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THE CHEMISTRY AND TECHNOLOGY OF HIGH EXPLOSIVES

BY: Ye. Yu. Orlova

English Pages: 752

PART III
Pages 568 through 752

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Part III

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PART III

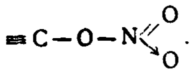
NITRIC ESTERS

CHAPTER IX

GENERAL DESCRIPTION OF NITRIC ESTERS

Nitric esters used to be of major industrial and military significance as ~~brisant~~ explosives. They were used in the pure form and as mixtures (dynamites). Toward this end, employment was made of glycerin and cellulose nitrates - nitroglycerin and pyroxylin. Today, these substances, as well as a number of other nitric esters ~~X~~ (nitroglycol and dinitroglycol) are employed to manufacture powder. PTEN is the only substance in this group now employed as a brisant explosive, and a very small number of other nitric esters are used to make industrial explosives - safety explosives and dynamites.[9] The employment of dynamites for industrial purposes is small, as compared to its past use, in most countries, with the exception of the USA. Today, high-percent dynamites are used for work in very hard rocks, as well as in cases in which the cartridges of explosives have to withstand the effects of water.

Nitric esters are sharply different from nitro compounds and nitramines in their properties due to the fact that the nitro group is attached to the carbon via oxygen as intermediary



$$\equiv C-O-N\begin{smallmatrix}O\\O\end{smallmatrix}.$$

Characteristic reactions of the nitric ~~X~~ esters are the saponification or hydrolysis reaction (in the presence of alkali)

$$RONO_2+H_2O \rightleftarrows ROH+HNO_3,$$

301 as well as the reduction reaction, at the consequence of which the initial alcohol, and ammonia, are produced on reaction with hydrogen at the moment of isolation

$$RONO_2 + 4H_2 \rightarrow ROH + NH_3 + 2H_2O.$$

The "~~peretherification~~" (re-esterification) reaction is also specific, particularly the reaction between nitric esters and sulfuric acid, in which the nitro group is displaced by the sulfo group:

$$RONO_2 + H_2SO_4 \rightleftarrows ROSO_3H + HNO_3.$$

The bond of the nitro group to the carbon atom of the molecule, through the oxygen, is unstable, and therefore nitric esters are considerably less stable than nitro compounds and are more sensitive to mechanical effects.

302 As distinct from the nitration reaction, the reaction resulting in the formation of nitric esters

$$ROH + HNO_3 \rightleftarrows RONO_2 + H_2O$$

is reversible (because of the hydrolyzing and saponifying effect of water). Both reactions are promoted by hydrogen ions. Hydrolysis is also accelerated by hydroxyl ions. Therefore, when nitric esters are being made, it is necessary either to have a considerable excess of nitric acid, or to remove the water formed by means of some substance that takes water up, such as concentrated sulfuric acid. Nitric acid diluted by water usually oxidizes alcohol. When the concentration of nitric acid is less than 77%, the etherification of alcohols such as glycerol, glycol, etc., does not occur, but yields to oxidizing and, in part, hydrolytic reactions, which intensify with dilution of the acid and increase in temperature. Therefore, either concentrated nitric acid or a mixture of nitric and sulfuric acids are employed to make nitric esters.

Sulfuric acid substantially accelerates the etherification reaction and reduces the oxidizing effect of nitric acids. The reason for this, in accordance with contemporary views, is that sulfuric acid reacts with nitric acid, converting it to an active nitrator, as well as to an etherifying form - the NO_2^+ cation - in accordance with the mechanism

$$HNO_3 + 2H_2SO_4 \rightleftarrows NO_2^{\oplus} + 2HSO_4^{\ominus} + H_3O^{\oplus}.$$

Etherification of alcohols by nitric acid is regarded by Ingold (Bibl.1) as O-nitration. It has been shown, by an investigation of the kinetics of this process, that here the same mechanism is at work with the nitronium cation as in C-nitration. This process goes in two stages: attachment of NO_2^+ (slowly) to the alcohol molecule, followed by cleavage of the hydrogen being replaced (rapidly) (Bibl.1).

Sulfuric acid also protects the apparatus against attack, and facilitates recovery of the spent acid.

The rapidity and completeness of the etherification reaction depends upon the composition of the mixed acid. The maximum velocity is achieved with the use of mixed sulfuric and nitric acids containing 9 - 10% H_2O, whereas further reduction in the water content does not increase the degree of etherification, but results in a noticeable reduction in reaction velocity.

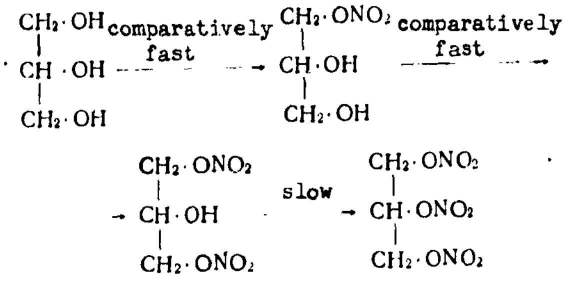
Theoretical explanation for this phenomenon was first offered by A.V.Sapozhnikov (Bibl.12), on the basis of nitration of cellulose. [illegible] as previously noted (p.33), Sapozhnikov provided graphic depiction on a triangular diagram, in which the relationship among the components was expressed in molar percent, of his numerous experiments in the esterification of cellulose (see Fig.1).

Those acid mixtures which yielded an identical degree of esterification proved to

302 be in specific regions of the triangle, and A.V.Sapozhnikov differentiated among them by curves. It proved that the region of highly-nitrated cellulose (eleven NO_2 groups) in the left portion of the triangle was bounded by a line of equal molecular ratios of H_2SO_4 and H_2O, and, in the right side of the triangle, by a line of ternary mixtures, in which the relationship of molecules of sulfuric to nitric acids were 2:1. Thus, the highest degree of esterification of cellulose occurs when nitric acid is present as the free monohydrates, and this is provided by an equally molecular relationship between sulfuric acid and water. Acid mixtures containing a larger amount of sulfuric acid yield cellulose that has been esterified to a low degree because of the decomposition of the nitric esters by unhydrated sulfuric acid.

The reactivity of alcohols varies. Thus, for example, methyl alcohol reacts with the nitronium cation approximately 25% faster than does toluene, while α,α'-glyceroldinitrate nitrates very slowly. In multi-atomic alcohols, the α-hydroxyl groups are considerably more reactive than the β-hydroxyl groups. According to a study

303 by Ingold (Bibl.1), the mechanism of glycerol etherification may be represented as follows:



The assumption that the etherification of alcohols is accompanied by a shifting equilibrium of the mixed acid:

$$R(OH) + H_2SO_4 \rightleftarrows R(OSO_3H) + H_2O;$$
$$R(OSO_3H) + HNO_3 \rightleftarrows R(ONO_2) + H_2SO_4,$$

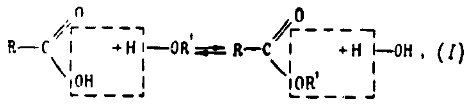
303 which allegedly determine the process rate in accordance with the relationships between the sulfuric and nitric acids and water in the starting mixture, and also in the spent acid, is not very probable, inasmuch as the rate of nitric ester formation is considerably more rapid than that of sulfuric ester.

An increase in the nitric acid content of the spent acid raises the yield of nitric ester, while an increase in the water content, on the other hand, results in a reduction in the yield of ester due to hydrolysis thereof.

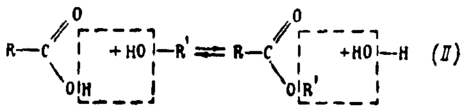
In determining the composition of the mixed acid, it is also necessary to remember that sulfuric acid acts not only as a factor accelerating esterification, but, when it is in a specific excess, it decomposes the esterification products, and the nitric esters are then able to convert to sulfuric esters.

For the esterification of alcohol, acetic anhydride or a mixture thereof with glacial acetic acid may be employed as the dehydrater (Bibl.3). This kind of esterification has the advantage, over esterification in the presence of sulfuric acid, that the formation of sulfates is prevented during the reaction. The presence of sulfates in explosive nitric esters is undesirable because they reduce their stability and make stabilization difficult.

Two mechanisms are possible for the esterification-hydrolysis reaction:



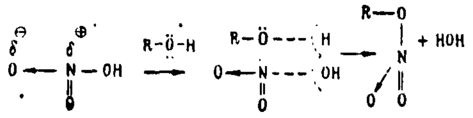
(I)



(II)

303 **When alcohols are esterified by nitric acid, mechanism (I) will hold.**

304 **The esterification mechanism may be represented by the following ~~diagram.~~ scheme**



With positively XXXX charged nitrogen, alcohol forms a bond due to the free oxygen electron pair in the alcohol. Simultaneously, OH in the transient ~~condition~~ state leaves as an anion, and H as a cation (Bibl.4). The reaction will go the more rapidly, the larger the partial positive charge ($\delta^{\oplus}$) on the nitrogen. The nitronium cation has a complete positive charge $NO_2^{\oplus}$, resulting from the reaction XXX of nitric and sulfuric acids when mixed. This renders the mixture of sulfuric and nitric acid a stronger esterifying agentXXXXXXXXXXX than is pure nitric acid.

The production of nitric esters is performed at a specific temperature.which is usually not high, inasmuch as an increase in the temperature increases the velocity not only of esterification, but of the reverse reaction of saponification, as well as of the oxidation processes. These harmful processes usually result in a reduced yield of nitrate, and increase the danger involved in this production process.

An increase in temperature during the process to above a specific level **may result in combustion of the mass because of the progressively increasing reaction velocities of esterification and oxidation. Because of the high heat effect of oxidation, the cooling surface of the apparatus does not provide complete removal of the heat XX emitted, the temperature of the reaction mass rises progressively, and is capable of attaining the spontaneous combustion temperature of alcohol and nitrate, which will result in explosion.**

304 Any increase in temperature during esterification is particularly dangerous, in the case of certain nitric acids, because of their low stability in the acid and unpurified forms. This may give rise to spontaneous decomposition of the resultant product, which is frequently accelerated by the presence of nitric oxides. The spontaneous decomposition of nitric esters is usually not susceptible to being stopped by cooling, and it terminates with burning or even an explosion.

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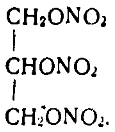
CHAPTER X

CHEMISTRY AND TECHNOLOGY OF NITRIC ESTERS

A. ~~Glyceryl~~ Glycerol Trinitrate

~~Glyceryl~~ Glycerol trinitrate (nitroglycerin) is an ester of glycerol and nitric acid. Its structural formula is



$$\begin{array}{c} CH_2ONO_2 \\ | \\ CHONO_2 \\ | \\ CH_2ONO_2. \end{array}$$

The designation nitroglycerin is inaccurate, as this compound does not contain nitro groups attached directly to carbon, but the name is universally accepted and has been retained in technology.

Nitroglycerin is one of the most powerful and sensitive of explosives, and its use requires particular attentiveness and care.

It was first produced by Sobrero in 1846 - 1847. Despite its high explosive properties, nitroglycerin was, for a long time, not employed, because of its high

305 ~~shock~~ impact sensitivity. The possibility of employing it was noted by the distinguished Russian chemist N.N.Zinin, who prepared a large amount of nitroglycerin and filled grenades with it in 1854 - 1855, during the Crimean War, jointly with V.V.Petrushevskiy, a military engineer.

The Swedish engineer Alfred Nobel, who visited N.N.Zinin in 1862, became familiar with his work. Having convinced himself of the future potential of this explosive, he built a plant to produce nitroglycerin, after his return to Sweden in 1863. In 1867, Nobel proposed that nitroglycerin be used in the form of dynamite, which made

306 it less dangerous to handle. That marks the beginning of the construction of enterprises for nitroglycerin production in the majority of the countries of Europe.

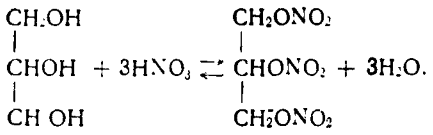
In an article titled "On Pyrocolloidal Powder", the great Russian chemist D.I.Mendeleyev, wrote in 1893: "Nitroglycerin was first used by the distinguished Russian chemist N.N.Zinin during the Crimean War, and then by the V.V.Petrushevskiy in the 60's, prior to its use by the inventor and developer of dynamite and other nitroglycerin preparations, Nobel" (Bibl.1).

N.Radivanovskiy has written in greater detail with respect to the work of N.N.Zinin and V.V.Petrushevskiy (Bibl.2).

At first, nitroglycerin was employed in the pure form for mining, and also in the form of dynamites, which are easier to handle because of their solid condition and greater safety. At the end of the Nineteenth Century, A.Nobel developed a powder of nitroglycerin and collodion. Smokeless powder employing nitroglycerin as a base has high ballistic properties and, today, virtually all nitroglycerin goes to the production of smokeless powder.

Section 1. The Chemistry of the Manufacture, the Properties, and the Applications of Nitroglycerin

Nitroglycerin is the ester of nitric acid and glycerol, obtained by the equation



$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + 3HNO_3 \rightleftarrows \begin{array}{l} CH_2ONO_2 \\ | \\ CHONO_2 \\ | \\ CH_2ONO_2 \end{array} + 3H_2O.$$

Theoretically, 1 mole glycerol and 3 moles nitric acid enter into the nitroglycerin formation reaction. Esterification proceeds in sequence, in three steps: the first yields glyceryl mononitrate, the second glyceryl dinitrate, and the third

305 glyceryl trinitrate. One hundred parts of glycerol should yield 247 parts of nitroglycerin. In practice, this yield is never attained, inasmuch as the esterification reaction is reversible, as a consequence of which a certain amount of unconverted glycerol remains, as well as products of incomplete esterification: glyceryl mononitrate and glyceryl dinitrate. The equilibrium contents of all these reactions depend on the process temperature, the quantity and composition of the mixed acid.

In order to achieve a maximum nitroglycerin yield, 20% more nitric acid is employed than the theoretically necessary. Usually, esterification is performed by a mixture of nitric and sulfuric acid. The maximum yield of nitroglycerin is obtained when anhydrous mixed acids are employed, containing 50% HNO_3 or more. Compositions of this type assure that the volume of spent acid will be minimal. This, in turn, means that there will be minimal losses of nitroglycerin with the spent acid.

306 It has been found (Bibl.3) that when glycerin is esterified with mixed acids, the result is always in the form of mononitromonosulfates, dinitromonosulfates, as well as mononitrodisulfates. The latter two readily hydrolize.

The quantity of mixed esters depends upon the composition of the mixed acid, of the composition of the spent acid, and the nitration time.

Spent acid containing considerable water (more than 12%), induces saponification upon contact with nitroglycerin:

$$C_3H_5(ONO_2)_3 + H_2O \rightleftarrows C_2H_5(ONO_2)_2OH + HNO_3;$$
$$C_3H_5(ONO_2)_2OH + H_2O \rightleftarrows C_3H_5(ONO_2)(OH)_2 + HNO_3.$$

When the HNO_3 content of the spent acid is low, or when it is entirely lacking, a process of conversion of the nitrate ester to sulfate ester will also occur:

$$C_6H_5(ONO_2)_3 + 3H_2SO_4 \rightleftarrows C_6H_5(OSO_3H)_3 + 3HNO_3,$$

306 in connection with which, the yield of nitroglycerin diminishes with the passage of time, as is evident from Table 97.

Table 97

a)	b)	c)
3	224,06	0,00
30	219,54	4,52
60	218,30	5,76
120	216,28	7,78

a) Contact time of nitroglycerin and spent acid, min; b) Nitroglycerin yield, gm, per 100 gm glycerin; c) Reduction in nitroglycerin yield, gm

If the spent acid contains less than 12% water, and more than 8% HNO_3, the process of saponification virtually fails to occur, but it is merely simple solution of the nitroglycerin that takes place.

Under industrial conditions, the average yield of nitroglycerin is 227 - 231 gm per 100 gm glycerin (91 - 94% of the theoretical).

The initial raw materials for production of nitroglycerin are glycerin, which in this case is termed dynamite glycerin, sulfuric, and nitric acids. The sulfuric acid is usually 20% oleum, and the nitric acid in the form of melange. Before it is employed, the initial acids are allowed to stand for 10 - 20 days, in order to free them from sediment, which may impair the conditions of separation, in the process of production.

For a long time, the sole source of glycerin was animal fat, which is an ester of glycerin and fatty acids. The fat is treated with caustic soda solution to obtain the glycerin. The saponification (or hydrolysis) reaction occurs when this is done:

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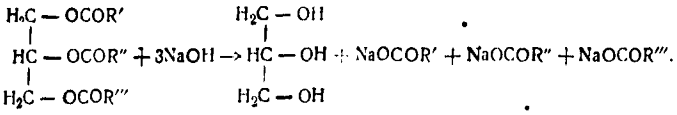


$$\begin{array}{l}H_2C-OCOR'\\ HC-OCOR''\\ H_2C-OCOR'''\end{array}+3NaOH\rightarrow\begin{array}{l}H_2C-OH\\ HC-OH\\ H_2C-OH\end{array}+NaOCOR'+NaOCOR''+NaOCOR'''.$$

The reaction products are glycerin and fatty acids salts - soaps.

In 1938, a method of obtaining glycerin from propylene (produced when petroleum is cracked) was developed. Glycerin synthesis from propylene goes in four stages.

1. The propylene is chlorinated to formation of allyl chloride:

$$CH_2=CH\cdot CH_3+Cl_2\rightarrow CH_2=CHCH_2Cl+HCl.$$

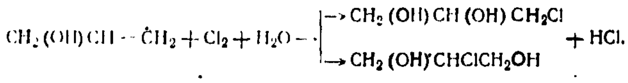
307 Chlorination is performed in a steel tube at 500°, with a large propylene excess (4 - 7 volumes propylene per volume of chlorine). Under these circumstances, it is primarily not the addition products of chlorine at the double bond that are obtained, but products of the substitution of one of the hydrogen atoms by chlorine, without saturation of the double bond. The chlorination products are separated by fractional distillation.

2. Allyl chloride is subjected to hydrolysis by a 5% alkali solution, with the formation of allyl alcohol as a consequence:

$$CH_2=CHCH_2Cl+NaOH\rightarrow CH_2=CH\cdot CH_2OH+NaCl+H_2O.$$

The process is performed in continuous-process autoclaves at 70 - 100°, under pressure (due to the high volatility of allyl chloride, which has a boiling point of 45°). The 5% aqueous salt solution of allyl alcohol obtained goes to a distillation column, in which the allyl alcohol is driven off.

3. Allyl alcohol converts to glycerol monochlorohydrin by the effect of the gaseous chlorine:



$$CH_2(OH)CH=CH_2+Cl_2+H_2O\rightarrow\left|\begin{array}{l}\rightarrow CH_2(OH)CH(OH)CH_2Cl\\ \rightarrow CH_2(OH)CHClCH_2OH\end{array}\right.+HCl.$$

4. The formation of glycerol by hydrolysis of chlorohydrin sulfate solution by strong caustic soda solution:

$$CH_2OHCH(OH)CH_2Cl + NaOH \rightarrow CH_2OHCHOHCH_2OH + NaCl;$$
$$CH_2OHCHClCH_2OH + NaOH \rightarrow CH_2OHCHOHCH_2OH + NaCl.$$

The glycerol solution obtained is vaporized under vacuum. The total yield of glycerol from propylene is 65 - 70% of theoretical.

Glycerol is a thick oily liquid with a melting point of 18.2°, which tends to considerable supercooling.

The degree of safety in the esterification process and the yield of nitroglycerin depend upon the purity and quality of the glycer~~in~~ol designed for the production of nitroglycerin. The following major specifications have to be met by dynamite glycer~~in~~ol:

1) water content of not over 1%;

2) specific gravity at 15° not less than 1.262;

3) absence of acrolein;

4) absence of sugar, glucose and other reducing agents;

5) absence of proteins and fatty acids;

6) glycerol diluted with water should have a neutral reaction on lithmus paper.

These requirements also limit the quantity of impurities in glycerol, ~~including~~ such as trimethyleneglycol (CH_3-CHOH-CH_2OH), polyglycerols (CH_2OH-CHOH-CH_2-O-CH_2-CHOH-CH_2OH) and others, which reduce the yield of nitroglycerin.

However, in the esterification of dynamite glycer~~in~~ol, which satisfies all the requirements of the technical conditions, undesirable phenomenon may occur, such as slow and incomplete separation from the spent acid, formation of a stable emulsion, poor settling out upon washing and, finally, low yield. The cause of this may be

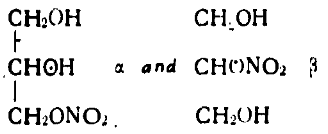
307 the existence of impurities not found in testing. Therefore, before glycerol is placed in production, a sample production of nitroglycerin therefrom is made.

To do this, 100 gm glycerol (50 gm in Germany) is slowly run into mixed acid of the following composition: 60% H_2SO_4 and 40% HNO_3 (in Germany, the mixture employed is: 55% HNO_3; 40% H_2SO_4 and 5% SO_3) at a temperature of 23° (30° in Germany). The process has to proceed without the emission of brown fumes. Glycerol run-in is performed for 20 min (15 min in Germany) and separation for 10 min. The separated liquids should not contain flakes or sediment. Separated nitroglycerin is run into water, washed, and determination of yield is made. If the quality of the initial glycerol was satisfactory, yield should be not less than 228 gm (92.5% of theoretical), and specific gravity not under 1.590.

Glycerol mononitrate is an intermediate product of glycerol trinitrate synthesis, and is therefore found therein as an impurity. As a consequence, of its high solubility,

30 the bulk remains in the spent acid, while the rest goes into the wash water in washing. It has no technical value as an independent product.

Glycerol mononitrate is a colorless viscous oil having a specific gravity of 1.41 at 15°. It exists in two forms, α and β, which apparently have the following structure:



$$\begin{matrix} CH_2OH \\ | \\ CHOH \\ | \\ CH_2ONO_2 \end{matrix} \quad \alpha \text{ and } \quad \begin{matrix} CH_2OH \\ \\ CHONO_2 \\ \\ CH_2OH \end{matrix} \quad \beta$$

Melting point 58° for the α-form and 54° for the β-form.

Glycerol mononitrate is highly hygroscopic. It is miscible with water and ethyl alcohol in any ratios. It is not soluble in ether. Chemically, it behaves like an alcohol and like a nitric ester. An aqueous solution thereof yields a neutral reaction.

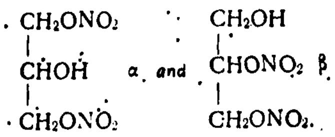
Glycerol mononitrate may be produced by saponification of glycerol dinitrate with hot water.

The explosive properties of glycerol mononitrate are very weak as a consequence of the markedly negative oxygen balance. The heat of explosive decomposition is 572 kcal/kg. Expansion of the liquid product in a Trauzl block is 75 cc. It is not sensitive to shock.

Glycerol dinitrate, like glycerol mononitrate, is an impurity glycerol trinitrate, and would also seem to be an intermediate product. Formerly, when nitroglycerin was produced with weak acids, glycerol dinitrate was obtained as a by-product, in considerable quantity. In view of its high solubility, it was found in the spent acid and in the wash water, from which it was separated by extraction.

Glycerol dinitrate crystallizes with difficulty, and therefore freezes at very low temperatures. Additions of up to 50% thereof to nitroglycerin renders this product virtually non-freezing under winter conditions. A shortcoming of glycerol dinitrate is its high solubility in water, which complicates manufacturing.

