1.11	5940
	1.01	5800
	0.91	5100
	0.75	5060
Nitrohexanone	1.51	7740
	1.42	7000
	1.25	5710
Nitrohexanol	1.44	7670
	1.28	6800
	1.00	5820
	0.81	5470

[122] *Z. ges. Schiess- u. Sprengstoffw.,* **29,** 332–333 (1934).