Glycerol dinitrate exists in two isomeric forms:



$$\begin{matrix} CH_2ONO_2 \\ | \\ CHOH \\ | \\ CH_2ONO_2 \end{matrix} \quad \alpha \text{ and } \quad \begin{matrix} CH_2OH \\ | \\ CHONO_2 \\ | \\ CH_2ONO_2 \end{matrix} \; \beta$$

The technical product is a mixture of these isomers and has a specific gravity of 1.51 at 15°. Glycerol dinitrate is a viscous colorless oil boiling at 148° and 15 mm pressure. At -40° it solidifies into a vitreous mass. Its volatility is twice that of

308 nitroglycerin. Glycerol dinitrate has a burning taste, is poisonous, and gives rise to headache. It is readily soluble in ether, acetone, alcohol, and chloroform, but is not soluble in carbontetrachloride and gasoline. At 15°, 8 gm glycerol dinitrate dissolves in 100 gm water, whereas 10 gm will dissolve at 50°. The product dissolves readily in dilute alkalies and acids. In strong sulfuric acid, it decomposes into glycerol mononitrate and glycerol dilsulfate.

Glycerol dinitrate will pick up almost 10% moisture from the air to form a hydrate $3C_3H_6N_2O_7 \cdot H_2O$ containing 3.2% H_2O. When the latter is heated to 40 - 50° or allowed

309 to stand in a des~~f~~icator with a water remover, it undergoes dehydration.

Glycerol dinitrate is readily converted to gelatin by collodion.

In its explosive properties, glycerol dinitrate is inferior to nitroglycerin. The heat of explosive decomposition is 1300 kcal/kg, and the Trauzl block expansion is 500 cc.

Glycerol dinitrate may be produced in the esterification of glycerol by mixed nitric and sulfuric acids, containing nitric acid in the quantity needed to introduce to nitro ester groups. However, when this method is employed, the product is contaminated with glycerol mononitrate and glycerol trinitrate. In order to produce pure glycerol dinitrate, the process is run with nitric acid alone, toward which end glycerol is mixed with three or four times the amount of concentrated nitric acid.

The rate of esterification of glycerol by nitric acid alone is less than by mixed nitric and sulfuric acid, and equilibrium sets in only after standing for a long period. Therefore, after glycerol has been dissolved in concentrated nitric acid (specific gravity 1.5), the solution obtained is held for several hours (2 - 6 hrs) so as to bring the reaction to completion. Nitric acid should contain not less than

309 90% monohydrate and should be free of nitrogen oxides.

The process is accompanied by agitation and cooling, with a temperature maintained at 15 - 20°. At its conclusion, the solution is decanted into chopped ice or into a mixture of ice and water, and marble or chalk is added until CO_2 emission ceases. As a consequence, the calcium nitrate solution resulting is so concentrated that its specific gravity exceeds the specific gravity of the glycerol dinitrate, and the latter flows to the top.

The raw product, despite complete neutralization by acid, remains acid, and therefore it requires stabilization. Stabilization is performed by washing, at 40 - 50°, with a table salt solution plus a little soda. In 30% NaCl solution, the solubility of glycerol dinitrate is considerably lower than in water (2 - 3% instead of 10%). The soda is removed by washing with fresh salt solution, and ~~it~~ is then recycled.

Glycerol dinitrate is hygroscopic, and ~~it~~ is dried by transmitting a stream of air through the heat of solution.

Glycerol trinitrate (nitroglycerin) is, in the pure form, an oily colorless and transparent liquid. The technical product is yellow or yellow-brown in color, depending upon the color of the initial glycerol.

At 15 - 20°, nitroglycerin has no odor, but at 50°, a weak and distinctive, sweetish odor is noticeable. The taste of nitroglycerin is sweetish and burning.

The specific gravity of nitroglycerin is $d^{20°}_{15°} = 1.596$ [according to Lewis (Bibl.4)]; at 15°, its density is 1.6009, and at 25° it is 1.5910 gm/cm^3. The specific gravity of frozen nitroglycerin is 1.735 (its volume diminishes by 8.26%). The viscosity of nitroglycerin is 0.360 poises. The vapor pressure of nitroglycerin at 20° is 0.00015 mm, 309 and at 60° 0.0060 mm, resulting in a loss of 0.45% in 10 days at 20°, and 1.68% at 50°. The heat of formation is $\Delta Hp = 88.63$ kcal/mole (Bibl.5), and the heat of combustion is $\Delta Hp = 1622$ cal/gm (Bibl.6).

Nitroglycerin decomposes with liberation of HNO_3 when steam-distilled.

As it hardens, nitroglycerin may form two forms - a labile, and a stable. They have different melting points and tend to supercool. The freezing point of the labile form is 2.1°, and the melting point is 2.8°; The corresponding data for the stable form are 13.2° and 13.5°. The heat of crystallization of nitroglycerin in the stable form is 33.2 cal/gm, and that of the labile form is 5.2 cal/gm. The heat of conversion of the labile to the stable form is 28.0 cal/gm (Bibl.7).

The susceptibility of nitroglycerin to spontaneous crystallization is very low, and its susceptibility to supercooling is significant. Usually, cooled nitroglycerin is compelled to crystallize out by seeding it with a crystal. If large quantities are involved, crystallization sets in more readily, as the possibility of formation of centers of crystallization increases. Nitroglycerin that has once frozen (if it has not been significantly heated upon thawing) will freeze rather readily without inoculation. When thawed nitroglycerin is heated to 50°, the tendency to supercooling

310 is again noted.

Chemically pure nitroglycerin is harder to solidify than technical nitroglycerin, and is always in the labile form. Technical nitroglycerin freezes more readily and, as a rule, in the stable form.

The labile form converts to the stable if the mixture is agitated with a glass rod, while in the quie~~t condition~~ [illegible], the labile form gradually (within one or two weeks) converts to the stable, which is now incapable of being converted to the labile form without

310 first being melted.

Crystals of the labile form of nitroglycerin are of the triclinic system, and those of the stable form are of the bipyramidalrhombic (orthorhombic holohedral) system (Fig.91).

When nitroglycerin is heated to over 60°, spontaneous increase in temperature due to decomposition is observed. Upon rapid heating to 180°, and when iron brought to red heat is placed in contact with it, nitroglycerin explodes (prior to the discovery of the capsule detonator, explosion of nitroglycerin was induced by bringing an iron rod brought to red heat in contact with it). Lightning will detonate nitroglycerin.

Fig.91 – Crystals of Nitroglycerin of the Triclinic System (Right) and the Bipyramidalrhombic (Left)

Nitroglycerin is distinguished for its high solubility in the majority of organic solvents. It is a good solvent itself, and is miscible in any proportions at room temperature with methyl alcohol, acetone, ethyl ether, amyl acetate, acetic ether, glacial acetic acid, benzene, toluene, xylene, phenol, pyridine, nitrobenzene, chloroform, dichloroethane, etc. The ready solubility in ethyl ether, chloroform, and dichloroethane ~~are~~ is employed for extraction of nitroglycerin from smokeless powder and explosive mixtures thanks to the boiling point of these solvents and the fact that chloroform and dichloroethane are virtually incombustible. Nitroglycerin is insoluble in glycer~~in~~ol.

In absolute ethyl alcohol at room temperature, nitroglycerin dissolves with difficulty, while at elevated temperature it is miscible in all proportions. The

310 solubility of nitroglycerin diminishes with increasing dilution of ethyl alcohol (it is poorly soluble in 50% alcohol, and, with further dilution by water, the nitroglycerin comes out of solution almost completely.

Nitroglycerin is difficultly soluble in carbon disulfide. This is employed in analysis, for example, in the separation of nitroglycerin from nitro compounds that are readily soluble in carbon disulfide.

Nitroglycerin readily dissolves nitro compounds. This is of significance in the manufacture of plastic and gelatinized explosives. One hundred grams thereof may retain about 35 gm dinitrotoluene or 30 gm TNT in solution at 20°.

Nitroglycerin forms low-melting eutectic mixtures with many nitro compounds. This has been examined in detail by Urbanski (Bibl.7). The compositions of these eutectics are presented in Table 98.

Nitroglycerin is capable of dissolving certain types of nitrocelluloses. Thus, a composition of 2.5% collodion and 97.5% nitroglycerin is a gelatinous mass. Aromatic nitro compounds dissolved in nitroglycerin facilitate gelatinization. This property is employed in making smokeless nitroglycerin powder and gelatin dynamites.

Nitroglycerin is readily miscible with many nitric esters. Mixtures thereof with nitroglycol, dinitroglycol, dinitroglycerin, and dinitrochlorohydrin are of high
311 practical significance for the manufacture of low-freezing dynamites.

The hygroscopicity of nitroglycerin in 24 hrs at 100% relative humidity is 0.12%. The solubility of nitroglycerin in water at various temperatures is (Bibl.6): 0.14 part in 100 parts at 25°, and 0.24 part at 60°. Hydrolysis sets in at temperatures in excess of 80° (Bibl.8).

Table 98

a)	b)		c)	
	d)	e)	d)	e)
Nitrobenzene	45,5	—15,2	57,5	—22,9
Meta-dinitrobenzene	82,5	5,0	88,0	—5,4
2,4-Dinitrotoluene	72,7	6,1	89,0	—4,1
2,4,6-Trinitrotoluene	82,9	6,3	90,0	—4,0
Tetryl	90,0	9,8	94,0	—0,6
Hexogen	99,5	12,3	99,7	1,2
Nitroglycol	about 20	about —30	about 10	about —40
PTEN	98,5	12,3	98,9	+1,3

a) Components of eutectic; b) Stable form; c) Labile form; d) Nitroglycerin content in eutectic, %; e) Temperature crystallization, °C

Acids dissolve nitroglycerin and simultaneously decompose it. Nitric acid is emitted and the ester of the corresponding acid is formed, as this occurs. This is the effect of sulfuric acid, for example. Concentrated nitric acid is miscible with nitroglycerin in all proportions, and the solutions obtained decompose rapidly as a consequence of the oxidizing effect of nitric acid. In cold hydrochloric acid, nitroglycerin is insoluble, but upon heating decomposition sets in gradually with formation of nitrosyl chloride.

Nitroglycerin that has not been washed free of acids decomposes readily, and this is revealed by the fact that it turns green (representing the appearance of nitrogen oxides in solution). Nitroglycerin going to the production of dynamite and smokeless powders must not contain even traces of acid. Alkalinity of no more than 0.001% is permissible.

Nitroglycerin is an ester by nature. When reduced, it forms glycerol, and is readily saponified by caustics, forming glycerates and other by-products when this occurs.

311 A characteristic reaction for nitroglycerin is the effect of aniline and sulfuric acid thereon, causing a purple-red coloration, which converts to green when water is added.

Nitroglycerin is amply stable at room temperature, but begins to decompose when heated to over 50°. The decomposition products are nitrogen oxide, glyceric acid, oxalic acid, etc. If large amounts of nitroglycerin undergo decomposition, the process may terminate in an explosion.

Nitroglycerin is extraordinarily poisonous (Bibl.9), and therefore the rules of safe handling must be rigorously adhered to in working with it.

The explosive properties of nitroglycerin are explained by its chemical structure. It has a positive oxygen balance (3.5%) and is one of the most powerful explosives. The explosive decomposition of nitroglycerin may be induced by heating, by mechanical
312 action (shock or friction), and by the effect of a detonating cap. It detonates when heated rapidly (to 200°).

Nitroglycerin is highly sensitive to mechanical effects. In this respect it approximates the initiating high explosives and the percussion compounds, and therefore its transportation is dangerous. Nitroglycerin production installations are always part of the plants in which it is used to manufacture powder or dynamite. In extreme necessity, the nitroglycerin may be transported in the form of solution (Bibl.10). Nitroglycerin detonates readily when iron strikes iron, or porcelain strikes porcelain. When frozen, it is less shock sensitive, but more sensitive to friction, and therefore considerably more dangerous.

Detonation of nitroglycerin may be caused by a weight of 2 kg dropped from a height of 4 cm. Heated nitroglycerin is even more shock sensitive. It explodes upon bullet

312 impact.

Nitroglycerin is comparatively insensitive to detonation: a No.8 cap is required to bring about complete explosion.

The heat of explosion of nitroglycerin is 1480 kcal/kg, the flash point is 200 - 205°, and the volume of gaseous explosion products 716 liter/kg. In a lead block it causes 550 ml expansion (Bibl.6).

The velocity of detonation of liquid nitroglycerin depends upon the test conditions, and chiefly upon the material and diameter of the tube in which it is packed, as well as upon the initial impulse. Under the usual test conditions, the velocity of detonation does not exceed 1100 - 2000 m/sec, but when tested in a steel tube of 25 mm diameter, it is 8000 - 8500 m/sec. K.K.Andreyev and A.Dserschkowitsch (Bibl.11) obtained a velocity of detonation of the stable form of nitroglycerin of 9150 m/sec when it was exploded in a steel tube of 22 mm diameter by a No.8 detonating cap.

The same pronounced dependence upon conditions, and particularly upon the initiating impulse, is observed in determining the brisant effect of nitroglycerin. When exploded by a cap of fulminating mercury, nitroglycerin causes 18.5 mm upset of a lead cylinder. A tetryl azide cap causes complete destruction of the cylinder, which testifies to the powerful crushing effect of this substance.

Section 2. Technology of Nitroglycerin Production

The production of nitroglycerin with subsequent separation from the spent acid is one of the most dangerous operations in chemical technology. Particularly careful monitoring both of the raw material and of the equipment is required. A necessary

312 safety conditions is precise adherence to the technology and the working rules, which must be carried out by highly skilled workers and well-trained engineers and technicians.

However, the possibility of explosion in nitroglycerin production is still [illegible] not completely ruled out thereafter. A fundamental solution of the problem of safe working conditions for personnel in this field is attainable only by completely automatic monitoring and remote control.

Batchwise Processes

During the past century, nitroglycerin was produced by a number of methods: the Copp method, the method of Bouthmie and Fochet, and the Nobel method.

The Nobel method is used in some countries to this day. Thus, in Germany, this was the method used to produce nitroglycerin, nitroglycol, and diglycoldinitrate at one of the largest plants in Germany (the Rheinsdorf Plant) during World War II.

313 Under the Nobel process, esterification of the glycerol is performed in a cylindrical nitrator having a conical bottom, from which a drain pipe with a three-way cock departs (Fig.92). Coils to deliver coolant water are provided in the nitrator. Agitation of the nitro mass is by compressed air introduced through narrow tubes, one of which approaches the cone bottom. The nitro mixture is run into the nitrator until it is half full, after the apparatus has been inspected, and the top has been lubricated with vaseline. The entire process of nitroglycerin production is performed in accordance with the

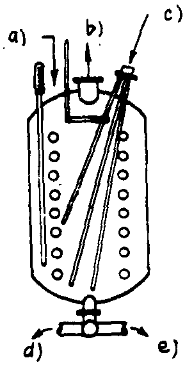


Fig.92 - Nobel Nitrator
a) Glycerol; b) To ventilation; c) Compressed air; d) To emergency vat; e) To separator

313 mechanism depicted in Fig.93.

From the ~~cast-steel~~ storage (material - cast steel) (1), a mixed acid consisting of 55% HNO_3 and 45% H_2SO_4 goes to a vessel resting on scales (2), and after weighing (1290 kg per batch), a pump delivers it to a pressure tank (3), and then to the stainless-steel nitrator (4), in which it is cooled to 0 - 5° while agitated by XXX compressed air (at about 2 atm). The compressed air used for stirring arrives from a compressor (18).

Cooling of the nitrators is by a system of coil condensers of stainless steel within the apparatus, and the salt solution is driven through these. The solution is pumped through tubes from the refrigerating device consisting of compressor (21), vaporizer (19), and condenser (20). The temperature of the salt solution is between -5 and -10°.

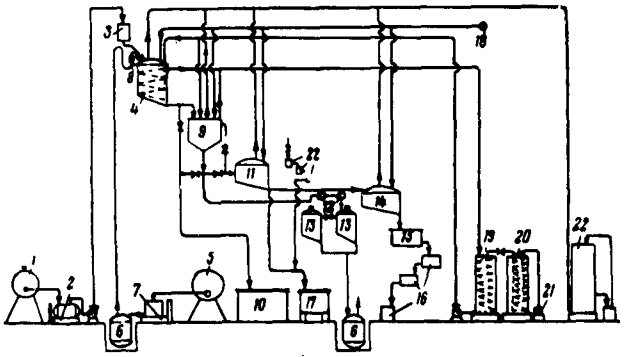


Fig.93 - Diagram of Nobel Method of Production of Nitroglycerin

1 - Mixed acid storage; 2 and 7 - Scales; 3 - Pressure tank; 4 - Nitrator; 5 - Glycerol storage; 6 - Rising device; 8 - Glycerol atomizer; 9 - Separator; 10 - Emergency vat; 11 - Preliminary washing vat; 12 - Ceramic pots; 13 - Settling vessels; 14 - Washing vats; 15 - Filter tables; 16 - Boxes; 17- Trap; XXX 18 - Compressor; 19 - Vaporizer; 20 - Condenser; 21 - Plungercompressor; 22 - Absorption column

From storage (5), the glycerol is transferred through pipes by compressed air, actuated by rising device (6), to the tilting vessel (a wooden box lined with lead) in

313 the nitration shop. It stands on scales (7). The glycerol is weighed (a single operation

314 employs 280 kg; but in Italy, England, and the USA up to 600 kg is employed), and is charged into a lifting device. Compressed air (at about 2 atm) sends the glycerol to the atomizer (8), of stainless steel, from which it enters (in atomized form) the mixed acid in nitrator (4). The rate at which the glycerol is run in is controlled by the temperature of the reaction mass.

The glycerol is run into the nitro mixture at a temperature of 0 - 15°, in 30 min time. Esterification at low temperature makes it possible for the run-in to go even more rapidly, and makes for a higher nitroglycerin yield. However, the danger of local freezing appears. If the apparatus is water-cooled, the run-in is extended to 50 min, even if the run-in of glycerol to the nitro mixture is performed in the 10 - 30° temperature intervals. The increase in the process time not only reduces the productivity of the system but intensifies the danger involved, inasmuch as the probability of spontaneous decomposition of the nitroglycerin rises.

If the temperature rises above 30°, the reaction mass is immediately dumped into emergency vat (10) to avoid decomposition or explosion. Here it is mixed with five times the amount of water.

At conclusion of esterification, the reaction mixture is cooled to 10°, subsequent to which it is transferred to separator (9) (stainless steel). The nitroglycerin emulsion separates into layers in the spent acid in the absence of agitation (this takes about 30 min). The nitroglycerin flows to the top, and the spent acid settles at the bottom. Two layers form. Separation of nitroglycerin from spent acid requires about 30 min.

The rate of stratification is determined to a considerable degree by the difference between the specific gravities of the liquids. The specific gravity of nitroglycerin, 314 as has already been indicated, is 1.6 at 15°, and the specific gravity of the spent acid is 1.7 (the composition thereof, for various mixtures, fluctuates within the following limits: 70 - 74% H_2SO_4; 9 - 10% HNO_3; 15 - 19% H_2O and 2 - 2.5% nitroglycerin). The difference between the specific gravities, which is 0.1, is adequate for comparatively rapid separation of the liquids if the initial products are pure. However, the usual type separation is interfered with not only by the high degree of emulsification that the liquids have undergone as a result of agitation by air, but also as a consequence of impurities entering with the glycerol and acids. Under unfavorable conditions, separation may take considerably longer.

The time required for separation is affected by:

1) the temperature of the mixture (a rise in temperature facilitates separation);

2) the shape of the separator (an emulsion layer of small height facilitates separation);

3) the amount of charging (large quantities separate comparatively more rapidly);

4) the impurities.

Utilization of the first factor - rise in temperature - is impermissible as a means of accelerating separation in nitroglycerin manufacture because of the low stability of the acid product. The second factor - the form of the separator - is usually taken into consideration. Separators are made of low height, or trays are introduced therein, with the purpose of reducing thickness of the layer of emulsion undergoing separation.

The impurities content of the initial products is limited. There are special

314 specifications for glycerol, as we have indicated above. The acids to be used in the making of the nitrating mixture are allowed to stand to settle out impurities, and at least two days are provided for this.

To reduce the separation time, a slight amount (0.05 - 0.2% of the weight of glycerol) of special additives, such as saturated hydrocarbons (paraffin, vaseline, paraffin oil) are introduced into the reaction mixture toward

315 the end of esterification. By changing the surface tension they accelerate the separation of the emulsion and make it easier for the drops of nitroglycerin to float to the top (the influence of a flo~~a~~tation effect cannot be ruled out here). In the process described here, 70 gm talc is added for this purpose. It goes without saying that these additives must be ~~indifferent~~ inert with respect to the nitro mass, and that they are removed by water when the nitroglycerin is later washed.

To eliminate colloid silicates, which also render separation difficult, Naoum (Bibl.12) recommends that hydrofluoric acid or NaF be added, inasmuch as they decompose silicates in accordance with the equation

$$4NaF + SiO_2 + 2H_2SO_4 \rightarrow SiF_4\uparrow + 2Na_2SO_4 + 2H_2O.$$

The formation of bubbles of SiF_4 gas also substantially promotes separation in this situation. Therefore, it is recommended that NaF be introduced into the nitro mass directly before separation in order for it to function most effectively.

The acid nitroglycerin is transferred from separator (9) into the preliminary washing vat ~~of~~ (material - stainless steel (11), filled half-way with cold water. If the temperature in the separator begins to rise, the nitroglycerin is cooled by letting salt solution into the coils. If noticeable decomposition of the nitro products sets

315 in, it is quickly dumped into the emergency vat (10).

The nitroglycerin flowing out of the separator contains up to 10% acid, the composition of which does not correspond to that of spent acid. Nitroglycerin holds in solution primarily nitric acid (4 parts HNO_3 per 1 part H_2SO_4), while 9 parts H_2SO_4 are required in the spent acid per 1 part HNO_3. The bulk of the acid is washed out with water in the preliminary washing vat, while removal of the residue requires very intensive cleaning processes.

Washing of the acid nitroglycerin in the preliminary wash vat (11) takes 5 min. The bulk of the acid is washed out under these conditions. If necessary, the vat may be cooled with water.

The acid fumes (up to 2% nitric acid enters the ventilating system) emitted from nitration apparatus (4), separator (9), and preliminary washing vat (11) along with the current of air, are directed to absorption tower (22) material (ceramic) where they are absorbed by water.

The nitroglycerin that has thus had its first washing is sent to the final washing shop through pipes, in the form of an aqueous emulsion, which is created by 5-minute strong mixing of the nitroglycerin with water.

Three hundred liters of 4% soda solution and all the nitroglycerin produced are charged into washing vat (14) (lead-lined wood). The vat contents are agitated with air. Washing continues for 20 min at 40°. The product, separated from the wash water, is sent to filtration to remove slimy impurities and other foreign matter.

Filtration of nitroglycerin is through flannel on a filtering table (15) (lead-lined wooden boxes). The filtered product is stored in wooden boxes (16), lined with

315 lead, and is filtered again before use. Nitroglycerin goes from the filtering department to the mixing shop of the dynamite or powder-manufacturing operation.

The acid wash water separated from nitroglycerin in the preliminary washing vat (11), goes to a trap installation having two rows of traps (17) (stainless steel). The nitroglycerin collected in the traps is sent to washing in the washing shop.

316 After separation of the nitroglycerin, the acid wash water from the trap goes to rising device (6) (stainless steel), from which it is sent through pipes to the destructive distillation column.

Spent acid, 850 kg in quantity, goes to further settling in ceramic pots (12), and from there to settling tanks (13), where it is held for 48 hrs, whereupon the nitroglycerin that has settled out is again separated off and washed, and the acid is raised by the riser (6) to the destructive distillation column, where the acid waters from the preliminary washing pot also go.

Two-stage settling of the spent acid makes it possible to increase the yield of nitroglycerin, but at the expense of a constant danger of decomposition in the settling columns.

The yield of nitroglycerin is about 94% of theoretical.

In 1943, the Rheinsdorf Plant made 6510 tons of nitroglycerin. The materials consumed per 1 ton of nitroglycerin were as follows:

Glycer~~in~~ol	429.7 kg
Nitro mixture	1982.5 kg
Recovered after treatment of spent acid:	
sulfuric acid	919.4 kg
nitric acid	253.9 kg
Steam	1950 kg
Electric power	81.90 kwh
Water	57.68 m^3
Air	273.1 m^3

The Nobel method has many inadequacies, The most important of these, aside from the fact that the process is batch-wise, is the presence of cocks on the nitroglycerin transfer pipes and the need to have the nitrator high up in the work area so as to provide gravity flow of the nitro mass into the separator. These design features significantly increase the danger of the work.

The batch-wise method of nitroglycerin manufacture developed by Nathan, Thompson and Rintula, first applied industrially in 1904, is still employed. This method is somewhat more advanced than Nobel's method. Its chief advantages are compactness, the use of clamps instead of cocks on the nitroglycerin lines, and the continuous pressure transfer of the nitroglycerin, layering out during separation, into the preliminary washing vat. This eliminates the accumulation of large quantities of unwashed (and consequently, of unstable) nitroglycerin in the separator, and that reduces the danger of the operation.

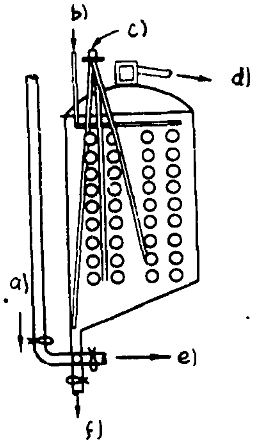


Fig.94 - Nitrator and Separator
a) Mixed acid or spent acid;
b) Glycerol; c) Compressed air;
d) Nitroglycerin; e) Spent acid;
f) To emergency vat

The compactness of the equipment employed in this method is due to the fact that esterification and separation are performed in the same apparatus.

The apparatus (Fig.94) is a cylindrical vessel with a sloping bottom making an acute angle with the vertical wall, and a conical upper portion. A vertical tube for acid delivery reaches to the bottom. Three pipes are attached to this tube, each at a distance of 30 cm from the bottom. One connects the nitrator to pressure tanks for mixed acid

316 and spent acid, a second to the spent-acid receiver, and a third to the emergency vat.
The tube is carried 30 cm below the bottom so that the nitroglycerin, when agitated,
cannot under any conditions enter the rising portion. The upper portion of the
nitrator terminates in a viewing glass and a tube joined to the preliminary nitroglycerin
317 washing tank. The nitrator is provided with a coil, a thermometer, and tubes for
leading in the compressed air.

Esterification is performed in the nitrator in the usual manner. The nitro mixture is charged into the lower portion, through a tube, and glycerin is delivered from above. At the end of the process, agitation by air is cutoff, and separation begins. The appearance of a layer of nitroglycerin is watched through the viewing glass. As soon as such a layer appears, the nitroglycerin that settles out is continually driven into the preliminary washing tank by spent acid delivered through the same tube through which the nitro mixture was charged in. This method of separation is more in accord with the requirements of safety. The spent acid is left in the nitrator over night, and this reduces corrosion thereof.

A schematic diagram of the method of producing nitroglycerin by the Nathan, Thompson, and Rentula procedure is illustrated in Fig.95.

The starting mixture is prepared in advance. Usually, mixtures of the following composition: 48 - 50% HNO_3; 47 - 51% H_2SO_4, and no more than 1% H_2O are employed. The mixture is permitted to stand for not more than 2 days. The quantity employed is computed so that the excess of HNO_3 over the theoretical will be 20 - 22% in the summer, and 18 - 20% in the winter. The bath module is 5:1.

317 Before esterification, the glycerol is heated to 45 - 50° and weighed on the decimal balance.

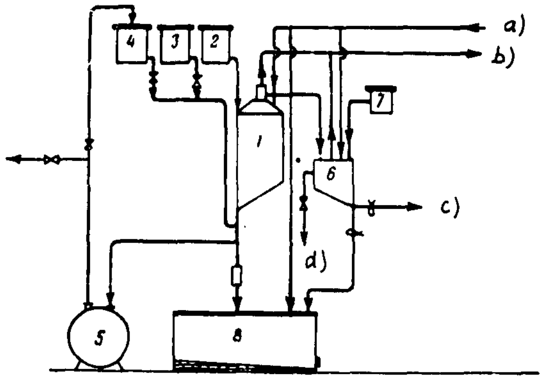


Fig. 95 - Diagram of Nitroglycerin Production by the Nathan, Thompson, and Rentula Method

1 - Nitrator; 2 - Glycerol metering tank; 3 - Mixed acid metering tank; 4 - Spent acid metering tank; 5 - Rising device; 6 - Preliminary washing tank; 7 - Water tank; 8 - Emergency vat

a) Compressed air; b) Absorption system; c) Nitroglycerin to final washing; d) Wash water

Before the process begins, the equipment is checked to make sure that it is in good order, the nitro mixture is charged into the nitrator, and it is cooled to 6 - 12°. Then, delivery of glycerin through a jet nozzle is begun. Run-in of the glycerin is performed so that the temperature of the nitrator content will rise to 23° in 10 min, subsequent to which it is held constant.

After run-in of the glycerol is completed, agitation for 5 min is performed, and the nitro mass is cooled to 17 - 18°, following which delivery of compressed air is cut off, and separation begins. When this is done, the cock for admission of spent acid

317 is opened, the spent acid raises the nitroglycerin layer to the run-off trough, through which it goes to the preliminary washing apparatus filled with water at 15 - 17°, and having closed air agitation.

318 Washing and filtration are performed in virtually the same way as with the Nobel process.

Safety techniques in batch-wise processes. The major condition for safety in nitroglycerin production is purity of the starting material. As already indicated, particularly regular specifications must be met by the glycerol. Proper composition of the mixed acid exercises a significant effect upon the level of danger, and therefore, this acid is subject to careful analysis before being permitted to go into production.

The danger of the process also depends upon the design of the apparatus. For example, a very important detail of the apparatus is the agitating device. Even when there are several tubes to deliver air, compressed air does not suffice to provide adequate agitation in all parts of the apparatus. The formation of dead zones, as well as cessation of agitation with the reaction incomplete, particularly during the run-in period, gives rise to local overheating, constituting centers of decomposition, and is therefore impermissible.

Should agitation cease and should there be no possibility of resuming it immediately, run-in of the components must be stopped, and the apparatus contents poured into the emergency vat.

Leakage of water by the coil is particularly dangerous, as this may give rise to pronounced local overheating. In order to prevent water from a damaged coil to enter the nitro mass, the water must enter the coil not under pressure, but by suction. Moreover, preventive measures to avoid coil leakage are important. Therefore, the coil is tested once a day to make sure it is waterproof. Usually, the coil is left overnight with the discharge cock closed, and under pressure, and is checked in the morning. It is not recommended that the work be run days on end in a single apparatus.

Cessation of delivery of water into the coil during component run-in immediately causes the mass to overheat, and this is impermissible. Therefore, if it is impossible to resume cooling at once, and if the reaction has not gone to completion, run-in of the components must be stopped and agitation increased, with observation of temperature. If the temperature rises to 30°, the nitrator contents must be dumped into the emergency vat.

When the process goes normally, the temperature of the nitro mass rises smoothly and is readily controllable by the rate of glycerol run-in (with simultaneous cooling by water or brine delivered into the coil). If the process goes abnormally, the temperature rises in jumps and this will testify to the existence of local overheating. If this occurs agitation is increased. If the temperature continues to rise it is necessary, without waiting for the mass to heat to 30°, to dump the apparatus contents into the emergency vat, having first disconnected glycerol delivery.

Separation is the most dangerous operation, inasmuch as the acid nitroglycerin is of low stability and, in the absence of agitation, local overheating may arise, resulting in decomposition of the nitroglycerin. These processes may arise most readily if the reaction has not gone to completion, and in the presence of incompletely denitrated glycerol or strong spent acid. For this reason, retention of the nitroglycerin in the separator is particularly dangerous.

#23

318 If the temperature in the separator should rise spontaneously, it is necessary to start agitation, and if this measure does not reduce the temperature, the separator contents must be dumped into the emergency vat.

In any instance in which danger arises and the need to dump the nitro mass into the emergency vat appears, the foreman conducting the process leaves the workshop after opening the dump valve, warning the other workers of the danger and of the need to go to a shelter.

319 The emergency vat must contain water in no less than five times the volume of the nitro mass in the nitrator or separator, and must have an air inlet for agitation. The bottom of the vat is inclined for convenience in collecting the nitroglycerin.

Dumping of the nitro mass into the emergency vat is accompanied by emission of a large quantity of nitrogen oxides, giving rise to the danger of explosion. Therefore, there are those who believe that the emergency vat should be outside the workshop. However, it must be borne in mind that removal of the vat to a distance may be the cause of explosion of the nitroglycerin in the pipe while the nitro mass is being dumped.

Naoum (Bibl.12) observes that dumping of the contents of nitrator or separator into the emergency vat does not always save the situation. Of every 100 such cases, 20 terminate with an explosion in the tank, and sometimes the residual nitroglycerin explodes in the nitrator. In order to achieve safer drainage of the nitro mass, the apparatus (nitrator and separator) are equipped with cocks that open automatically, for example, under the action of compressed air. This automatic equipment can be started not only directly from the work station of the apparatus

319 operator, but also from the shelter.

When the automatic equipment for dumping the nitro mass into the emergency vat is turned on, signals that warn all persons in the given building of danger start to operate.

Continuous nitroglycerin production processes. When nitroglycerin is produced by batch-wise methods, a considerable amount of it accumulates in the department. As a consequence, should an explosion occur, great destruction may ensue. The danger in nitroglycerin production may be reduced substantially by using continuous-action apparatus, which is coming into ever wider use.

In the continuous method, a comparatively small amount of explosive is in the process at any time, as a consequence of which there is a substantial reduction in the possibility that the explosion will be transmitted to other shops, and the amount of ~~danger~~ damage done by explosion is reduced to a minimum.

Carter (Bibl.13) illustrates the foregoing by the following percentage values in terms of hourly output: the maximum amount of nitroglycerin in the nitrator when the periodic method is used is 200 kg, that in the separator 200 kg, while in the continuous method the figures are 36 kg and 4 kg respectively.

At the present time, the control of the continuous process has been completely automated. Control is carried out in a special booth beyond the shop embankment and makes for a considerably greater degree of dependability in the functioning of the apparatus (Bibl.14).

A stimulus to the development of continuous processes has also been the considerable rise in the production of powders based on nitroglycerin.

319 Continuous-process apparatus exist today in many countries: England, the USA, France, Germany, Belgium, Sweden, Canada, etc. (Bibl.13,15,16).

The first continuous-method installation, of 100 kg hourly output, was setup in 1928 by A. and K. Schmid in Csechoslovakia, whereupon the Schmid process modified somewhat by the DAT Company was employed in Germany (Bibl.17, 18, 19) and in Austria (Bibl.20). The capacity of installations employing the Schmid process today attain 1200 kg nitroglycerin per hour.

Figure 96 presents a diagram of the flow of nitroglycerin production in German enterprises by the Schmid method as carried out by the Meissner Company (Bibl.17). The most important factor in the system is simultaneous delivery of glycerol and the nitro mixture in the required quantities.

In the first installations, the components were metered into the nitrator by plunger pumps. The piston pump provided delivery of a constant stream of glycerol, regardless of its viscosity. The glycerol and nitro-mixture pumps were mounted on a
320 single shaft, and the inside dimensions of the pumps were chosen so that the glycerol and mixed acid would be delivered in the required quantities.

At modern installations, automatic metering of all the components (including the wash water) takes place through metering devices, in the following sequence. The nitro mixture, having passed through the filter into the metering device, goes, further, to a special receiver setup in the nitration workshop. When the latter has been filled, a pressure of exactly 1 atm (gage) is established therein by means of compressed air. This is held constant during the entire period of operation of the apparatus. The constancy of the pressure in the receiver is established by the compressed-air delivery control. The metering device is also connected to a small air vessel by means of a

320 line going to the bottom of the metering device. This vessel is also designed to maintain a constant pressure in the receiver should the delivery of nitro mixture therein be increased.

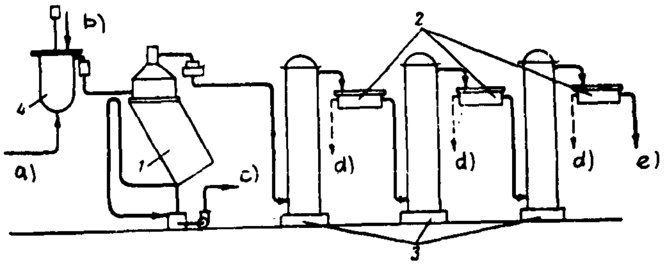


Fig.96 - Diagram Illustrating Continuous Production of Nitroglycerin (NGTs)

1 and 2 - Separators; 3 - Washing columns; 4 - Nitrator

a) Nitro mixture; b) Glycerol; c) Spent acid; d) Water; e) Nitroglycerin

The glycerol is heated by a device that automatically regulates its temperature, prior to delivery into the nitration apparatus. The purpose of this is to hold the viscosity constant. At the end of the line delivering the glycerol, there are two spray nozzles, which, if the delivery of air is constant, are set to deliver the required amount of glycerol into the apparatus.

In order to make sure that the amount of gXXXX glycerol passing through the spray hozzles is what it should be, the nozzles are connected to a very sensitive XXXXXXXX monitoring device which cuts off delivery of glycerol to the nitration apparatus if the agitator should cease to operate. A variable-area flow meter is also provided along the acid line. These metering devices make for a very high accuracy of metering (a deviation of no more than 0.3%) will occur).

320 Esterification of the glycerol takes place in a nitrator. The glycerol is delivered from above, at first into weak and virtually spent acids. The fresh nitro mixture is delivered from the bottom, dilutes the spent acid in the apparatus, and is delivered by an agitator through the condensing volume of the apparatus. Inasmuch as the amounts of reacting components corresponds precisely to the capacity of the cooling surface, capable of removing the heat emitted, no sharp rise in temperature will occur during the process.

In the continuous-process nitrators, the conditions of esterification are less severe than in batch-type systems, inasmuch as the reaction occurs in a spent-acid medium. The productivity of the nitrator depends upon its cooling surface.

Figure 97 illustrates the design of a Schmid nitrator, and Figure 98 that of a Meissner nitrator. In the second type of nitrator, the cooling surface is larger.
321 It consists of 300 vertical tubes installed along the perimeter. The cooling brine enters the space between the tubes from below and emerges at the top.

In both the first and the second apparatus, the nitro mixture is delivered beneath a plate which directs the mixture to the outer walls of the nitrator for cooling. The nitro mass flows out of the upper portion of the nitrator into the separator.

The agitator installed in the nitration apparatus functions like a propeller-type pump to raise the reaction mixture from the bottom and drive it through a system of coils within the apparatus.

Thanks to the creation of a fine emulsion of nitroglycerin in spent acid, the reaction mass becomes completely safe in terms of explosion, as has been demonstrated by special experiments. Even the bursting of a No.8 cap will not cause it to detonate.

321 In view of the rapidity of the esterification reaction, and as a consequence of the use of mechanical agitation, volatilization of nitric acid out of the apparatus virtually does not occur. As a consequence, the yield of nitro product is more than 1% higher than when batch-type nitration is employed.

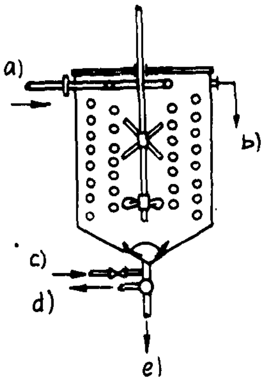


Fig.97 - Schmid Nitrator

a) Glycerol; b) Emulsion; c) Nitro mixture; d) To separator; e) To emergency tank

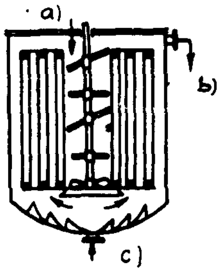


Fig.98 - Meissner Nitrator

a) Glycerol; b) Emulsion; c) Nitro mixture

The nitroglycerin, emulsified in spent acid, goes to a separator.

To speed separation, A.Schmid designed a separator so as to reduce to a minimum the thickness of the layer of emulsion and to facilitate separation of the drops of nitroglycerin. The separator (Fig.99a) is a tapered prism terminating in two pyramids. The emulsion enters one of the pyramids, and the spent acid leaves through the other. Within the separator, there are corrugated plates, arranged parallel to each other. As the emulsion moves through these plates, the nitroglycerin rapidly separates from the spent acid over a short portion of the route and, combining with the rest of the nitroglycerin that has separated out and has gathered on the inside surfaces of

321 the plates, rapidly moves upward along a trough.

Figure 99b shows the improved Schmid separator (employed by the Meissner Company) constituting a box in the form of a parallelepiped with a square base. Within the separator, there are 30 corrugated partitions. The emulsion inlet is above the partitions, in the upper portion of the separator. This makes for superior separation of the spent acid from the nitroglycerin, inasmuch as emulsified acid separates more rapidly from the nitroglycerin than does emulsified nitroglycerin from acid. The cover terminates, in its upper portion, with a glass cylinder for nitroglycerin removal. The spent acid is removed from the lower portion of the separator through a U-tube
322 in such fashion that the acid removal is 30 cm lower than the nitroglycerin removal. Before the separator starts to function, it is filled with spent acid from the preceding operation. After separation, the spent acid in this type of separator usually contains 0.1 - 0.3% emulsified nitroglycerin, and is of approximately the following composition: 12% HNO_3; 72% H_2SO_4; 14% H_2O; about 2% dissolved nitroglycerin and 0.3% nitroglycerin in emulsion.

The nitroglycerin arriving from the separator is transparent. However, a rather large quantity of nitric acid (as much as 7%) is dissolved therein, as well as 0.5% H_2SO_4, 0.1% H_2O, and 1.5% dinitroglycerin. The bulk of the acid is very readily washed free of the acid products. However, the residual acid may only be washed free by intensive agitation of nitroglycerin with wash water or with soda solution over a long period of time.

Washing of the acid nitroglycerin is performed in washing columns consisting of 25 glass plates between which are compressed sheets of perforated stainless steel.

322 The acid nitroglycerin, the wash water, and compressed air are delivered into the lower portion of the column. The nitroglycerin rises, in the form of emulsion, and goes to the separator, from which it goes to the next column. All told, the system contains 5 - 6 washing columns and an equal number of separators. In the first two columns, washing is by hot water, in the second by weak soda solution, and in the third by weak soda solution, and in the fourth again by water.

The two-stage washing of nitroglycerin makes for reduced product losses and reduced separation time, even with the parallel flow of components. Washing is performed in a glass column, with a perforated partition at its bottom (Bibl.21). The wash liquid is driven through the bottom of the column by means of a jet, and, together with compressed air which emulsifies the nitroglycerin therein, rises to the top of a column and flows over its edge into the intermediate separator. From the separator, the nitroglycerin collected at its bottom goes to another, identical column, while the wash water passes through a settling tank in which the nitroglycerin is collected.

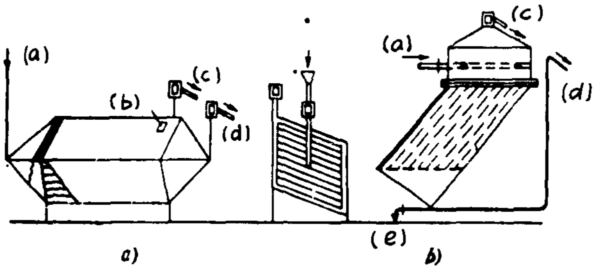


Fig.99 - Separators

a) Schmid; b) Meissner

(a) Nitro mixture;(b) Viewing window; (c) Nitroglycerin; (d) Spent acid

(e) To emergency vat

322 Reduction in the number of washings diminishes nitroglycerin losses. The coefficient of distribution of nitric acid between the nitroglycerin and the water is such that, with an equal volume of water, one can obtain nitroglycerin of less than 0.2% HNO_3 acidity by a single washing of the nitroglycerin, if good mixing and sufficiently careful separation is provided. Under these conditions, the remaining acid may be removed by a single washing with weak soda solution.

323 Table 99 illustrates the conditions of stabilization by the two-column method.

Table 99

a)	b)	c)	d)	e)		h)
				f)	g)	
1	9	i)	1:1	22	19	30
2	11	j)	2:3	40	29	34

a) Column number; b) Inside diameter, cm; c) Wash liquid; d) Ratio of wash liquid to nitroglycerin by volume; e) Temperature at column inlet, °C; f) Wash liquid; g) Nitroglycerin; h) Temperature of liquid at outlet, °C; i) Water; j) 2.5% Na_2CO_3 solution

With this method of washing, nitroglycerin losses reach no more than 0.22%, whereas with washing in three columns they reach 0.31%, and in five columns - 0.49%.

In Germany, nitroglycerin has been washed in three columns by a countercurrent method (Bibl.17). This made it possible further to increase the yield of nitroglycerin by reducing the amount of wash liquid which carries off a portion of the product after washing. By the countercurrent method, the same portion of solution is employed in all three columns. Washing was performed with cold water (15°) and a

323 3 - 5% soda solution.

In addition to the Schmid-Meissner apparatus we have described, a number of Biacci installations were used in Germany at various plants. These have a rather improved design of nitrators and separators (Bibl.17). The first continuous nitroglycerin plants in Canada (Bibl.13) and in the USA (Bibl.15) were designed to use the Biacci method (Bibl.16).

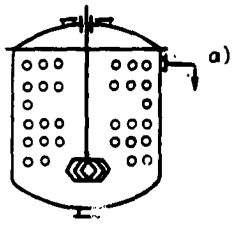


Fig.100 Biacci Nitrator

a) Emulsion

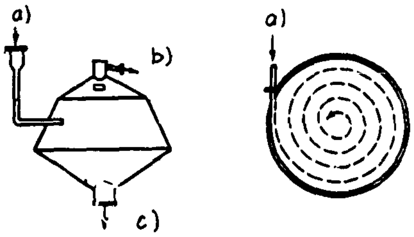


Fig.101 - Biacci Separator

a) Nitro mass; b) Nitroglycerin;
c) Spent acid

Under the Biacci method (Bibl.16,17), the nitrator is a cylindrical vessel with a spherical top and bottom (Fig.100). It is provided with a turbine agitator which makes for intensive stirring and circulation of the nitro mass. The initial products are introduced from above. They are taken into the middle of the turbine by suction and are thrown toward the periphery, The liquid emerging from the turbine acquires a circular and spiral motion. The heat emitted in the reaction is drawn off by coils which fill the entire apparatus.

The separator (Fig.101) is a low round reservoir with conical top and bottom. The upper portion terminates in a glass cylinder. The emulsion of nitroglycerin and spent

323 acid enters the overflow tube of the nitrator in the upper portion of the side wall of the separator at a tangential direction, and is always in rotary motion. As a consequence of the rotary motion of the emulsion, consisting of drops of nitroglycerin
324 and spent acid, a kind of centrifuging is set up. The drops of nitroglycerin merge into large ones, and rapid separation of the emulsion occurs. The easy flow of emulsion also prevents local overheating.

Complete separation of the nitroglycerin and spent acid occurs in 13 min, with an apparatus capable of producing 700 kg/hr. However, the bulk of the nitroglycerin is separated in 3 min. A separator of 240 ltr capacity suffices for an output of 700 kg/hr.

The separated nitroglycerin may be seen in the upper portion of the viewing glass. The level of nitroglycerin is regulated by a special device for running in the spent acid. The spent acid enters the second separator for further settling of the nitroglycerin and then goes to denitration.

Figure 102 illustrates a Biacci apparatus.

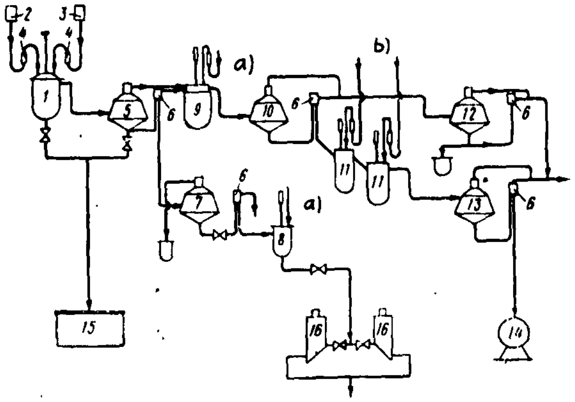


Fig. 102 - Diagram of Biacci Apparatus

1 - Nitrator; 2 and 3 - Glycerol and nitro mixture containers; 4 - Metering devices; 5,7,10,12,13 - Separators; 6 - Additional separators; 8 - Diluter; 9,11 - Washing apparatus; 14 - Nitroglycerin receiver; 15 - Emergency vat; 16 - Settling vessels
a) Water; b) Soda solution

324 Glycerol and nitro mixture from reservoirs (2) and (3), under a constant 2 atm pressure, are delivered to nitrator (1). The temperature of the acid is 5 - 10°, and that of the glycerol 15°. The quantity of entering components is controlled by metering devices (4). The temperature in the nitrator (25°) is sustained with the aid of the cooling brine, fed to the coil. The mixed acid contains 50% H_2SO_4 and 50% HNO_3; at a module of 1:5.

From the nitrator (1), the nitro mass is fed into a first separator (5) from which the spent acid goes through an additional separating box (6) to a second separator (7) and from there to settling [before settling it is diluted with 3% water in the reservoir (8)].

From the first separator (5), the nitroglycerin is sent to a preliminary washing apparatus (9) where it is mixed with cold water and is then treated in a third separator (10). From the separator (10), the nitroglycerin is sent to a washing apparatus (11), while the water again goes to separation in a fourth separator (12). In the washing apparatus (11) the nitroglycerin is washed with a 5% soda solution at 30° and the resultant emulsion is fed to the separator (13) from where the nitroglycerin is supplied to the receiver (14) and then sent to the consumer.

In the case of current cutoff, power reserve is provided by storage batteries. In the nitrators and separators, contact thermometers are mounted.

325 which, at 30°, cut in a signal while, at 33°, the mass is dumped into the emergency vat (15) filled with conc. sulfuric acid, in which the nitroglycerin saponifies very rapidly.

The washing system of such arrangements is of conventional location.

In the case of shut-down of water inflow into the reservoir, into which the nitroglycerin is admitted, the latter may be detonated by means of a mechanical mixer.

The literature (Bibl.14) contains brief references to a plant in Ardur (Scotland) where IX nitroglycerin is produced by the Biacci process.

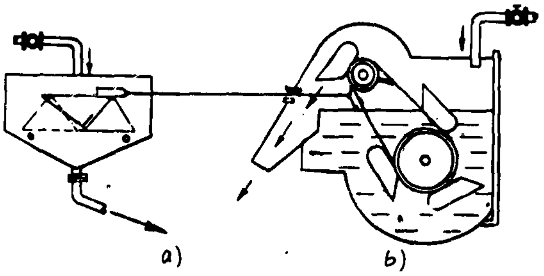


Fig.103 - Metering Device for Acid and Glycerol

a) Meter for acid; b) Meter for glycerol

Rachinskiy (Bibl.22) has developed a system for the continuous nitration of glycerol, in general design coinciding with the Schmid-Meissner scheme.

An original stage in this system is the continuous metering of the mixed acid and glycerol. The metering interferes with interacting components and can only work in synchronism. The design of such a metering device is shown in Fig.103.

The metering device for glycerol constitutes a receiver with a constant liquid level, inside of which a slowly rotating disk is mounted with reinforced scoops of special design. The scoops maintain a constant volume of liquid, raising and forcing this liquid through a tube into the nitrator. An advantage of this metering device lies in the fact that it works independently of the temperature of the ambient medium; this is very important inasmuch as the viscosity of glycerol strongly fluctuates with XXX variations in the temperature.

Transfer of nitroglycerin from one to the other is usually effected by gravity through pipelines.

325 To prevent transmission of detonations through the pipeline to another section of the plant, detonation interrupters are installed. The design of such detonation interrupters has been described in a book by Naoum (Bibl.12). There are water-filled vessels in which the stream of nitroglycerin is broken by a layer of water. However, this method does not completely guarantee that a detonation will be interrupted. Emulsions containing 1.5 volume water per 1 volume nitroglycerin detonate readily (Bibl.23).

Long-distance transportation of nitroglycerin is done in mixtures with acetone or other solvents, subsequent to which it is separated from the acetone by dilution of the mixture with water (Bibl.6, 10). It is necessary to prevent ignition of the solvent in transportation (Bibl.24).

Problems of denitration of the spent acid and extraction of the nitroglycerin from the wash water are important in nitroglycerin production.

Denitration of the spent acid, with subsequent concentration of the sulfuric acid is similar, in general outline, to the denitration of spent acids derived
326 in the production of aromatic nitro compounds. A peculiarity of the production process is the presence of nitroglycerin and the substantial quantity of nitric acid in the spent acid. The presence of nitroglycerin greatly increases the danger of denitration, and therefore the spent acid is subjected to long-term settling before this process.

Settling may be avoided if, prior to denitration, the spent acid is sent through a destructive distillation column. A description of the operation of this column is provided below, on p.331. The spent acid passing through the destructive distillation column is simultaneously separated from the basic component containing nitric acid (Bibl.25).

Nitroglycerin, dissolved in the wash water, usually is not extracted. It is only the nitroglycerin, present in the form of emulsion, that is trapped in special settling devices and thus removed from the wash water.

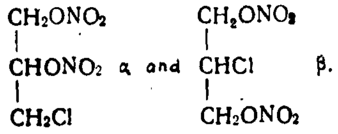
One British patent (Bibl.26) proposes that the wash waters containing nitroglycerin be treated with mononitrotoluene. This latter extracts the nitroglycerin. The mononitrotoluene, containing nitroglycerin, should, it is recommended, be employed as an explosives component.

B. Other Explosive Glycerol Esters

Monochlorohydrindinitrate and diglycerintetranitrate are of practical significance as the basis of non-freezing dynamites. Prior to the Second World War, monochlorohydrindinitrate was made use of in Germany, and diglycerintetranitrate in the USA. Diglycerintetranitrate was also employed as a non-volatile solvent in powders.

Section 1. Monochlorohydrindinitrate (Bibl.12)

Monochlorohydrindinitrate is an ester of chlorohydrin and nitric acid, having two isomers:



$$\begin{array}{l} CH_2ONO_2 \\ | \\ CHONO_2 \\ | \\ CH_2Cl \end{array} \ \alpha \ \text{and} \ \begin{array}{l} CH_2ONO_2 \\ | \\ CHCl \\ | \\ CH_2ONO_2 \end{array} \ \beta.$$

The first isomer predominates in the technical product. Monochlorohydrindinitrate is a transparent and colorless oil, having less viscosity than nitroglycerin. It has a mildly aromatic odor and a specific gravity of 1.54 at 15°. The technical product has a yellow-brown color. The freezing point of the α-isomer is -5°, and that of the β-isomer 16.2°. The product is susceptible to considerable supercooling and may, for a long period, remain in the supercooled condition at -20° without crystallization.

326 The freezing point of the technical product is not constant.

Monochlorohydrindinitrate is not hygroscopic. Its volatility is somewhat higher than that of nitroglycerin. It is readily soluble in ethyl and methyl alcohol, ethyl ether, acetone, acetic ethyl ether, glacial acetic acid, chloroform, benzene, etc. It is of low solubility in water (0.23% at 15°), carbon disulfide and benzene.

Monochlorohydrindinitrate is miscible in any ratios with nitroglycerin. A mixture thereof with 25% nitroglycerin is non-freezing, for all practical purposes, at -20°.

Pure monochlorohydrindinitrate gelatinizes collodion rather weakly, but when mixed with nitroglycerin, its gelatinizing capacity is high.

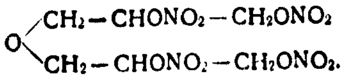
In the chemical sense, monochlorohydrindinitrate performs as a nitric ester and,
simultaneously, as though chlorine-substituted. It has a negative oxygen balance and,
327 in addition to the incomplete combustion products - CO and H_2, also releases a poisonous
hydrogen chloride, which is a shortcoming thereof as an explosive.

Monochlorohydrindinitrate is considerably more shock sensitive than is nitroglycerin. The heat of its explosive decomposition is 1140 kcal/kg, which is 23% lower than that of nitroglycerin.

Monochlorohydrindinitrate is produced in the same apparatus and virtually by the same technology as nitroglycerin. However, its production is less dangerous than the manufacture of nitroglycerin, inasmuch as less heat is liberated in esterification. Separation goes more rapidly thanks to the lower specific gravity of the nitro product (1.54 as against 1.60).

Section 2. Diglycerintetranitrate (Bibl.12)

This is an ester of nitric acid and diglycerin ether:



It was first obtained in 1861 by Lourenzo (Bibl.6).

Diglycerintetranitrate is a viscous oil, not hygroscopic, insoluble in water, readily soluble in alcohol, ether, and other organic solvents. It does not crystallize even when cooled deeply. Its gelatinizing capacity is insignificant, but a mixture with nitroglycerin gelatinizes collod

As an explosive, diglycerintetranitrate is weaker than nitroglycerin. Its heat of explosive decomposition is 1370 kcal/kg. Its sensitivity to mechanical effect is somewhat lower than that of nitroglycerin.

Diglycerintetranitrate is obtained by etherification of diglycer~~in~~ol with a sulfuric acid mixture in the same apparatus and by the same technology as that employed in production of nitroglycerin. However, before it is meted into the nitrator, diglycer~~in~~ol has to be heated to 50 - 60°, to reduce its viscosity, which is eleven times as great as that of glycer~~in~~ol. The high viscosity of the product complicates esterification and creates particularly great difficulties of separation and stabilization as a consequence of the formation of stable emulsion. Stabilization is performed with a table salt solution to combat the formation of a stable emulsion.

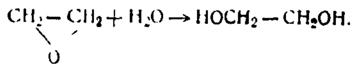
The product yield is 81% of theoretical.

C. Ethyleneglycoldinitrate and Diethyleneglycoldinitrate

Ethyleneglycoldinitrate and, particularly, diethyleneglycoldinitrate were widely employed during World War II as substitutes for nitroglycerin in dynamite and powders.

Efforts to discover substitutes for glycer~~in~~ol were begun as far back as World War I, inasmuch as manufacture of this product is based chiefly upon the use of foodstuffs. The most fruitful work proved to be the utilization of ethyleneglycol instead of glycer~~in~~ol to make nitric esters. Ethyleneglycol is made synthetically from ethylene or from hydrolyzed alcohol, and therefore has distinctive advantages over glycer~~in~~ol.

Today, ethyleneglycol is obtained primarily by hydration of ethylene oxide:



$$\underset{\diagdown O \diagup}{CH_2-CH_2}+H_2O \rightarrow HOCH_2-CH_2OH.$$

328 The process is run in a neutral medium under a pressure of 10 - 12 atm at 160 - 180° in a continuous autoclave, consisting of a steel column 10 m high and 1 m in diameter. The solution emerging from the autoclave is vaporized in a two or three-section steaming apparatus, and is vacuum-distilled.

A small portion of the ethyleneglycol is obtained by hydrolysis of dichloroethane:

$$ClCH_2-CH_2Cl+Na_2CO_3+H_2O \rightarrow HOCH_2-CH_2OH+2NaCl+CO_2.$$

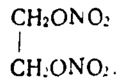
Despite its good gelatinising properties and great power, ethyleneglycoldinitrate could not be used to make powders because of its high volatility. It has gained application only in dynamite.

Contrariwise, diethyleneglycoldinitrate (the raw material for which is a synthetic product - diethyleneglycol, obtained from ethyleneglycol) proved to be superior even to nitroglycerin as a solvent for nitrocellulose. It plasticizes nitrocellulose more readily, and powders based on this substance are more elastic, while their stability is higher than that of nitroglycerin powders. Moreover, the production of diethyleneglycol powders is less dangerous than the production of nitroglycerin powders (Bibl.17).

During World War II, triethyleneglycoldinitrate - an ester of nitric acid and diethyleneglycol - was employed to produce a powder clamined to have the lowest ratio of rate of combustion to temperature.

Section 1. Ethyleneglycoldinitrate (Nitroglycol)

Ethyleneglycoldinitrate is an ester of nitric acid and glycol:



$$\begin{array}{c} CH_2ONO_2 \\ | \\ CH_2ONO_2 \end{array}$$

It was first obtained by Henry in 1870 (Bibl.6), and is used only as a component in low-freezing dynamites.

Nitroglycol is a transparent and rather free-flowing liquid of specific gravity $d^{20^\circ}_{20^\circ}$ = 1.489 (Bibl.6). Its viscosity is considerably less than that of nitroglycerin, and is 4 centipoises. The freezing point is -21.7.

The distillation of nitroglycol at normal pressure is accompanied by decomposition. It is more readily steamed distilled than nitroglycerin.

The vapor pressure of nitroglycol is high (Bibl.17). Its values at various temperatures (Bibl.7) is presented in Table 100. The volatility of nitroglycol is considerably higher than that of nitroglycerin.

Table 100

a)	b)
0	0,0044
20	0,038
40	0,26
60	1,3
80	5,9
100	22,0

a) Temperature, °C; b) Vapor pressure, mm Hg

Nitroglycol is of low hygroscopicity, is readily soluble in tetryl and methyl alcohols, ether, chloroform, acetone, benzene, nitrobenzene, and toluene, and is difficultly soluble in carbon tetrachloride. In 100 g water, 0.52 gm and 0.85 gm nitroglycol will dissolve at 25° and 60° respectively (Bibl.6). As is evident from the data adduced, the solubility of nitroglycol in water is considerable, and this must be borne in mind in washing it.

Nitroglycol is readily gelatinized by collodion at room temperature.

In its chemical properties and physiological effects nitroglycol is analogous to nitroglycerin. Because of its high volatility, safety rules must be rigidly adhered to.

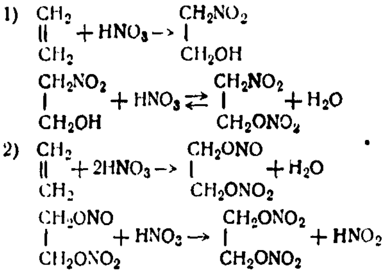
329 Nitroglycol has a zero oxygen balance and exceeds nitroglycerin in potential energy. The heat of explosive decomposition of nitroglycol is 1655 kcal/kg (Bibl.6), the volume of gaseous explosion product is 737 ltr/kg, and expansion in the Trauzl block is 600 ml. Nitroglycol is substantially less sensitive to shock

than is nitroglycerin. It detonates when a 2 kg load is dropped from a height of 10 - 12 cm, whereas nitroglycerin detonates when the same load is dropped from the height of 4 - 5 cm. Moreover, the detonation sensitivity of nitroglycol is considerably higher than that of nitroglycerin. Upon contact with flame it ignites and burns with hissing, while local overheating may result in an explosion, although the tendency to explode is less than that of nitroglycerin.

Nitroglycol is produced on the same kind of equipment as is nitroglycerin, and by a highly similar technological cycle. Because of the low freezing temperature of nitroglycol, the nitration process may be run at a lower temperature and this reduces losses due to volatilization and solution in the spent acids. In washing nitroglycol, it is recommended that excessively high wash-liquid temperatures and large volumes thereof be avoided, so as to eliminate possible losses of product due to volatility and the comparatively high solubility. The tendency of acid nitroglycol to decompose is less than that of acid nitroglycerin, and this reduces the danger in its production.

Nitroglycol may also be obtained by direct nitration of ethylene without conversion thereof to glycol. Nitration is performed by transmitting ethylene through mixed acid at 50° in the presence of $AgNO_3$ or Ag_2SO_4 as promoter. The result is an oily product of specific gravity 1.47, consisting primarily of a mixture of nitroglycol and of nitroethylalcohol. The nitroglycol is separated out of the mixture by live-steam distillation (Bibl.27). The nitration reaction

mechanisms are:



Nitroethylalcohol;

Nitroethylnitrate;

Glycolnitritenitrate;

Nitroglycol

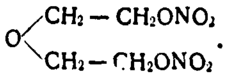
The two reactions go simultaneously, and the result is a mixture of 40 - 50% nitroglycol and 50 - 60% nitroethylnitrate, the total being 60 - 70% of the ethylene absorbed.

The mixture of nitro products obtained is a brisant explosive and may be employed in the manufacture of dynamite.

The best mixed acid for nitration has the following composition: 50% H_2SO_4, 45% HNO_3, and 5% H_2O. Nitration is run at 20 - 25°. The production of a virtually pure stable nitroglycol is achieved by treating the oil with ammonia which dissolves the unstable components of the oil. The amount of nitroglycol released is 25% in terms of the ethylene.

Section 2. <u>Diethyleneglycoldinitrate (Diglycoldinitrate)</u>

Diethyleneglycoldinitrate is an ester of nitric acid and diethyleneglycol ether:



It was first described by Rinkenbach in 1927 (Bibl.6).

330 Starting in 1933, in Germany, broad studies of diglycoldinitrate were made with the purpose of using it to produce powders, and in 1938 - 1939 complete conversion of the industry to nitrodiglycol powders was virtually achieved. Nitrodiglycol powder is today being made in place of nitroglycerin powder in other countries as well.

The major advantage of diethyleneglycoldinitrate is the fact that it can be produced from synthetic raw materials. Moreover, according to the data of German specialists, it enjoys a number of other advantages as well. The superior plasticizing capacity of diethyleneglycoldinitrate permits smaller quantities of this substance than of others to be used in making powders. Thus, in Germany, a powder containing only 15% nitrodiglycol was developed.

The powder mixture based on diethyleneglycoldinitrate is more readily rolled, more plastic, and rolling is accompanied by a smaller number of flashes. The use of this powder mixture permits larger quantities of non-plasticizing crystalline substance (for example, nitroguanidine) to be included.

Diethyleneglycoldinitrate permits readier production of "cold" powders, and this increases the service life of the weapon. It must, however, be ordered that this powder has considerably less power than does nitroglycerin.

Diethyleneglycoldinitrate is a colorless liquid having a specific gravity of $d^{20^\circ}_{15^\circ}$ = 1.385 (Bibl.6) and a viscosity of 8 centipoises at 20°. Two forms of diethyleneglycoldinitrate exist: the stable form, with a freezing point of 2°, and the labile form having a freezing point of -10.9°.

The vapor pressure of diethyleneglycoldinitrate at 20 and 60° is 0.0036 mm and 0.130 mm Hg respectively. Thus, its volatility is just as great as that of nitroglycerin, but only one fourth that of nitroglycol.

Diglycoldinitrate is readily soluble in nitroglycerin, glycoldinitrate, ether, and methanol. It is insoluble in ethanol, carbon tetrachloride, and carbon disulfide. Its solubility in water is 0.40 and 0.46 gm per 100 gm water at 25 and 60° respectively. It readily plasticizes nitrocellulose (substantially better than does nitroglycerin, but somewhat less satisfactorily than does nitroglycol).

The chemical properties of diglycoldinitrate are analogous to those of nitroglycerin, and its toxicity is the same. Its explosive properties are lower than those of nitroglycerin. The heat of explosive decomposition is 948 kcal/kg, the flashpoint is 210 - 215°, the volume of gaseous explosion products is 919 ltr/kg, and expansion in the Trauzl block is 425 ml. Shock sensitivity is low and is 175 - 180 cm when a 2 kg weight is employed (Bibl.12).

Diethyleneglycoldinitrate is produced by esterification of diethyleneglycol with mixed sulfuric and nitric acid on apparatus of the same design as that used to produce nitroglycerin (Bibl.7), but the technological process has certain specific features. More rigorous demands must be met by the starting raw material, particularly, the diethyleneglycol. The latter, like glycerin, is subjected to test esterification in addition to the standard tests for the purpose of holding impurities to very narrow limits.

In Germany, esterification of diethyleneglycol at the majority of enterprises is performed by the Nobel method (as is the case with glycer~~in~~ol), and only at a few plants is it done on continuous-action apparatus employing the Meissner method.

Diethyleneglycol is esterified by a mixed acid of the following composition: 33 - 35% HNO_3; 64 - 65% H_2SO_4, and 0 - 2% H_2O. The specific features of the process are the following: a coolant brine at -15° is introduced into the nitrator coils, and the entire process is run at 15 - 20°, whereas at its conclusion, 331 the mixture is cooled to 10°. The separator is provided with coils to cool the reaction mixture should the temperature rise to over 10°. The reaction mass contains 4 - 6% diethyleneglycoldinitrate, tending to decomposition, in dissolved form.

Talc is added at some plants toward the end of the separation period to accelerate the process.

Cooling is also sustained in the first washing vat, as a considerable quantity of nitric acid is present in solution in the products separated from spent acids. For the rest, the process is wholly identical to nitroglycerin production.

The spent acid is of approximately the following composition: 60% H_2SO_4; 10 - 11% HNO_3; 23 - 25% H_2O and 3 - 4% diethyleneglycoldinitrate. Because of the readier oxidizability of diethyleneglycoldinitrate, and because of the higher content thereof in spent acid, the latter is less stable, and long-term settling thereof, as is the case in nitroglycerin production, is not permissible. Therefore, the spent acid is immediately sent to stabilization and then to denitration. Stabilization is performed in a destructive distillation column by the procedure illustrated in Fig.104.

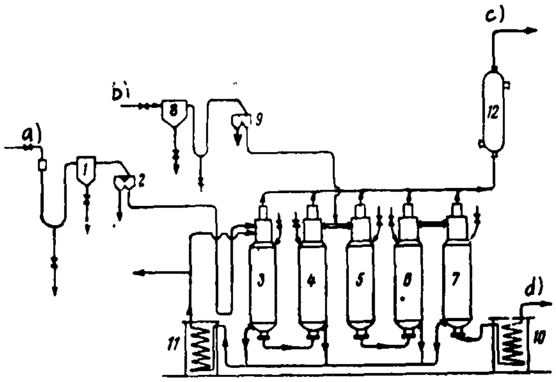


Fig.104 - Diagram of Stabilization of Spent Acid

1 - Spent-acid collector; 2, 9 - Metering tanks; 3, 4, 5, 6, 7 - Destructive distillation columns; 8 - Trap; 10, 11, 12 - Condensers

a) Spent acid; b) Wash water; c) To absorption; d) To denitration

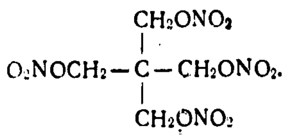
The spent acid goes to collector (1), from which, through a metering tank (2), it goes to the first vessel of the destructive distillation column (3), which has five such vessels (3 - 7). The interior of these vessels is of thermosilid, and the heated jacket is of cast steel. The acid wash water goes to trap (8), where another small quantity of entrained nitro products is removed. From trap (8), the wash water goes to metering tank (9) and then to the third vessel of the destructive distillation column (5).

Before the start of the work, the destructive distillation column is filled with 70% sulfuric acid and heated with steam (3 atm) to 90 - 100°. Subsequently, this temperature is maintained by the heat of reaction emitted. During the period required for the spent acid to pass through the column, the nitro products it contains decomposes in its entirety. The heated acid from the final vessel of the destructive distillation column (7) goes to condenser (10), and from there to denitration and concentration. The dilute nitric acid goes through a common line from the five vessels of the destructive distillation column to condenser (11), and from there back to the destructive distillation column. The nitric oxides, both from the condenser (11), and from the vessels, go to absorption via condenser (12).

332 Denitration and concentration of the/spent acids freed from organic substances may be performed in any concentration column, with addition of the corresponding quantity of sulfuric acid.

D. <u>Pentaerythritoltetranitrate (PETN, Pentrite)</u>

Pentaerythritoltetranitrate (PETN) is a nitrate ester of a multiatomic alcohol of pentaerythrite. It is first obtained by Tollens in 1891. It is the most stable of the nitric esters and is an explosive of comparatively low sensitivity to mechanical effects. Its formula is



$$O_2NOCH_2-\overset{\displaystyle CH_2ONO_2}{\underset{\displaystyle CH_2ONO_2}{C}}-CH_2ONO_2.$$

PETN is one of the powerful brisant explosives, the production of which has available a virtually unlimited supply of raw materials, as the primary materials for its manufacture are synthetics. The expansion of organic synthesis ~~XXX~~ has made it possible to reduce the cost of production of the initial products for the manufacture of pentaerythrite - formaldehyde and acetaldehyde, and this was the stimulus to the development of PETN production. Formaldehyde is today manufactured in large quantities from ~~XXX~~ synthetic methanol. Acetaldehyde from acetylene by catalytic hydration in the presence of mercury salts.

Nevertheless, the cost of PETN is today still high, and therefore it is employed in peacetime industry chiefly in percussion caps and goes to the production of detonating fuzes. PETN caps have considerable higher initiating capacity than caps of ~~XX~~ fulminating mercury or tetryl ~~XXXX~~ azide.

Because of its high sensitivity to mechanical effects, PETN is not used in the pure form to fill munitions.

In Italy, PETN, ~~XXXXXXXXXX~~ rectified with 20% paraffin, and called "pentrit F" was used to fill 75 and 77 mm armour-piercing shells, while a mixture consisting of 80% ammonium nitrate and 20% PETN, ~~XXXXXXXXXXXXXXX~~ rectified by 20% paraffin, and designated ~~XX~~ PNP, was employed to fill fragmentation and contact-fragmentation shells of medium calibers. In Germany, PETN was produced both in the pure and in the ~~XXXXXXXXXX~~ rectified form. In some case, the ~~XXXXXXXXXX~~ rectifier content achieved 40%.

Unrectified PETN employed to manufacture ~~XXX~~ detonating fuze and as a secondary charge in percussion caps. PETN rectified with 5 and 10% synthetic wax was employed in the pressed form for supplementary detonators and to fill fragmentation-tracing, fragmentation, and fragmentation-incendiary small-caliber shells (to 50 mm).

PETN containing 15 - 20% rectifier ~~were~~ was employed to fill armour-piercing shells and armour-piercing tracer shells. PETN with 30 - 40% rectifier and dye was employed to fill signaling and smoke camouflage shells.

Section 1. Chemistry of Production, Properties, and Application of PETN

PETN, or pentaerythritol tetranitrate is a nitric ester of quadri-atomic pentaerythrite alcohol.

Pentaerythrite itself $C(CH_2OH)_4$ is obtained by condensation of acetaldehyde and formaldehyde in the presence of calcium hydroxide, in accordance with the following reaction:

$$2CH_3COH+8HCOH+Ca(OH)_2 \rightarrow 2C(CH_2OH)_4+(HCOO)_2Ca.$$

Pentaerythrite is a white crystalline substance melting at 260°, odorless, and sweetish to the taste. It is readily soluble in water (5.55 parts pentaerythrite dissolved in 100 parts water at 15°).

333 Pentaerythrite, particularly the technical product, contains a considerable quantity of impurities. The major impurities - dipentaerythrite - is a product of the condensation of two molecules of pentaerythrite:

$$2C(CH_2OH)_4 \rightarrow H_2O+C(CH_2OH)_3-CH_2-O-CH_2-C(CH_2OH)_3.$$

The dipentaerythrite present in pentaerythrite reduces the melting point of the latter, forming a eutectic mixture melting at 100° (Fig.105)

(70% penta- and 30% dipentaerythrite). The dipentaerythrite melt at 221°. Technical pentaerythrite with a melting point of 235° contains 10% dipentaerythrite.

A second inevitable impurity in pentaerythrite consists of sugary substances, which form as a consequence of the aldol condensation of formaldehyde in an alkaline medium

$$6HCHO \rightarrow CH_2OH(CHOH)_4-CHO.$$

The content of these impurities attains 0.26%.

A third impurity consists of resins which give the product a yellowish color. Of the inorganic impurities, the most important is lime, which causes the product to contain up to 0.25% ash.

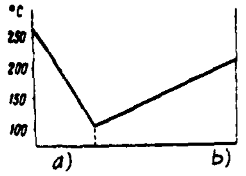


Fig.105 - Diagram of Fusibility of Mixtures of Penta- and Dipentaerythrite
a) Penta-; b) Dipenta-

The high content of oxidizing and sugary substances in pentaerythrite gives rise to side reactions when the nitric ester is produced, a result of these reactions being an increase in temperature. Sudden and strong increase in temperature upon the esterification of pentaerythrite by nitric acid may give rise to crackling and even to explosion, and therefore it is necessary carefully to follow the process to make sure the content of such impurities does not exceed the standards provided by the specifications.

The quality of the pentaerythrite also affects the yield of PETN. The yield of crystalline PETN from pentaerythrite at a melting point of 210° is about 80%, and, with a melting point of 238° - about 92%.

The pentaerythrite employed to produce PETN should have a melting point of not less than 240°, and should, upon test esterification, result in a PETN yield of not less than 90% theoretical.

By the effects of nitric acid, pentaerythrite may readily be converted to ester on the following reaction:

$$C(CH_2OH)_4 + 4HNO_3 \rightleftarrows C(CH_2ONO_2)_4 + 4H_2O.$$

When this occurs, the concentration of acids should not be less than 86% HNO_3. With increase in the concentration of initial nitric acid, the product yield rises. The bath module is chosen so that the spent acid will contain 80 - 82% HNO_3. Reduction in the bath module and concentration of the initial nitric acid results in intense acidifying processes.

The reaction temperature and nitric oxides also affect the oxidizing processes. Therefore, the temperature of esterification should not exceed 20°, and the nitrogen oxides content of the nitric acid should not be more than 2%.

The process of pentaerythrite esterification is exothermic and proceeds at high speed. Therefore, very vigorous agitation, good cooling, and batch-wise addition of alcohol to acid is required if the necessary temperature is to be sustained.

Stettbacher (Bibl.29) recommends that after the mixing of the pentaerythrite and nitric acid is concluded, three- or four-fold the quantity of commercial sulfuric acid (measured against the pentaerythrite) be run into the nitrator

334 to complete the reaction and for more complete separation of the PETN from the acids. Later investigations have demonstrated that this operation is unnecessary. Esterification by nitric acid alone goes quite completely, and the resultant PETN comes down as crystals from the spent acid because of its low solubility in dilute acids. Complete separation of the PETN is achieved by additional dilution of the spent acid with water to a concentration of 40 - 50% in terms of HNO_3.

By another method, PETN is produced via sulfuric ester with subsequent reesterification at 55 - 60° by addition of nitric acid (Bibl.30).

In some respects, this method is convenient in the performance of a continuous nitration process, inasmuch as it is easier to meter liquid components than solid (pentaerythrite). Moreover, in view of the higher temperature of the process, tap water, rather than cooled brine, may be used for cooling.

When sulfuric acid is reacted with pentaerythrite, pentaerythrite sulfate, and ester, is produced by the following reaction

$$C(CH_2OH)_4 + xH_2SO_4 \rightleftarrows C(CH_2OH)_{4-x}(CH_2OSO_3H)_x + xH_2O.$$

Here, x equals two or three, i.e., reaction with sulfuric acid yields either pentaerythrite disulfate or pentaerythrite trisulfate.

Conversion of this product to nitric esters is performed with concentrated nitric acid or with melange in accordance with the following equation

$$C(CH_2OH)_{4-x}(CH_2OSO_3H)_x + 4\,HNO_3 \rightleftarrows C(CH_2ONO_2)_4 + \\ + (4-x)\,H_2O + xH_2SO_4.$$

The ~~super~~re-esterification of pentaerythritedi- or pentaerythritetrisulfate is more difficult than the esterification of pentaerythrite. If the esterification of the latter by nitric acid goes with sufficient rapidity even at 0°, reesterification of the former begins at 35 - 40°, and occurs with sufficient rapidity only at 55 - 60°.

An intermediate product of the ~~super~~re-esterification of pentaerythritedi- or pentaerythritetrisulfate is pentaerythritedinitrate disulfate

$$[C(CH_2ONO_2)_2(CH_2OSO_3H)_2],$$

which does not completely convert to PETN, but remains in part therein (Bibl.30).

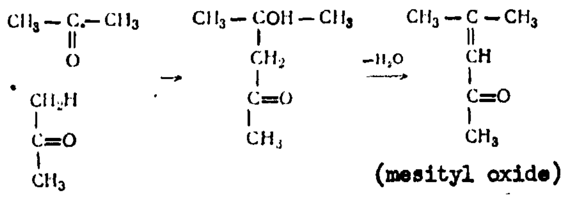
The mixed esters are unstable and constitute the cause of the low stability of unstabilized PETN. In order to obtain stable PETN, free of mixed esters, esterification of pentaerythrite disulfate by nitric acid is performed at an elevated temperature of the order of 55 - 60°. However, in order for complete removal of unstable impurities to occur, the PETN has to be subjected to special stabilization - boiling with soda solution (soda cooking) and recrystallization.

The PETN, washed with water, is treated for an hour with boiling soda solution, and then, after filtration, is dissolved in acetone. Ammonium carbonate is added to the solution obtained to neutralize the mineral and, probably, organic acids in the PETN. The solution is filtered free of excess $(NH_4)_2CO_3$ as well as of other mechanical impurities, and is cooled or run in a stream into two or three times the quantity of water, in order to separate out the PETN crystals.

When PETN is crystallized out of acetone solution by addition of water, it is necessary to bear in mind the possibility that impurities poorly dissolved in aqueous solutions of acetone, which reduce the quality of the PETN, may also come down at the same time.

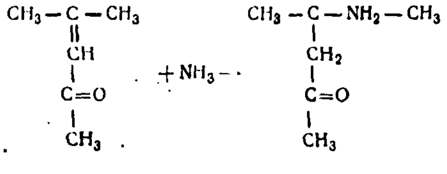
Ammonium carbonate has important shortcomings as a PETN stabilizer. In hot acetone solution, it decomposes into ammonia and carbon dioxide, which, entering the reflux condenser jointly with the acetone fumes, recondense, whereupon the ammonium carbonate thus formed clogs piping with the result that the withdrawal ventilation is interrupted.

335 Moreover, the ammonium carbonate gives rise to partial condensation of acetone with formation of an unsaturated isopropylideneacetoneketone or mesityl oxide, /in accordance with the following mechanism:

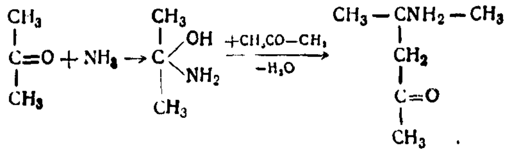

(mesityl oxide)

Mesityl oxide is a highly reactive substance and will therefore readily react with ammonia obtained from the ammonium carbonate, and thus forms 2-amino-2-methylpentanone or diacetone amine:

$(NH_4)_2CO_3 \rightarrow 2NH_3 + CO_2 + H_2O;$



We also XX know that acetone reacts directly with ammonia, forming acetone amine in the process, and this latter readily condenses with acetone, to yield diacetone amine in accordance with the following mechanism:



The use of soda instead of the ammonium carbonate is capable of eliminating these shortcomings.

The method of crystallizing PETN by suspension of a solution thereof in nitromethane, in water, followed by driving off the azeotropic mixture of solvent with water, has been described (Bibl.31).

Properties of PETN. PETN (Bibl.32, 33) is a white crystalline substance with a melting point of 141 - 142°, and a specific gravity of 1.77. PETN presses poorly. Pressing permits a density of 1.70 gm/cm^3 to be obtained. The specific heat of PETN is 0.4 kcal/gm°C.

PETN is nonhygroscopic; its solubility in water at 19° is 0.01%, and at 100° - 0.035%. The solubility of PETN in other solvents (Bibl.32, 34) is presented in Tables 101, 102, 103, from which it is evident that acetone is the best solvent thereof.

PETN is a neutral substance and does not react with metal. It decomposes after a long-term reaction with bases and acids (Bibl.35).

PETN yields eutectic mixtures (Bibl.32), presented in Table 104, with many nitro compounds.

When a eutectic of PETN and TNT, PETN and tetryl, and similar substances, are heated, above their melting points, decomposition of the PETN will occur (Bibl.36).

PETN is of adequate stability, and exceeds many nitrates of multiatomic alcohols in stability. This property is explained by the fact that four methoxyl groups are located around the central atom of carbon: it is possible that the fact that PETN is a solid, is also of significance (Bibl.37, 38).

Decomposition of PETN with liberation of nitrogen oxides at 140 - 145° achieves a significant velocity within half an hour of the beginning of the experiment. At 175°, the product intensively emits brown fumes of nitrogen oxides, and detonation occurs at 215°.

336 PETN deflagrates with difficulty, but when ignited (in small quantities) it burns quietly.

One of the major impurities of PETN is dipentaerythritehexanitrate

$$(CH_2ONO_2)_3C - CH_2 - O - CH_2 - C(CH_2ONO_2)_3,$$

which reduces its melting point.

Table 101

a)	b)				
	c)	d)	e)	f)	g)
0	0,19	0,07	0,20	—	0,15
10	0,24	0,08	0,22	0,15	0,17
20	0,45	0,16	0,25	0,30	0,23
30	0,71	0,27	0,34	0,45	0,43
35	—	—	0,45	—	—
40	1,16	0,42	—	1,16	0,62
50	1,8	0,71	—	2,01	1,10
60	2,60	1,21	—	3,35	2,49
62	—	—	—	—	—
65	3,24	—	—	—	—
70	—	2,22	—	5,40	3,29
74	—	3,79	—	—	—
80	—	—	—	7,90	5,85
90	—		—	—	9,12
100	—	—	—	—	15,92
113	—	—	—	—	30,69

a) Temperature, °C; b) Solubility of PETN, gm, in 100 gm solvent;

c) Methyl alcohol; d) Ethyl alcohol; e) Ethyl ether; f) Benzene; g) Toluene

Table 102

a)	b)						
	c)	d)	e)	f)	g)	h)	i)
25	1,1	1,8	0,9	1,5	3,0	0,8	26,4
100	24,6	33,1	19,3	25,4	32,5	15,8	42,6

a) Temperature, °C; b) Solubility of PETN, gm, in 100 gm solvent; c) Cellosolve;

d) Methyl cellosolve; e) Carbitol; f) Methyl carbitol;

g) Carbitol acetate; h) Butyl carbitol; i) Dimethyl formamide

Table 103

a)	b)						
	0	2,5	6,25	9,07	10,0	14,29	30
10	—	—	—	—	16,4	--	—
25	31,4	25,6	—	20,0	22,0	9,4	3,4
45	50,6	—	33,7	29,9	33,0	22,1	—
55	66,6	60,0	46,0	—	37,5	30,7	9,7
62	—	—	—	--	42,7	--	—

a) Temperature, °C; b) Solubility of PETN, gm, in 100 gm acetone containing various quantities of water, gm

337 Table 104

a)	b)	c)
Meta-dinitrobenzene	20	82,4
2,4-dinitrotoluene	10	67,3
α-trinitrotoluene	13	76,1
Tetryl	30	111,3
Nitromannite	20	101,3

a) Components of eutectic; b) PETN in eutectic, %; c) Melting point, °C

Dipentaerythritohexanitrate was first obtained in 1932 by Bruen (Bibl.33).

Its melting point is 73.6°, its specific gravity $d^{15^\circ}_{15^\circ} = 1.630$. It differs from PETN by its good solubility in conc. nitric acid and, therefore, a considerable quantity thereof remains in the spent acid. The solubility of dipentaerythritohexanitrate in acetone is similar to the of PETN.

Technical PETN contains up to 5% dipentaerythritohexanitrate.

Because of its inferior explosive properties (20% lower than those of PETN), dipentaerythritohexanitrate reduces the power of the latter, and therefore, the presence of dipentaerythritohexanitrate as an impurity in PETN is undesirable.

PETN is highly sensitive to impact. When a weight of 2 kg is dropped from 17 cm it will detonate virtually everytime, but in some cases detonation will occur when the height is only 15 cm, and sometimes even at 10 cm.

The major explosive properties of PETN and dipentaerythritohexanitrate (Bibl.33) are presented in Table 105.

Table 105

a)	b)	c)
Sensitivity to impact at 2 kg weight dropped from height, in cm	17	14
Heat of explosive decomposition in kcal/kg	1385	1092
Volume of gaseous explosion products in kcal/kg	790	903
Velocity of detonation m/sec	8300	7410
Expansion in ~~Tetryl block, ml~~ Trautzl block,ml	500	380
Limiting weight of detonation, gm:		
fulminating mercury	0,17	—
lead azide	0,03	0,18

a) Characteristic; b) PETN; c) Dipentaerythritohexanitrate

The data presented in the Table show that PETN is a powerful brisant explosive.

It is employed as a secondary charge in percussion caps for the production of detonating fuzes and for the manufacture of detonators for artillery explosives.

In order to reduce the sensitivity of PETN, there have been experiments in its employment alloyed with various nitro derivatives. Investigation of these alloys showed that they are lower in sensitivity and are of adequate stability.

Thus, when a cast mixture of PETN and TNT (50:50) was stored for 3 yrs at ordinary temperatures, the pH diminished from 6.58 to 5.46. The stability of PETN also diminishes when other nitro derivatives of benzene and toluene are added thereto. The maximum reduction in stability is caused by the mononitro derivatives.

138 Vaseline, paraffin, and ozocerite are good rectifiers for PETN, but they significantly reduce its power.

The specifications that have to be met by the crystallized PETN are the following:

1) Appearance - fine crystalline powder, white in color (slightly grayish is permissible) without foreign impurities visible to the eye and without visible signs of moistness;

2) Melting point between 138 - 140°;

3) Not more than 0.1% moisture and volatiles;

4) Not more than 0.1% acetone-insoluble impurities at ordinary temperatures;

5) Ash content not over 0.2%, and no more than 0.01% silica;

6) Absence of free acids;

7) Stability, determined by the concentration of hydrogen ions at 110° for 8 hrs, not less than 5.5;

8) Stability to iodized starch test, 1 hr at 80°.

Section 2. Technology of PETN Production (Bibl.17, 30, 32, 39)

A special feature of the PETN production process is the fact that the initial product, pentaerythrite, is a solid with a high melting point. Metering of the solid initial component is considerably more difficult than metering of liquids.

Industrial production of PETN may be performed in two ways: a two-stage method with prior production of pentaerythritol sulfate then converted to nitrate, and a single-stage method involving direct production of pentaerythritol nitrate.

In both cases, the process is carried out by addition of pentaerythritol to the corresponding apparatus filled with sulfuric or nitric acid. The pentaerythritol dissolves in these acids. The solution process precedes esterification and apparently determines the overall speed of the process. Good agitation and the presence of sufficiently fine pentaerythritol (not clumped) is a necessary condition for the technology of esterification.

The two-stage method. This method was suggested before the single-stage (Bibl.30), inasmuch as it appeared that the chances of its application were greater. The process consisted of two stages, the first - production of pentaerythritol sulfate and the second - production of pentaerythritol nitrate. Both the first and second stages may be run at elevated temperatures XXX (50 - 60°), without fearing oxidation even in the second stage, inasmuch as the hydroxyl groups are protected in deriving the nitrate, and, moreover, the nitrogen oxides giving rise to this process are bound by sulfuric acid. The elevated temperature necessary to replace the sulfo group by the nitro group makes it possible to employ river water for cooling.

Esterification by mixed acid may be run in carbon-steel equipment. However, the single-stage method of production of PETN requires condenser XXXXXXXXXX and alloy steel apparatus.

It was assumed that the two-stage method of production of PETN would be considerably easier to carry out in continuous apparatus than the single-stage one inasmuch, as in this instance, XXX it will not be pentaerythritol, but a solution of its sulfonic ester in sulfuric XXXXX acid that will be metered into the apparatus. Continuous metering of liquid components is doubtless simpler and more precise than that of solid components.

339 The following diagram for the production of PETN by a two-stage process has been described (Bibl.30). In the first stage, a 10 - 15% solution of pentaerythritol in sulfuric acid is prepared. In the second stage XX this solution is introduced into the premixing apparatus simultaneously with the nitric acid. This premixing apparatus has an agitator and a coolant surface, where a temperature of 12° is maintained. The mixture is transmitted to the

lower portion of the second apparatus, which is a column (with jackets, in which water at a temperature of 40 - 50° is circulated). The reaction mass in the column is heated to 55 - 60°, raised, and discharged through a flange at the top. The rate of motion of the liquid in the column is so regulated that the process of trans-etherification is able to come to an end completely before the moment when it emerges from the apparatus.

It is difficult to carry out the two-stage method of producing PETN in a continuous apparatus because of the low stability of the product. Experience has shown that PETN, produced in this manner, has exceedingly low stability in the unpurified form. Any retention of this kind of PETN in the apparatus, for example, adhesions to the inside of the cover or the wall, or to the coils, results in spontaneous decomposition of the product, which may terminate in an explosion. Careful washing of the apparatus is required to avoid this.

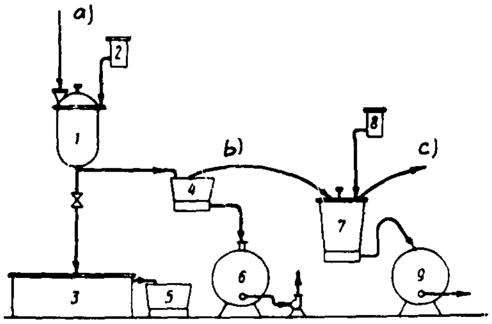


Fig.106 - Diagram of Manufacture of PETN by the Single-Stage Method
1 - Nitrator; 2 - Nitric acid metering tank; 3 - Emergency baths; 4 and 5 - Vacuum filters; 6 - Vacuum collector for spent acids; 7 - Diluting tank; 8 - Water tank; 9 - Vacuum collector for wash water
a) Pentaerythritol; b) Acid PETN; c) PETN to **washing**

PETN produced from pentaerythritol sulfate requires special stabilization. Unstabilized PETN tends to decomposition even at room temperature.

The single-stage method. Under this method, the technological process breaks down into a series of operations:

1) drying, pulverization, and screening of the pentaerythritol;

2) production of PETN;

3) washing of PETN;

4) crystallization of PETN;

5) drying of PETN;

6) screening and packaging of PETN.

Pentaerythritol going to the production of PETN is first ground, dried, and screened. The drying of pentaerythritol is usually performed in a drum dryer at a temperature of not more than 100° (Bibl.40).

Production of PETN goes in accordance with the diagram illustrated in Fig.106.

300 kg Nitric acid (93 - 95%) is run into the nitrator (1) from metering tank (2), and 60 kg pentaerythritol is gradually charged, with the agitator working 340 at a speed that will assure that the temperature does not rise over 20°. After introduction of all pentaerythritol, the mass is allowed to stand for 30 min. In the esterification process, PETN is formed, and this comes down out of the spent acid (specific gravity 1.43) as crystals.

The reaction mass is discharged from the nitrator to a vacuum filter (4), where the PETN is separated from the spent acid, collected in the vacuum collector (6). Then the acid PETN is transferred to preliminary washing in diluting tank (7), filled with water.

The diluter is a tank with an agitator and a false bottom of porous ceramic materials. The agitator is required, to prevent local overheating when the acid PETN is run into the water. 6.5 Parts water are run into the diluting tank in advance, for each part of PETN.

The acid PETN is stirred with the water for 15 min, whereupon the agitator is stopped, and the acid water is removed by vacuum through the false bottom of the diluting tank. Then, the PETN is washed thrice in the diluting tank by a 50% greater quantity of water. After this washing, the acidity of the PETN is about 1%.

The PETN is then sent to final washing, which is performed as follows.

A 1% soda solution (8 - 10 times the quantity of PETN) is charged into the washing vat. It is heated to 90°, whereupon the PETN is gradually run in, resulting in foaming of the mixture as a consequence of the liberation of carbon dioxide. After charging is complete, the mixture is stirred for an hour with the temperature at 85 - 90°. During the entire washing period, the medium must remain alkaline. Clumps of PETN crystals undergo a noticeable break-up during the washing, and the acid between them is neutralized by the soda.

After the soda cooking, the PETN is filtered free of water on a vacuum filter.

The resultant raw PETN has an acidity of about 0.5 - 0.8%. To achieve an acidity of less than 0.3% by multiple washing of PETN is something that has not been accomplished, apparently because of the presence of intracrystalline acid. To eliminate this acid, PETN is recrystallized from acetone. With this object, the PETN dissolves in acetone, whereupon ammonium carbonate is added to neutralize the acid, and the solution is boiled for a certain period. The PETN is then precipitated from solution either by cooling or by diluting the solution with water.

Inasmuch as the PETN going to stabilization contains 15 - 18% water, which reduces its solubility, solution requires that excess acetone (2.2 - 2.5 parts by weight) be employed per part of PETN. Finely ground ammonium carbonate is sifted into this solution so as to provide a 100% excess over the quantity required to neutralize the acidity of the PETN. Solution of the PETN and stabilization are run at 58° for 1 hr.

109 After the conclusion of this period of time, the solution is forced through a filter into a crystallizer preheated to 50°.

The hot acetone solution of PETN must not be run into a cold apparatus, as otherwise the product may crystallize on the walls and in the piping. Therefore, the solution is slowly cooled with water delivered into a jacket. If the cooling is rapid, a crust will form, which may be dissolved by heating the apparatus to 58°.

At the conclusion of crystallization, the PETN is separated from the acetone on a vacuum filter. Thereupon, the PETN contains 15 - 20% mother acetone liquor, which is removed by washing with alcohol.

The acetone is employed three times, with the addition of fresh acetone to the mother liquor on each occasion. The spent acetone goes to fractional distillation.

The filtered PETN, containing 15 - 20% alcohol, goes to chamber dryers, where it is dried at 40° for 12 hrs. The dry PETN is screened and packed in calico sacks.

341 This is the method of PETN manufacture employed during World War II in Germany, where it was carried out in continuous-action apparatus. Two methods of producing PETN were employed in Germany, the filtering and stabilization of the spent acid being different in the two methods. Let us present a brief description of the two processes of PETN production (Bibl.17, 32).

The direct method of producing PETN, with continuous filtering off the spent acid, is illustrated in the diagram in Fig.107.

Into nitrators (2) (50 ltr capacity each) with agitation, pentaerythritol and nitric acid (97 - 98% HNO_3) in a ratio of 1:5, and at a temperature of 10 - 25°, are delivered through metering devices. From nitrators (2), the reaction mixture goes continually through a V-type buffer nitrator (3) (40 ltr capacity), in which the mixture is cooled to 10 - 15°.

From the buffer nitrator, the reaction mixture goes continually to vacuum filter (4) (rotating at 0.75 rpm, and having a filtering surface of 0.5 m^2). On

341 the filter, the PETN is separated to 12 - 15% acidity, and goes continually to washing column (5), where it is washed with cold water. Discharge of the washing column is performed periodically on vacuum filter (7). Here, the PETN is washed twice with hot and once with cold water, and is filtered to 12 - 15% moisture. The washed PETN is unloaded manually into sacks and sent to crystallization.

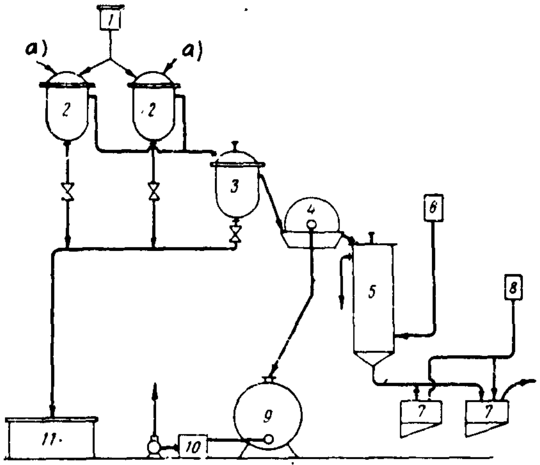


Fig.107 - Diagram of PETN Manufacture with Continuous Filtering of Spent Acid

1 - Nitric acid pressure XXXXXXXX tank; 2 - Main nitrators; 3 - Buffer nitrator; 4 - Vacuum filter; 5 - Washing column; 6 and 8 - Pressure tanks for water; 7 - Vacuum filter; 9 - Spent acid settling tank; 10 - Collector; 11 - Emergency tank

a) Pentaerythritol

The wash waters, containing 8 - 12% HNO_3 are discharged through traps into the waste-water system. The spent acids go to aluminum settling tanks (9) for 24 hrs, are then run into collector (10), from which they go to the spent-acid reservoir. The composition of the spent acid is as follows: 80 - 82% HNO_3;

342 0.5 - 0.75% N_2O_3 and 1.0 - 1.5% nitro substances. After settling, the spent acid contains about 0.75% nitro substances.

342 The nitrous gases emitted are absorbed by water in an absorption column and the acid obtained in the column is returned to production after concentration.

For purposes of stabilization, the spent acid goes after settling to what is called a destructive distillation column, consisting of five columns connected in series, and having steam-heated jackets for attainment of a temperature of 90 - 100°. After passing successively through all five columns, the acid is separated from the nitro product and goes to a condenser, where it is cooled to 25 - 30°. The bulk of the nitro substances decomposes in the first two columns. To strengthen the decomposition of the nitro substances, water is delivered into the third column, as a consequence of which the nitric oxides emitted therewith accelerate the process of acidification. The spent acid contains 65 - 70% HNO_3 and is free of nitro substances after stabilization.

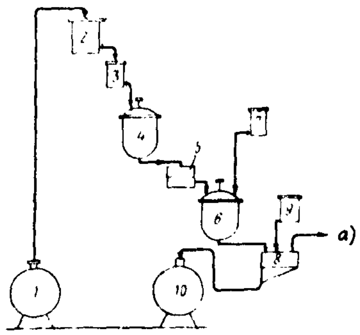


Fig.108 - Diagram of PETN
Recrystallization

1 - Acetone storage; 2 - Automatic acetone metering tank; 3 - Preheater; 4 - Solution tank; 5 - Filter; 6 - Crystallizer; 7 and 9 - Water metering tank; 8 - Vacuum filter; 10 - Mother liquor collector

a) PETN to drying

Crystallization of PETN (diagram in Fig.108) is performed in a separate building, containing two apparatus for dilution, with a capacity of 600 ltr each, and two crystallizers having 1100 ltr capacity each.

342 The apparatus for solution, and the crystallizers, are made of aluminum, and are provided with agitators making 150 rpm, and with reflux condensers.

Acetone, ~~360 ltrs of which is~~ in a quantity of 360 ltr, is delivered by compressed air (or nitrogen), from storage unit (1) to automatic metering tank (2), and from the latter through a protective vessel into heater (3), where it is heated to 50°. It then goes to dilution tank (4), into 112 kg moist (equivalent to 100 kg dry) PETN, and 750 gm sodium bicarbonate. After the PETN has been dissolved (30 min) the solution is sent through filter (5) to crystallizer (6), where another 750 gm sodium or ammonium bicarbonate is added. The sodium bicarbonate is added in two portions, so as not to create a powerfully alkaline medium, which would induce corrosion of the aluminum apparatus.

Gradually 600 ltrs of cold water are run into the acetone solution ~~in~~ from the ~~crystallizer~~ the metering tank(7) at 30 ltr/min, with the agitator operating. PETN of good free-flowing qualities is obtained when precipitation is performed in this manner.

The acetone, diluted to 30% with the discharged PETN, ~~emitted~~, is sent from the crystallizer to vacuum filter (8), where the PETN is filtered out, and washed twice with warm and once with cold water. The PETN separated from the water (PETN of 10 - 15% moisture content) is loaded into sacks and sent either to drying or to phlegmatization.

~~Phlegmatization~~ Rectification is performed with a synthetic wax. PETN and water (1:2) is charged into the ~~phlegmatizer~~ rectifier, and molten wax is added with agitation. The temperature in the ~~phlegmatizer~~ rectifier is held at 4 - 5° lower than the melting point of the wax. Then, the temperature in the ~~phlegmatizer~~ rectifier is raised to 2 - 3° above the melting point of the wax, and after 15 - 20 min agitation, the ~~phlegmatizer~~ rectifier contents are cooled and filtered.

342 With the purpose of producing more homogeneous material, the phlegmatized PETN
343 (1000 kg) is mixed under water and sent for drying after repeated filtration.

The finished PETN should have a melting point of not less than 138°, should contain 17.4% nitrogen, and not more than 0.3% acetone-insoluble substances.

The diluted acetone goes to fractional distillation in a Holzen-Grimm fractionating column ~~fractional distillation~~ (to 98% concentration), subsequent to which it is again used for crystallization.

This method of producing PETN is of adequate simplicity, comparatively safe, of high output, and provides a high yield and a high quality of finished product at comparatively low rates of consumption.

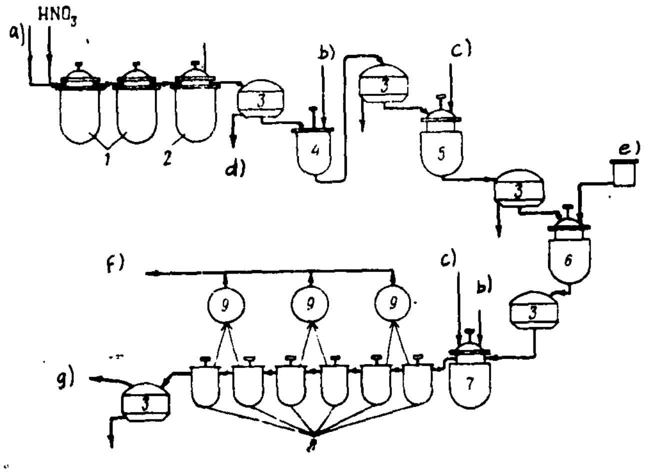


Fig.109 - Diagram of PETN Production with Periodic Separation of Spent Acid

1 - Nitrators; 2 - Diluter; 3 - Filters; 4 - Washing apparatus; 5 - Neutralizer; 6 - Solution tank; 7 - Crystallizer; 8 - Distillation column; 9 - Acetone condensers a) Pentaerythritol; b) Water; c) Soda solution; d) Spent acid; e) Acetone; f) Acetone to recovery; g) PETN to drying

Figure 109 illustrates the continuous method with periodic separation of spent

343 acid.

The pentaerythritol is metered into the main nitrator (0.5 m^3 volume) to the vacuum filter and automatic scales, by means of a worm conveyer. From storage, 99% nitric acid is simultaneously sent to the main nitrator through the metering device. Nitric acid, 5 - 6 parts by weight, is metered per 1 part pentaerythritol by weight. The temperature in the nitrator, which comes to 15°, is maintained by means of brine cooled to -11°.

From the main nitrator, the nitro mass goes to a buffer nitrator (0.17 m^3 volume), and then to the diluting tank (0.17 m^3 volume), into which water is metered. The quantity of water should be such that the concentration of spent acid diminishes from 80 to 40% in terms of HNO_3. The temperature in the buffer nitrator is held at 10°, and that in the diluting tank at 15° (these are also cooled by brine). Upon dilution, the PETN crystallizes out, and the entire mass goes to the vacuum filter.

The vacuum filter has an aperture in the center of the filtering ~~fabric,~~ cloth; to this aperture is attached a pipe connecting it to the washing tank. During loading and filtration, the aperture is closed by a plug. After the acid has been taken off by suction, the plug is removed, and the crystals of PETN are washed into the washing tank. From the washing tank, the mass goes to a filter, and after separation of the

344 acid water, the PETN is sent by a powerful stream of water to a tank in which the acid PETN is neutralized by soda solution. The PETN, treated with soda, is discharged onto a filter, and after separation, it is sent to the continuous ~~cleansing apparatus~~ scrubber.

The PETN is dissolved completely in the dissolving tank, to which it is sent simultaneously with acetone. The solution is filtered and flows into the tank for dilution with water. Upon dilution, the PETN crystallizes out of

344. solution. The entire mass is sent through stills to remove the acetone. The hot mass is cooled and filtered upon leaving the final still. When the phlegmatized PETN has been produced, montan wax (lignite wax), in melted form, is run into the third distillation column.

The nitrators are in a separate building, and the agitator shafts are introduced through the roof. The installation is equipped with control[illegible] and metering instruments, and the entire operation is automated.

The refrigeration apparatus and tanks for storing the acid are located alongside the nitration building. The building for treatment of raw PETN with soda is at the same place.

After washing, the PETN is sent to the next building for recrystallization and phlegmatization.

Acetone losses in batch-wise recrystallization are 0.125 ton per ton of finished PETN, and 0.055 ton when continuous recrystallization is performed.

The spent acid is settled and then concentrated under vacuum to 98 - 99%.

Consumption of material per ton of PETN:

pentaerythritol	0.435 - 0.447 ton
nitric acid (97 - 98%)	0.918 - 1.110 ton
acetone (lost)	0.055 - 0.125 ton
nitric acid lost	0.120 - 0.200 ton
yield of ready PETN	96%

Safety procedure. The manufacture of PETN is dangerous at all stages.

In the esterification of pentaerythritol, it is necessary to assure careful monitoring of the accuracy with which the components are metered, the work

344 of the agitators, and the temperature regime. When the technological process is steady, this latter factor is controlled by XX delivery of coolant solution into the coils. Decomposition of the PETN is indicated by the appearance of nitrogen oxides and sudden rise in temperature, and when this phenomenon occurs the nitro mass must immediately be dumped into an emergency container from the nitrator.

The operation of dilution of the nitro mass with water, in which a considerable quantity of nitrogen oxides is liberated, is also [illegible] dangerous. At elevated temperature, these may cause decomposition of PETN and ignition thereof. Therefore, if the temperature in the diluting tank should rise suddenly, it is necessary immediately to dump the nitro mass into the emergency container.

Monitoring and control of the processes is most reliably realized by automatic instrumentation.

~~After~~ Dilution of the nitro mass is followed by the operation whereby PETN is filtered free of the spent acids ~~follows~~. This operation is no less dangerous than the preceding ones. Uncrystallized and unwashed PETN is of low stability because of various impurities, and primarily, the acids it contains. PETN of this quality is very sensitive to heat, and therefore special measures must be taken in handling it. Thus, for example, the dust of unpurified PETN will readily take fire upon contact with steam lines or other heated portions of equipment, and therefore any such possibility must be prevented.

In drying and packaging PETN, careful grounding of all apparatus must be assured, and other measures must also be taken to remove static electricity, inasmuch as PETN readily undergoes electrolysis.

B. Nitric Esters of Other Alcohols

Section 1. Methyl Nitrate

Methyl nitrate CH_3ONO_2 is a ~~nitrate~~ nitric acid ester of methyl alcohol.

It was manufactured, in large quantities, over a long period, for the dye industry (for purposes of methylation). As a consequence of destructive explosions which accompanied its manufacture and application, its production for peacetime purposes was stopped.

Methyl nitrate is a brisant explosive, more powerful than hexogen. At the end of World War II, a mixture of methyl nitrate and ethyl alcohol, called Mirol was employed in Germany to fill aerial bombs.

Methyl nitrate is a colorless, transparent liquid with an aromatic aroma similar to that of chloroform. Inhalation of its fumes induces headaches. The specific gravity of methyl nitrate at 15° is 1.21. Its solubility in water at 20° is 3.8%. It is of high volatility, and readily plasticizes collodion. At 65°, it will distill without decomposition.

Methyl nitrate readily undergoes combustion and burns quietly with a strong, nonluminous flame. The fumes of methyl nitrate are highly explosive when ignited, and explosion will also occur when they are heated to 150°.

The ~~shock~~ impact sensitivity of methyl nitrate is less than that of nitroglycerin. It detonates when a 2 kg weight is dropped from a height of 40 cm.

Methyl nitrate has a small (-10.4%) negative oxygen balance. The volume of gaseous explosion products is 874 ltr/kg, the heat of explosive decomposition is 1600 kcal/kg, expansion in the Trauzl block is 657 cm^3, and Hess brisance is 24.5 mm.

345 The fact that methyl nitrate is less viscous than nitroglycerin makes for a greater velocity of detonation if the container is weak. The velocity of methyl nitrate detonation in a glass tube 3 mm in diameter is 2480 m/sec, and that of nitroglycerin under the same circumstances is 1500 m/sec.

Methyl nitrate is produced by careful esterification of methyl alcohol by nitric acid (specific gravity 1.4) or by a mixture of sulfuric and nitric acid. One part methyl alcohol is introduced, with vigorous agitation, into 6.3 parts cooled mixed acid (40% HNO_3 and 60% H_2SO_4) at 0 - 10°. Agitation is with a mechanical impeller, inasmuch as air is unsuited to this use because of the high volatility of the starting and final products. The ester is separated from the spent acid, washed with cold water, and then with soda solution. The yield is 81% of theoretical.

A method of producing methyl nitrate by the action of a mixture of sulfuric and nitric acid upon excess methanol has been described. Distillation is employed to obtain a 60% solution of methyl nitrate in methanol (Bibl.41).

In Germany, a continuous method of producing methyl nitrate by esterification of methanol with 60% nitric acid has been developed (Bibl.42 - 43). When this is done, solutions of methyl nitrate in methanol of various concentrations, from 60% to pure 100% methyl nitrate, may be obtained as end products. Methyl nitrate manufactured in this way is chemically pure and requires no further stabilization. A full year of operation of the apparatus did not result in a single accident. Methyl nitrate was used in the form of a 72 - 75% solution in methanol, inasmuch as the use of pure methyl nitrate is quite dangerous, in view of its volatility.

The mixture called Mirol has the following properties: specific gravity 1.06;

345 volume of gaseous explosion products 1075 ltr/kg; heat of explosion 1106 kcal/kg; expansion in Trauzl block 370 ml; velocity of detonation 6300 m/sec.

346 Section 2. Nitroisobutylglycer~~in~~ol ~~Trinitrate~~

Nitroisobutylglycer~~in~~ol trinitrate NO_2-$C(CH_2ONO_2)_3$ is the ~~nitrate~~ nitric acid ester of nitroisobutylglycer~~in~~ol. First obtained by Hofwimmer in 1912. The explosive and physical-chemical properties of nitroisobutylglycer~~in~~ol trinitrate are the same as those of nitroglycerin. However, it freezes at a lower temperature and is less volatile. The possibility of expanding nitroisobutylglycer~~in~~ol trinitrate production involves development of the production of nitromethane, constituting the raw material for this purpose.

Nitroisobutylglycer~~in~~ol trinitrate is a slightly yellowish, viscous, syrupy substance having a specific gravity of 1.68 at 15°, odorless, and burning to the taste. The freezing point is below -35°.

Its chemical properties are analogous to those of nitroglycerin. The product has a zero oxygen balance. Its heat of explosion is 1707 kcal/kg (7% higher than that of nitroglycerin).

Nitroisobutylglycer~~in~~ol trinitrate is obtained by nitration of nitroisobutylglycer~~in~~ol with mixed acid of the following composition: 60% H_2SO_4 and 40% HNO_3. The process goes in accordance with the following equation:

$$NO_2C(CH_2OH)_3 + 3HNO_3 \rightleftarrows NO_2C(CH_2ONO_2)_3 + 3H_2O.$$

Product yield is 90%.

When nitroisobutylglyc~~erin~~erol trinitrate is washed with soda, a stable emulsion is formed from which it is extracted by chloroform or ether. Moreover, the product is highly sensitive to the effects of ~~XXXXX~~ alkaline substances, and this complicates

346 its stabilization.

The initial product - nitroisobutylglyceri~~n~~ol - is produced by condensation of 1 molecule of nitromethane with 3 molecules of formaldehyde in the presence of $KHCO_3$:

$$NO_2-CH_3+3HCOH \rightarrow NO_2C(CH_2OH)_3.$$

Its melting point is 130 - 160°. It is purified by recrystallization from alcohol, and then dried.

Section 3. Mannitol Hexanitrate (Nitromannite) (Bibl.6,12,44,45,46)

Mannitol hexanitrate is a nitr~~ate~~ic ester of mannite obtained from manna sap:

$$O_2NOCH_2(CHONO_2)_4CH_2ONO_2.$$

The product was first obtained in 1847 by Domante and Minard. In appearance, it is a white crystalline powder (thin needles). The melting point of mannitol hexanitrate is 112 - 113°, its specific gravity 1.604. It is readily soluble in acetone, ether, and hot ethyl alcohol, weakly soluble in cold ethyl alcohol, and insoluble in water.

The chemical stability of mannitol hexanitrate is low. American patents (Bibl.47) indicate that its stability may be increased by additions of 0.5 - 3% ammonium salts, as well as by urea derivatives.

Mannitol hexanitrate takes fire with difficulty, and frequently detonates when ignited. When slowly heated, it decomposes completely at 150°, with the evolution of red fumes, without crackling. Its sensitivity to shock is the same as that of nitroglycerin. The heat of explosion is 1510 kcal/kg, expansion in the Trauzl block is 560 ml, and velocity of detonation is 8260 m/sec.

The use of mannitol hexanitrate is inhibited by its high sensitivity and inadequate stability.

The method of producing it was developed by N.V.Sokolov (Bibl.48). Into a vessel containing 1 part mannite, there is gradually added 5 parts concentrated nitric acid (specific gravity 1.51). To the transparent solution obtained, there is added, gradually, with cooling, 10 parts concentrated sulfuric acid, and the mannitol hexanitrate comes down as a thick white porridge-like mass which is sucked through a filter and washed first with water, and then with a weak bicarbonate solution. A raw product is recrystallized from boiling alcohol.

Section 4. Nitrates of a Mixture of Sugar and Glycerol (Bibl.12)

Nitrates of sugar and glycerol are employed in the USA and, to some degree, in Germany. They are produced by esterification of a solution of sugar (beet or cane) in glycerol, as soon as the sugar nitrates in dissolved condition undergo ~~XXXXXXXXX~~t stabilization.

Usually, mixtures containing 20 - 25% sugar nitrates and 75 - 80% nitroglycerin are employed. These mixtures constitute a syrupy liquid having a specific gravity of 1.605 (20—80 mixture) at 20°, and 1.612 (if the composition is 25 - 75). The chemical stability of these products is lower than that of nitroglycerin, but may be increased by the addition of 0.1 - 0.2% ~~XXXXXXXXXXXXXXX~~ diphenylamine. The explosive properties of these mixtures approximate those of nitroglycerin: Trauzl fugacity of the 20 - 80 mixture is 560 cm^3, and that of the 25 - 75 mixture is 530 cm^3.

To produce nitrates of the mixture of sugar and glycer~~in~~ol, a solution of sugar in glycer~~in~~ol is made. Solutions containing 20 - 25% sugar are esterified by mixed sulfuric and nitric acid under conditions analogous to the esterification of glycer~~in~~ol. The nitrates obtained are washed with water then with soda solution, and are moderately agitated to avoid the development of a stable emulsion. Solutions of

347 table salt are employed to accelerate separation of the wash liquid.

Methods of obtaining nitrates of sugar have been described which involve treatment of a suspension of sugar in acetic anhydride by a mixture of acetic anhydride and fuming nitric acid (Bibl.49), and by the action of a mixture of nitric acid with sulfuric or acetic acid (Bibl.50) upon saccharose. As a result of this esterification and subsequent washing, crystalline compounds are obtained, whose stability has to be higher than that of the mixtures of sugar and glycer~~in~~ol nitrates described above.

F. Cellulose Nitrates (Bibl.51)

Nitrocellulose was first produced in France by Braconnot in 1832 by reacting nitric acid with cellulose, and in 1838 by Pelouze by reacting nitric acid with paper. In 1846, Schoenbein, and a year later, Boettger again obtained nitrocellulose by reacting cotton with a mixture of nitric and sulfuric acids, and made a detailed study of the conditions of its formation, and of its explosive properties.

The production of nitrocellulose on an industrial scale became possible only in 1869, when Abel in England proposed that pyroxylin (the name given to nitrocellulose by Pelouze in 1838) be reduced in size on beating machines for the purpose of extracting the acids from the interior portions of the fibers, which are difficult of aceess. This made it possible to produce a stable nitrocellulose capable of being stored for a long period.

Starting in 1879, nitrocellulose began to be employed on a large scale as a propellant (powder) in artillery and as a brisant high explosive, in the form of pressed cartridges. In 1885, a gelatin of nitrocellulose and nitroglycerin, was developed, called "blasting gelatin." This came into use as a brisant explosive.

347 Later(in 1889), nitroglycerin gelatins of this kind, with high-nitrocellulose were developed as powders. Nobel's substance was called "ballastite", and Abel's was

348 called "cordite". These were smokeless and more powerful powders than the black powder previously used. Today, it is only smokeless powders that are used in the armies of all countries.

Nitrocellulose is also employed for civilian purposes, as for example in the form of the celluloid of motion-picture film, fast-drying lacquers, etc.

In Russia, the production of pyroxylin was begun in 1892 at the Okhta Powder Works.

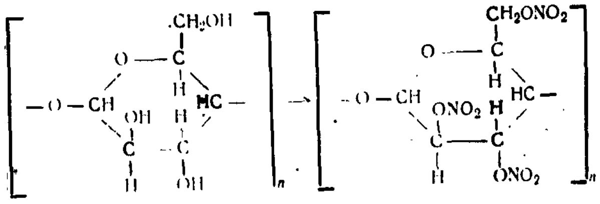
Braconnot, Pelouze, and even Schoenbein actually XX knew very little, practically speaking, XXXX about the chemical nature of nitrocellulose, because it was taken, on the one hand, as a salt-like compound of cellulose and nitric acid, and, the other, as a peroxide compound. XXX It was only in 1852 that Bechan showed that XXXXX nitrocellulose is an ester of cellulose and nitric acid.

Section 1. <u>Chemistry of Production, Properties, and Application of Cellulose Nitrates</u>

Cellulose is a high-molecular compound, and therefore XX as many as three nitrate groups (14.14% nitrogen) may be introduced into a single ring.

The process of formation of cellulose nitrates may be expressed by the following equation:

$$[C_6H_7O_2(OH)_3]_n + n\,[3HNO_3] \rightleftarrows [C_6H_7O_2(ONO_2)_3]_n + n\,[3H_2O];$$



348 The reaction of formation of cellulose nitrate is incompletely reversible, as the phenomenon of nitrocellulose denitration is usually accompanied by the side processes of oxidation and hydrolysis. Complete substitution of all the hydroxyl groups in the cellulose results in a tri-substituted cellulose nitrate containing 14.14% nitrogen. If two hydroxyl groups are substituted in the cellulose, the result is a nitrocellulose containing 11.13% nitrogen, whereas if a single nitro group is replaced, the result will contain 6.77% nitrogen.

The nitrate groups are distributed nonuniformly in the nitrocellulose micromolecule because of the nonuniform ease of substitution of the hydroxyl groups in the glucose residue, and the unequal accessibility of the macromolecules in the various portions of the fiber.

Thus, nitrocelluloses are nonhomogeneous in both the chemical and physical respects. If one takes into consideration modern concepts of nitrocellulose as a high-polymer substance, which is most frequently nonhomogeneous in terms of the size of the macromolecule, a particular type of nitrocellulose cannot be regarded as an individual product, the composition of which may be expressed by some empirical formula. Even a nitrocellulose containing 14.14% nitrogen, in which all hydroxyl groups are replaced, may reveal substantial differences in terms of the size of the macromolecules, i.e., it may be a physically nonhomogeneous substance.

The degree of esterification of nitrocellulose is usually characterized by its nitrogen content in %.

349 The specific gravity of nitrocellulose is 1.65, but it varies somewhat in accordance with the nitrogen content.

In addition to the nitrogen content, the other properties of nitrocellulose are

349 also of major practical importance: solubility and swelling in various solvents; degree of polymerization (the viscosity of the solutions); thermal stability.

The following groups of nitrocellulose solvents exist:

1) solvents as such, which are capable of dissolving nitrocellulose, i.e., of causing, first, swelling, and then going into solution;

2) mixed solvents - mixtures of substances, each of which individually is incapable of inducing solution of the nitrocellulose, but which, as a mixture, are of good solvents;

3) plasticizers. A group of nonvolatile (high-boiling) solvents of nitrocellulose, introduced into products made therefrom to improve their mechanical properties.

The solubility of nitrocellulose in various solvents depends, as already indicated, upon many factors, primarily upon the nitrogen content of the nitrocellulose, and upon the conditions under which it was obtained.

The selection of solvents is governed by the type of product. In the manufacture of powder, it suffices to convert the nitrocellulose to a swollen condition. However, in the production of lacquers, the nitrocellulose has to be dissolved in its entirety, in which case the solvents selected also have to dissolve the other components of the lacquers.

The viscosity of nitrocellulose solutions is also of major practical significance, inasmuch as it affects the mechanical properties of the products. Usually, the strength of the products rises with an increase in the degree of nitrocellulose polymerization. The viscosity of nitrocellulose solutions depends, in the first place, 349 upon the degree of polymerization of the initial cellulose, and also upon the conditions of esterification, stabilization, and the presence, in the solutions, of mineral salts readily absorbed by nitrocellulose.

Nitrocellulose is capable of adsorbing organic solvents and acids. This substantially complicates the job of separating it from acids in production.

Concentrated solutions of mineral acids destroy nitrocellulose. Nitric acid results in destruction of the nitrocellulose molecule, with formation of substances soluble in water and acids. Sulfuric acid behaves in the same manner. Bases readily saponify nitrosellulose. On the other hand, nitrocellulose is relatively stable to the effect of oxidizers. Reducing agents frequently restore it to cellulose, the process being accompanied by oxidation and reduction of the reaction product.

Light causes slow decomposition of nitrocellulose. It is also susceptible to spontaneous decomposition, which is regarded as intramolecular oxidation. This process may be accelerated by various factors, in the first instance, the effect of heat. An increase in temperature of 5° doubles the rate of decomposition. Decomposition of nitrocellulose is catalyzed by nitrogen oxides.

In the dry state, nitrocellulose readily catches fire, whereas when ignited it will burn and deflagrate. Friction readily electrifies it, and the potential difference arising under these conditions reaches several kilovolts.

It has been noted that, in the dark, nitrocellulose may be weakly phosphorescent.

Cellulose-nitrates have the most various applications in the manufacture of various types of powders, lacquers, motion-picture film, celluloid, etc. Depending upon the object sought, the nitrocellulose is changed, and the specifications it must satisfy are modified.

In some cases, for example, in the manufacture of powders,the nitrogen content is of particular significance, as it is an indirect indicator of the heat of combustion of powder. The other indices of the quality of nitrocellulose must be completely determinable under these conditions inasmuch as, for example, its solubility in organic solvents governs the consumption of volatile solvents in the manufacture of powders, whereas its viscosity governs the mechanical strength of the finished powder, etc. In other cases, for example, in the production of lacquers, it is desirable to have products with the smallest possible nitrogen content, readily soluble, and of the lowest possible viscosity.

In practice, the following, most important nitrocelluloses have come to be defined:

1) collodion No.2, containing 11.5 - 12% nitrogen. Employed in the manufacture of lacquers, celluloid, film, nitroglycerin powders, etc.;

2) No.2 pyroxylin, containing 12.05 - 12.4% nitrogen. Employed in a mixture with No.1 pyroxylin to make pyroxylin powders;

3) pyrocollodion, containing 12.6% nitrogen (first obtained by D.I.Mendeleyev). Employed to manufacture pyroxylin powders;

4) No.1 pyroxylin, containing 13 - 13.5% nitrogen. Employed in a mixture with No.2 pyroxylin to manufacture pyroxylin powders.

In practice, a large quantity of cellulose nitrates of various properties are made use of.

The term pyroxylin powders is applied to powders made with volatile solvents (a mixture of alcohol and ether). Nitrocellulose designed to be used in pyroxylin

350 powders is freed of the water which it contains when produced. This used to be done by an exceedingly dangerous operation - the drying of nitrocellulose in driers. At the suggestion of D.I.Mendeleyev, drying was replaced by alcohol dehydration, and this was later adopted in all countries.

Nitrocellulose, dehydrated by alcohol, is treated in mixers with a mixture of alcohol and ether, resulting in the plasticization thereof. The other components of the powder, such as stabilizers, etc., are introduced at this point. Hydraulic presses are employed to press powder from the powder mass obtained. In order to remove the volatile solvent, the powder is dried in the open air, wetted in water, and then dried with moderate heating.

In the manufacture of nitroglycerin powders of the ballistite type, nitrocellulose is heated with a large quantity of water, to which the nitroglycerin and other components of the powder are then added. At the end of the "cooking", the nitrocellulose and the products absorbed therein are filtered free of water, and the resultant powder mass goes to hot rolls where it is separated from excess water, plasticized, and converted into a soft and elastic web. The web, rolled on reels, goes to hydraulic presses, the rolls of which are heated to 80 - 85°, and the nitroglycerin powder is pressed out. Thanks to the use of a nonvolatile solvent - nitroglycerin - the technological process is substantially condensed and simplified.

In the production of nitroglycerin powders of the cordite type, the nitrocellulose is treated in mixers by a solution of nitroglycerin in a volatile solvent. The mass resulting is pressed into powder, which is first spread out to dry at room temperature, and then dried at elevated temperature. Thus, the volatile solvent is removed from the powder, whereas the nonvolatile - the nitroglycerin - remains in the powder

350 as a component.

In the manufacture of celluloid, the nitrocellulose (collodion) in the mixers is treated with an alcohol solution of camphor. The resultant mass is plasticized by

351 treatment on rolls and in special block presses.

In manufacturing lacquers, the nitrocellulose is dissolved in a mixture of solvents, to which other substances - plasticizers, stabilizers, pigments, etc., are also added.

Section 2. Technology of Nitrocellulose Production

Nitrocellulose may be produced by reaction of nitric acids of greater than 77% strength upon cellulose. This results in a nitric acid ester. A weaker nitric acid results in the formation of an addition compound which is readily decomposed into the starting substances even by the effects of cold water. The nitrogen content of the nitrocellulose rises as the nitric acid concentration increases.

The treatment of cellulose by mixtures of sulfuric and nitric acids constitute the usual method of producing nitrocellulose. By changing the composition of the mixed acid and, primarily, the water content thereof, one may produce various types of cellulose. Inorder to obtain various types of nitrocelluloses, various compositions of acid mixtures may be employed, depending upon the form of cellulose, apparatus, the module of the bath, etc. (Table 106) (Bibl.6).

Table 106

Composition of Mixed Acids, %	Nitrogen Content of Nitrocellulose, %		
	8—12	12—12,75	13—13,5
HNO_3	25—35	23—25	25—26
H_2SO_4	47—55	59—62	63—69
H_2O	17—20	15—16	9—11

351 As a consequence of the need for good wettability of the loose mass of cellulose, as well as for reversibility of the esterification process, it is necessary to employ considerable excesses of the mixed acid, Usually, 30 to 50 times as much acid as cellulose is used, in weight, and in some cases even 80 - 100-fold excess is employed.

The nitrating agent in the mixed acids is nitric acid. Investigation (Bibl.52) of the mechanism of cellulose esterification by a mixed acid has shown that reaction is conditioned by interaction between the hydroxyl ions of cellulose and the NO_2^+ ions. This is confirmed by the fact that when mixed acid enriched by O^{18} is employed in esterification, the resultant nitrocellulose contains a nitrate group, in which two oxygens constitute O^{18}. From this, the conclusion has also been drawn that the oxygen of the hydroxyl group in cellulose does not separate out upon esterification and, consequently, it is unchanged.

Theoretically, 63.6 gm nitric acid is consumed in producing 100 gm cellulose trinitrate. However, the practical consumption thereof is considerably higher, inasmuch as, upon separation from the acids, at the end of esterification, a considerable amount of mixed acid remains in the cellulose, which is lost when washing with water is performed.

In the esterification of cellulose, side processes - hydrolysis and oxidation - occur, in addition to the basic process of formation of the cellulose ester.

Increase in temperature upon esterification accelerates the process, without changing the quantity of nitrate groups introduced. The side processes are intensified with rise in temperature, and
352 therefore rise in temperature always results in a reduction in the nitrocellulose yield.

The module has a significant effect upon the speed of the esterification process, and the result thereof. The effect of the module is diminished somewhat when the most active mixed acids, containing maximal HNO_3 and minimal H_2O.are employed.

Nitrogen oxides are, as a rule, a harmful impurity, particularly in mixtures containing much water. In anhydrous mixtures or mixtures containing a little water, the oxides are combined in nitrosyl sulfuric acid, and therefore do not affect the esterification process.

The quality and form of the cellulose exercise a considerable effect upon the quality of the nitro product. The cellulose should be such that, when it is charged into the acid mixture, it wets readily and rapidly, and absorbs a considerable quantity thereof. This requirement is met (both) by the chemical composition of the mixed acid, and by the shape in which the cellulose is employed. The purity of the material is of decisive significance, as is the structure of the fiber.

Cotton cellulose is distinguished by high purity and the good wettability of the mixed acid. Wood cellulose contains many impurities (resin, lignin, etc.) and requires special cleaning: bleaching and purification. In the etherification of wood cellulose, more active mixtures are employed (with elevated HNO_3 and reduced H_2O content).

After esterification, nitrocellulose, washed with water to neutral reaction, remains quite unstable. When stored for long periods, or dried, it decomposes, with production of nitrogen oxides. The spontaneous decomposition of nitrocellulose accelerates with time, and, where large masses of the product are involved, may result in spontaneous combustion and explosion.

352 A complex of operations, termed stabilization, ~~are~~ is employed to improve the stability of nitrocellulose. For purposes of stabilization, nitrocelluloses are boiled in weak acid and weak alkaline waters, and the fiber is ground, followed by neutralization of the "encapsulated" acids that are thus liberated.

The technological process of nitrocellulose production is composed of preparation of the XXXXX initial raw material, esterification of the cellulose, stabilization of the nitrocellulose, and dehydration of the nitrocellulose. In some cases, the process of reduction of viscosity is added in the production of collodion.

1. Preparation of the Raw Material

The mixed acids and the cellulose constitute the raw material. The mixed acids, of specific composition, are prepared in a special shop, where the pure and the spent acid are stored.

The cellulose reaches the factory in the form of cotton fiber pressed into bales, or in the form of rolls of paper. The bales of cotton are loosened by XXX a willowing machine, and the rolls of paper are broken down into pieces of specific size by special machinery. The fine material is dried (usually in pneumatic driers) to 1 - 2% moisture content, and cooled.

2. Esterification of Cellulose

The Thomson method. Esterification is performed in flat ceramic cups, 1 m in diameter and 0.25 m high. At the bottom of the bowl is a pipe to drain the spent acid. At a temperature of 28 - 30°, 300 - 400 kg mixed acid is run into the bowl
353 and 9 kg cellulose is charged in, and mixed with the acid. Then, perforated segments are placed over the top, and water is carefully poured onto this to a thickness of

XXX

353 1.5 - 2 cm to prevent evaporation of the acid. At the termination of the process (1 - 2.5 hrs), the cock for draining the nitric acid is opened, and cold water is carefully run-in from above. Seeping through the fibers, this water displaces the spent acid. About 80% of the spent acid is obtainable in undiluted form, the rest being diluted by water and subjected to concentration.

An inconvenience of the method is the partial denitration of the nitrocellulose as the spent acid is displaced by water.

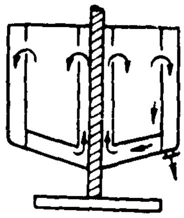


Fig.110 - Centrifuge

Esterification in centrifuges. Centrifuges with bottom drive, sometimes having jackets for external heating by warm water (Fig.110) are employed. The centrifuge is filled with mixed acids, started at low speed (25 rpm), and the cellulose is charged into it as rapidly as possible. Upon esterification, the mixed acid is thrown toward the wall of the centrifuge, under the action of the centrifugal force, and from the wall it flows downward and again enters the spent cellulose through holes in the walls of the basket (through the centrifuge cone). This circulation of the acid improves the condition of esterification. At the end of the process, the centrifuge is switched to fast operation (750 - 1000 rpm), and the spent acid is separated from the nitrocellulose. After the separation, the nitrocellulose is unloaded manually into a large volume of water, and sent to stabilization.

When this method of work is used, cases of spontaneous combustion of the material are not uncommon, because of the poor wetting of the cellulose by the mixed acids. Moreover, considerable quantities of acid are lost as a consequence

353 of evaporation.

__Esterification in nitrators.__ The process is run in special nitrators with good mechanical agitation. The nitrator (Fig.111) is of oval cross section, has a conical bottom, and is equipped with a valve for draining its entire contents into an acid-removing centrifuge, at the end of the process. The nitrator is closed with a cover and has a special flue, as well as two agitators rotating in opposite directions. The acid is sent into the nitrator from above through a spraying device, which improves the wetting of the cellulose.

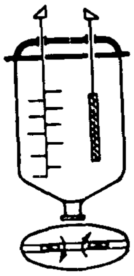


Fig. 111 - Nitrator

The mixed acid is charged into the nitrator, followed by the cellulose. The process lasts 30 - 45 min. At the end of this period, the valve at the bottom of the nitrator is opened, the contents are discharged into the acid-removing centrifuge, and the separation of the spent acid is completed within 5 - 10 min. The centrifuge discharges at the bottom, and the opening is closed by a rising cone. After the separation, the nitrocellulose is forced through the opening in the bottom of the centrifuge by iron prongs into a "washing" device below, and consisting of a large funnel with angular nozzles for the delivery of water. From here, the nitrocellulose goes to a bulk transporter, in which water transports it to an intermediate basin with an agitator (turbidizer).

The conditions for producing nitrocellulose from cotton are presented in Table 107.

Table 107

a)	b)			c)	d)
	H_2O	HNO_3	H_2SO_4		
Pyroxylin No.1 (for powder)	9,5	22,5	68,0	30	20
Pyroxylin No.2 (for powder)	14,5	22,5	63,0	30	30—40
Collodion	20,5	22,5	57,0	60	40
Collodion for nitrocellulose silk	18,3	19,7	62,0	60	40—50
Collodion for motion-picture film	17,0	20,0	63,0	60	40—50
Collodion for celluloid	20,0	20,0	60,0	60	40

a) Type of Collodion; b) Composition of mixed acid, % (module 40 - 50);

c) Esterification time, in min; d) Temperature of mixture, °C

3. Stabilization of Nitrocellulose

The process of stabilization resolves itself to washing the nitrocellulose, reducing its size in soda solution, and the final washing.

Washing is performed by hot water in special vats (of wood or stainless steel), having a false bottom, below which ~~XXXXXXX~~ live steam is introduced to heat the vat contents. The liquid from the vat is drained at a point beneath the false bottom.

Pipes are installed in the vat to circulate the liquid during cooking.

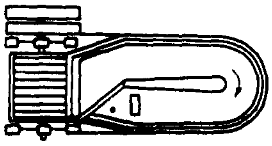


Fig.112 - Beating Machine (Hollander)

The nitrocellulose charged into the vat is first washed with cold water, then with hot water having 0.3 - 0.5% sulfuric acid added thereto. The nitrocellulose is first cooked with acid solution and then with soda solution (0.1% Na_2CO_3), then washed with water and sent for crushing to beating machines or other apparatus such as cone mills.

354 A beating machine (Fig.112) has a ~~bath~~ tub, oval in shape, made of iron or concrete, lined with dutch tiles. A longitudinal partition divides the ~~beating machine bath~~ hollander tub into two halves. At one end of the machine is the breaker mechanism, consisting of a system of knives: some of them are mounted to the bottom of the ~~bath~~ tub, and some to the surface of the rotating drum. The fibers, passing between the knives, are cut and crushed.

Water, a little soda, and then the nitrocellulose, are charged into the beating machine. After it has been crushed, the material in the ~~beating machine~~ hollander is transferred, to complete stabilization, in lavers, where hot washing (at 90 - 95°) is employed to remove the residue of soda and unstable impurities that have come out during the grinding.

The lavers are cylindrical vessels of up to 30 m^3 capacity, with agitators. Treatment of the nitrocellulose with hot water (two hot washings of 2 - 3 hrs duration each) is performed at a module of 8 - 10. After the washings, the water is removed by syphon. From the lavers, the nitrocellulose goes to mixers in which they are mixed with a larger lot.

The mixers are large containers (100 to 300 m^3) or basins having powerful agitators. A 10% nitrocellulose in water suspension is delivered to the mixers from
355 the lavers. Here, the contents are stirred for a long period to achieve homogeneity of the nitrocellulose in the large lots. The suspension is purified of particles of iron by means of electromagnets, and from sand by sand traps.

The nitrocellulose then goes to an agitator, and from there to centrifuges for separation of the water. Nitrocellulose, with a moisture content of about 30%, is

355 stored in wooden hoppers. Removal of the water from the nitrocellulose by drying in special driers is not performed, because of the extreme danger thereof.

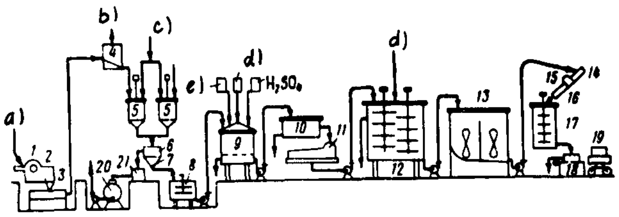


Fig.113 - Diagram of Nitrocellulose Manufacture

1 - Willowing machine; 2 - Funnel; 3 - Pneumatic drier; 4 - Bunker; 5- Nitrator; 6 - Acid-removing centrifuge; 7 - Washing apparatus; 8 - Turbidizer; 9 - Hot washing vat; 10 - Filter; 11 - Beating machine; 12 - Laver; 13 - Mixer of large batches; 14 - Trough; 15 - Electric~~al~~ magnet; 16 - Sand trap; 17 - Agitator; 18 - Water-removing centrifuge; 19 - Car; 20 - Spent-acid collector; 21 - Acid filter

a) Cotton; b) To dust chamber; c) Mixed acid; d) Water; e) Soda

Figure 113 illustrates the manufacture of nitrocellulose.

In manufacturing collodions, the production of nitrocellulose of low viscosity is necessary. To accomplish this, it is boiled in water at a pressure of up to 6 atm. Reduction of viscosity is controlled by the time and temperature of cooking. The process is carried out in autoclaves, usually constituting a pipe ($d = 10$ cm, $l = 1200$ m) heated by steam entering the jacket. The rate at which the nitroglycerin suspension passes through the autoclave, the pressure, and the temperature are regulated within the necessary limits.

Collodion to be used to make motion picture film is dehydrated by ethyl alcohol, which is run on to the centrifuge in three portions after removing the water.

355 G. **Starch Nitrates (Bibl.66, 53, 54)**

Nitrostarches are employed in the USA and in a number of other countries for the production of powder (Bibl.55), and are also used as explosives. Nitrostarch was first produced by Bracannot in 1833.

Nitrostarch contains 13.0 to 13.5% nitrogen. It is more hygroscopic than nitrocellulose, is virtually insoluble in water, and is readily soluble in acetone. Chemically, it is similar to nitrocellulose, it is capable of undergoing hydrolysis, and of undergoing saponification, etc.

Nitrostarch, dispersed into an ether-alcohol mixture, will frequently dissolve. When the solvent is removed, the result is a colloidal film or mass similar to nitrocellulose.

In its explosive properties nitrostarch is also similar to nitrocellulose. Nitrostarch containing 13.52% nitrogen, reveals a detonation velocity (at $\Delta = 0.9$)
356 of 4970 m/sec, while its fugacity exceeds that of picric acid by 17%. It ignites readily and burns at a rate of 1 m in 22 - 27 sec. The flame is not smoky. It is highly sensitive to mechanical effects (Bibl.53, 56).

Nitrostarch is produced by esterification of starch (potato or wheat) by a nitro mixture of the following composition: 50% HNO_3 and 50% H_2SO_4 at 15°. The resultant nitric ester is separated from the spent acid on filters and is subjected to washing and stabilization. The nitric ester is washed with a large quantity of cold water. Stabilization consists of a preliminary stabilization by cooking the product with water at a temperature of about 80 - 90° for several hours, followed by final stabilization. This last is performed by cooking the product in ethyl alcohol with addition of magnesium oxide to the mass to neutralize the residual acid.

Colors of Nitro Compounds in Alkaline Solutions

Nitro Compound	Solution in Acetone		Solution in Alcohol	
	with 1 part 10% KOH solution	with NH_3 or 10% NH_4OH	with 10% KOH solution	with NH_3 or 10% NH_4OH
Nitrobenzene	Violet (in the presence of traces of dinitrobenzene)	Pink	Pink	-
1,2-Dinitrobenzene	Crimson	-	-	-
1,3-Dinitrobenzene	Violet-red	Pale red	Brown	-
1,4-Dinitrobenzene	Colorless	-	-	-
1-Chloro-2,4-dinitrobenzene	Red, crimson; wine red when CH_3COOH is present	-	-	-
1-Chloro-3,5-dinitrobenzene	Bluish changing to fuchsia red	-	-	-
1,3,5-Trinitrobenzene	Blood red	-	-	-
Meta- and para-nitrotoluenes	Colorless			
2,4-Dinitrotoluene	Vivid dark blue	No coloration	Lt. pale blue	-
2,6-Dinitrotoluene	Vivid red with bluish tinge	Same	Bright red	-
α-Trinitrotoluene	Dark red	Dark red	Dark brown	Bright red
β-Trinitrotoluene	-	Green changing to red	-	-
γ-Trinitrotoluene	-	Dark blue turning to red	-	-
Technical trinitroxylene	Black, then dark violet	Dark brown	Dark brown	-
2,4,6-Trinitroxylene	Dark green	-	-	-
2,3,5-Trinitroxylene	Red brown	-	-	-
2,4,6-Trinitroethylbenzene	Red	-	-	-
α-Dinitronaphthalene	Bluish red	-	-	-
Trinitronaphthalene	Reddish brown	Reddish brown	Yellowish red	Yellowish red
Ortho-nitrophenol	Yellowish	-	-	-
Meta-nitrophenol	Reddish yellow	-	-	-
Para-nitrophenol	Bright yellow	-	-	-
2,4-Dinitrophenol	Yellowish	-	-	-
Trinitrophenol	Orange	-	-	-

APPENDIX 2

Specifications to be Met by Technical Sulfuric Acid

Indicator	Acid		Commercial Sulfuric Acid				Oleum	
	Chamber Process	Tower Process	Tower Process	Contact Process	Unrecovered Acid	Recovered Acid	For Nitration	For Other Purposes
Monohydrate content, not less than, %	65,0	75,0	90,5	92,5	91,0	75,0	—	—
Free sulfuric anhydride content, not less than, %	—	—	—	—	—	—	20,0	18,5
Calcined residue content, not more than, %	—	—	0,4	—	0,2	0,2	0,2	0,15
Iron content, not more than, %	—	—	—	—	—	—	0,04	—
Nitro compounds content, not more than, %	—	—	—	—	0,2	0,4	—	—
N_2O_3 content, not more than, %	0,01	0,03	0,07	—	0,01	0,05	—	—

Note 1. In oleum for nitrating mixtures produced by introducing commercial sulfuric acid into contact systems, the following ~~specifications~~ contents are permissible:

sulfuric anhydride, %, not less than 18.5
nitric acids computed as N_2O_3, %, not more than 0.05
Arsenic, %, not more than 0.03
calcined residue, %, not more than 0.25
iron, %, not more than 0.04

2. In commercial sulfuric acid produced by concentration of spent acid in a three-chamber concentrator, the following contents are permissible:

monohydrate, %, not less than 95
nitrogen oxides, computed as N_2O_3, %, not more than 0.01
calcined residue, %, not more than 0.20
nitro products, %, not more than 0.20

358

APPENDIX 3

Specifications to be Met by Technical Nitric Acid

Specifications	Weak Nitric Acid		Strong Nitric Acid		Acid Melange	
	Grade I	Grade II	Grade I	Grade II	Grade I	Grade II
HNO_3, %, not less than	49	60	98	96	89,0	87,0
Nitrogen oxides (N_2O_3), %, not more than	—	—	0,3	0,4	0,4	0,6
Sulfuric acid, %, not more than	—	—	Not more than 0,1	0,2	Not less than 7,5	7,5
Solid residue, %, not more than	0,07	0,05	0,05	0,07	0,12	0,15
Water, not more than	—	—	—	—	3,0	4,5

359

APPENDIX 4

Freezing Point of Alloys of 2,4-Dinitrotoluene and Para-Mononitrotoluene

Freezing point, °C	69,54	62,45	55,41	47,3	37,8	83,45	28,65	31,1	36,95	42,5	47,35	51,25
2,4-Dinitrotoluene	100	90	80	70	60	55	50	40	30	20	10	0
Para-mononitrotoluene, in %	0	10	20	30	40	45	50	60	70	80	90	100

APPENDIX 5

Solubility of Trinitrotoluene Isomers in 100 gm Alcohol, gm

Temperature, °C	Trinitrotoluene Isomers		
	α (2, 4, 6)-	γ (2, 4, 5)-	β (2, 3, 4)-
25	1,5	1,4	1,9
30	1,8	1,7	2,4
35	2,3	2,1	2,9
40	2,9	2,7	3,5
45	3,7	3,4	4,5
50	1,6	4,2	5,4
55	6,1	5,9	6,9
60	8,3	7,3	8,5
65	11,4	8,5	11,0
70	15,5	12,7	14,7

359

APPENDIX 6

Solubility of Trinitrotoluene Isomers, gm, in 100 gm of Benzene and Alcohol Mixture, at 25°

Trinitrotoluene Isomer \ Benzene to Alcohol Ratio	1:1	1:2	1:3	1:9
2,4,6-	20,4	8,7	5,3	2,5
2,4,5-	12,2	6,6	4,7	2,3
2,3,4-	9,5	6,4	4,7	2,9

APPENDIX 7

Solubility of Isomers of Trinitrotoluene, gm, in 100 gm Toluene, at 35°

Trinitrotoluene isomers	2,4,6-	2,4,5-	2,3,4-
Solubility	67,0	23,2	13,7

360

Appendix 8

Freezing Points of Alloys of 2,4,6-Trinitrotoluene and 2,4-Dinitrotoluene

Content of 2,4,6-trinitrotoluene alloyed with 2,4-dinitrotoluene, %	Freezing Point, °C	Trinitrotoluene Content in Alloy with 2,4-dinitrotoluene, %	Freezing Point, °C
100	80,35	55	50,49
90	74,40	40	50,35
—	—	30	55,65
70	61,50	20	61,00
60	54,30	10	65,70
—	—	0	69,54

Freezing Points of Alloys of Technical Trinitrotoluene and Dinitrotoluene

Trinitrotoluene Content in Alloy with Dinitrotoluene, %	Freezing Point, °C	Trinitrotoluene Content in Alloy with Dinitrotoluene, %	Freezing Point, °C	Trinitrotoluene Content in Alloy with Dinitrotoluene, %	Freezing Point, °C
0	56	41,0	36	68,8	58
2,7	55	44,4	37	70,0	59
5,9	54	45,9	38	71,2	60
9,0	53	47,1	39	72,5	61
10,9	52	48,2	40	73,8	62
12,9	51	49,4	41	75,0	63
14,9	50	50,5	42	76,5	64
16,9	49	51,6	43	78,0	65
19,0	48	52,7	44	78,5	66
21,1	47	53,7	45	81,3	67
22,8	46	54,8	46	83,1	68
24,4	45	55,9	47	85,0	69
25,9	44	57,1	48	87,0	70
27,3	43	58,3	49	89,0	71
28,6	42	59,4	50	90,7	72
29,8	41	50,5	51	92,1	73
31,2	40	61,7	52	93,6	74
32,5	39	62,8	53	95,0	75
33,9	38	63,9	54	96,8	76
35,0	37	65,0	55	98,6	77
36,3	36	66,2	56	100	78
37,5	35	67,3	57		

APPENDIX 10

Density of Solid and Liquid Trinitrotoluene at Various Temperatures

Temperature, °C	Specific Gravity	Specific Volume	Aggregate Condition
25	1,6407	0,6095	Solid
40	1,6369	0,6109	"
50	1,6318	0,6128	"
55	1,6305	0,6133	"
60	1,6299	0,6135	"
65	1,6274	0,6145	"
70	1,6242	0,6157	"
72	1.6151	0,6192	"
75	1,5671	0,6381	"
78	1,5149	0,6601	"
79,5	1,4982	0,6672	"
81	1,4638	0,6832	Liquid
82	1,4634	0,6833	"
88	1,4584	0,6857	"
93	1,4516	0,6889	"

APPENDIX 11

Specific Vapor Pressure of Trinitrotoluene

Temperature, °C	85	100	190	245—250
Vapor pressure, mm Hg	0,053	0,106	2	50

APPENDIX 12

Change in Specific Heat of Trinitrotoluene with Temperature

Temperature, °C	0	20	50	80
Specific heat, cal/gm/°C	0,309	0,328	0,353	0,374

APPENDIX 13

Effect of Light upon Freezing Point and Sensitivity of 2,4,6-Trinitrotoluene

Exposure Time, Hrs.	Freezing Point, °C,	Shock Sensitivity (p = 10 kg, h = = 25 cm) of 0103 gm Sample, in % explosions	Deflagration, °C
0	80,1	10	295—298
65	79,3	6	295—298
165	78,7	20	293—295
300	78,3	24	293—295
450	76,7	32	285—290
512	76,4	30	280—285

APPENDIX 14

Explosive Properties of Mixtures of TNT and RDX and Aluminum Powder

Name of Explosive	Filling Temperature, °C	Density of Cast Alloy, gm/ml	Velocity of Detonation, m/sec	Brisance due to Kast, mm	Gas Volume, ltr/kg	Heat of Explosion, kcal/kg	Temperature of Explosion, °K	Fugacity, ml	Shock Sensitivity at p = 10 kg, cm
TNT/RDX									
90/10	82	1,62	7070	4,4	—	—	—	316	24
80/20	82	1,63	7210	4,5	—	—	—	320	12
70/30	82	1,64	7420	4,7	—	—	—	353	8
60/40	82	1,67	7510	4,9	—	—	—	357	10
50/50	—	1,70	7570	5,1	791	1180	3820	368	12
40/60	—	1,70	7670	5,2	830	1200	3910	388	8
TNT/RDX/Aluminum									
70/15/15	85	1,72	6960	4,5	—	—	—	—	24
50/25/25	85	1,85	7680	4,9	—	—	—	397	24
50/20/30	85	1,80	7400	4,7	—	—	—	—	24
40/45/15	90	1,79	7500	5,3	—	—	—	478	24
TNT/Aluminum 90/10	85	1,65	6590	4,4	730	1195	3800	416	12

APPENDIX 15

Freezing Point of Alloys of Mononitrobenzene and Dinitrobenzene

Composition, %		Freezing Point, °C	Composition, %		Freezing Point, °C
Mononitrobenzene	Dinitrobenzene		Mononitrobenzene	Dinitrobenzene	
0	100	80,8	2,50	97,50	78,40
0,25	99,75	80,5	2,75	97,25	78,20
0,50	99,50	80,2	3,00	97,00	77,90
0,75	99,25	79,95	3,50	96,50	77,40
1,00	99,00	79,7	4,00	96,00	76,90
1,25	98,75	79,45	4,50	95,50	76,45
1,50	98,50	79,25	5,00	95,00	76,00
1,75	98,25	79,00	5,50	97,50	75,60
2,00	98,00	78,80	6,00	94,00	75,20
2,25	97,75	78,60	8,00	92,00	73,60
			10,00	90,00	72,20

APPENDIX 16

Change in Specific Gravity of Mononitrobenzene Relative to Dinitrobenzene Content thereof (at 15°)

Specific Gravity of Nitrobenzene at 15°	Dinitrobenzene, %	Specific Gravity of Nitrobenzene at 15°	Dinitrobenzene, %	Specific Gravity of Nitrobenzene at 15°	Dinitrobenzene, %
1,206	0,0	1,223	6,5	1,245	16
1,208	0,5	1,224	7,0	1,248	17
1,210	1,0	1,225	7,5	1,251	18
1,211	1,5	1,226	8,0	1,254	19
1,212	2,0	1,227	8,5	1,257	20
1,213	2,5	1,228	9,0	1,259	21
1,214	3,0	1,229	9,5	1,261	22
1,215	3,5	1,230	10,0	1,265	24
1,216	4,0	1,232	11,0	1,268	25
1,217	4,6	1,234	12	1,271	26
1,218	5,0	1,237	13	1,272	27
1,220	6,5	1,240	14	1,273	28
1,222	6,0	1,243	15	1,275	29
				1,280	30

APPENDIX 17

Solubility of Trinitroxylene and Xylyl Oil in Various Solvents

Solvents	Trinitroxylene Isomers	Solubility, %, at Various Temperatures, °C														
		10	15	20	25	30	35	40	45	50	55	60	65	70	75	80
Benzene	meta-	0,7	0,8	1,0	1,2	1,4	1,7	2,1	2,5	3,0	3,6	4,4	5,1	5,9	—	—
	para-	—	3,3	4,4	5,5	6,9	8,1	10,2	11,9	13,8	16,2	19,3	—	—	—	—
Toluene	meta-	0,6	0,7	0,9	1,1	1,3	1,5	1,8	2,1	2,5	3,0	3,7	4,5	5,4	6,5	7,7
	para-	2,1	2,7	3,4	4,1	5,1	6,0	7,0	8,3	9,8	11,2	13,6	16,5	19,2	22,1	26,5
Acetone	meta-	0,8	1,0	1,2	1,5	1,9	2,4	2,8	3,5	4,3	5,1	—	—	—	—	—
	para-	6,2	7,2	8,8	10,4	12,1	14,4	16,8	19,3	21,9	24,5	—	—	—	—	—
96% Alcohol	meta-	—	—	0,01	0,03	0,06	0,08	0,11	0,14	0,17	0,21	0,27	0,35	0,43	0,51	0,60
	para-	0,13	0,16	0,2	0,3	0,4	0,5	0,6	0,8	1,0	1,4	1,7	2,1	2,7	3,2	3,7
	xylyl oil	—	—	8,9	10,8	12,8	15,3	18,5	22,2	27,5	43,6	51,6	—	—	—	—
Mixture of 20% benzene and 80% automotive gasoline	meta-	0,04	0,05	0,06	0,07	0,08	0,1	0,13	0,17	0,22	0,27	0,34	0,42	0,56	—	—
	para-	0,11	0,14	0,17	0,22	0,28	0,36	0,45	0,57	0,8	1,0	1,2	1,3	1,4	—	—
	xylyl oil	—	—	—	6,7	7,5	8,7	10,1	11,9	14,1	16,0	18,5	21,3	25,5	31,1	—
Mixture of 30% benzene and 70% automotive gasoline	meta-	0,10	0,12	0,15	0,18	0,23	0,27	0,37	0,48	0,56	0,70	0,87	—	—	—	—
	para-	—	0,22	0,32	0,41	0,53	0,69	0,90	1,08	1,33	1,58	2,0	—	—	—	—
	xylyl oil	—	11,7	13,5	15,4	17,5	19,9	22,4	26,1	30,0	34,8	40,3	46,2	52,5	—	—

APPENDIX 18

Heat of Combustion and Formation of Naphthalene and its Nitro Derivatives

Substance	Molecular Heat of Combustion in kcal		Heat of Formation kcal/mole
	when v = const	when p = const	
Naphthalene	1230,33	1229,17	—11,6
1-Nitronaphthalene	1189,95	1190,09	— 7,3
1,5-Dinitronaphthalene	1153,48	1152,61	— 3,6
1,8-Dinitronaphthalene	1154,74	1153,87	— 4,8
1,3,8-Trinitronaphthalene	1119,75	1117,86	— 2,9
1,4,5-Trinitronaphthalene	1122,72	1120,83	— 5,8
1,3,6,8-Tetranitronaphthalene	—	—	— 1,6

APPENDIX 19

Melting Point of Alloys of 1,5- and 1,8-Dinitronaphthalenes

Percentage Composition		Melting Points, °C	
1,5-Dinitronaphthalene	1,8-Dinitronaphthalene	Initial	Final
100,0	0	215	215
90,9	9,1	195	206
78,9	21,1	183	200
66,7	33,3	183	193
50,0	50,0	183	185
33,3	66,7	148	155
22,1	77,9	145,5	145,5
90,1	90,9	149	161
0	100	170	171

APPENDIX 20

Solubility of Isomers of Trinitrotoluene in Various Solvents

Trinitrotoluene Isomers	Solvent	Temperature of Solution, °C	Solubility, %
1, 3, 8-	Dichloroethane	19	0,60
1, 2, 5-	"	19	3,72
1, 3, 8-	65% HNO_3	19	0,07
1, 2, 5-	65% HNO_3	19	0,25
1, 2, 5-	Chloroform	19	2,01
1, 3, 8-	Acetone	19	2,99

Continued

Trinitrotoluene Isomers	Solvent	Temperature of Solution, °C	Solubility, %
1, 2, 5-	Acetone	19	25,42
1, 3, 8-	95% Alcohol	19	0,02
1, 2, 5-	95% Alcohol	19	0,43
1, 4, 5-	Gasoline	55	0,07
1, 2, 5-	Gasoline	65	0,06
1, 3, 5-	Acetic acid	80	0,73
1, 4, 5-	same	Boiling point	Insoluble
1, 2, 5-	Carbon disulfide	same	same
1, 3, 8-	Carbon disulfide	-	-
1, 3, 8-	Water	-	-
1, 2, 5-	Water	-	0,04

APPENDIX 21

Specific Gravity of Mixture of Benzene and Chlorobenzene at 15°

Composition in %		Specific Gravity	Composition in %		Specific Gravity	Composition in %		Specific Gravity
Benzene	Chlorobenzene		Benzene	Chlorobenzene		Benzene	Chlorobenzene	
0	100	1,1125	35	65	1,0206	70	30	0,9425
5	95	1,0988	40	60	1,0092	75	25	0,9321
10	90	1,0852	45	55	0,9979	80	20	0,9220
15	85	1,0718	50	50	0,9866	85	15	0,9124
20	80	1,0585	55	45	0,9755	90	10	0,9031
25	75	1,0454	60	40	0,9644	95	5	0,8939
30	70	1,0327	65	35	0,9534	100	0	0,8848

APPENDIX 22

Specific Gravity of Mixture of Chlorobenzene and Dichlorobenzene at 15°

Composition in %		Specific Gravity	Composition in %		Specific Gravity	Composition in %		Specific Gravity
Chlorobenzene	Dichlorobenzene		Chlorobenzene	Dichlorobenzene		Chlorobenzene	Dichlorobenzene	
100	0	1,1125	75	25	1,1541	50	50	1,1999
95	5	1,1207	70	30	1,1632	45	55	1,2093
90	10	1,1290	65	35	1,1722	40	60	1,2183
85	15	1,1374	60	40	1,1812	35	65	1,2285
80	20	1,1458	55	45	1,1906	30	70	1,2385

APPENDIX 23

Heat of Formation and of Combustion of Organic Substances

(Starting and Intermediate Materials for Powders and High Explosives)

Substance	a)	b)	c)		d)		
			kcal/mole	kcal/kg	Q kcal/kg	q_v kcal/mole	q_p kcal/mole
Akardite 1, asymmetrical (diphenylurea)	$C_{13}H_{12}ON_2$	212,24	1605,4	7 564	103,9	22,0	26,4
Akardite 2, (N-methyl-NN'-diphenylurea)	$C_{14}H_{14}ON_2$	226,27	1771,4	7 829	77,3	17,5	22,4
Akardite 3, (N-ethyl-NN'-diphenylurea)	$C_{15}H_{16}ON_2$	240,29	1923	8 002	115,1	27,7	33,2
Anisole	C_7H_8O	108,13	904	8 360	224,2	24,2	26,8
Aniline	C_6H_7N	93,12	810	8 700	−104,3	−9,7	−7,4
Acetone	C_3H_6O	58,08	427,2	7 355	989	57,1	59,4
Benzene	C_6H_6	78,11	780	9 982	−166,6	−13	−11,3
Glycerol	$C_3H_8O_3$	92,09	395,5	4 295	1700	156,6	159,8
Dibutylphthalate	$C_{16}H_{22}O_4$	278,34	2055	7 383	689	191,9	199,5
Dimethylaniline	$C_8H_{11}N$	121,18	1142,7	9 429,8	−158,52	−19,21	−15,73
2,4-Dinitroanisole	$C_7H_6O_5N_2$	198,13	821,4	4 145,7	198,5	39,3	43,1
2,6-Dinitroanisole		198,13	820,7	4 142	202,2	40,0	43,8
2,4-Dinitrotoluene	$C_7H_6O_4N_2$	182,13	848,7	4 660	65,9	12,0	15,5
2,6-Dinitrotoluene		182,13	854,4	4 691	34,8	6,3	9,8
Dioxane	$C_4H_8O_2$	88,10	561,2	6 370	964	84,9	87,8
Diphenylamine (solution	$C_{12}H_{11}N$	169,22	1537	9 083	−291	−37,4	−32,9
Diphenylnitrosoamine	$C_{12}H_{10}ON_2$	198,22	1526	7 700	−304,7	−60,4	−56,6
Dichloroethane	$C_2H_4Cl_2$	98,97	296,5	2 396	374,4	37,1	38,8
Diethyleneglycol	$C_4H_{10}O_3$	106,18	568,2	5 354	1371	145,5	149,3
Diethylphthalate	$C_{12}H_{14}O_4$	222,23	1422	6 400	804	178,7	183,9
Camphor	$C_{10}H_{16}O$	152,23	1411	9 271	453	69	73,9
Meta-xylene	C_8H_{10}	106,16	1087	10 239	25,4	2,8	5,7
Mannitol	$C_6H_{14}O_6$	182,17	723	3 969	1722	313,7	319,5

a) Formula; b) Molecular weight; c) Heat of combustion (v = const); d) Heat of formation

Continued

Substance	a)	b)	c) kcal/mole	c) kcal/kg	d) Q kcal/kg	d) q_v kcal/mole	d) q_p kcal/mole
Methyl alcohol	CH_4O	32,04	173,5	5 415	1732	55,5	57
Trimethylenemethylmethane (metriol)	$C_5H_{12}O_3$	120,15	650,6	5 847	1438	172,8	177,2
Urea	CH_4ON_2	60,06	153,3	2 530	1249	75,7	77,7
Naphthalene	$C_{10}H_8$	128,16	1232	9 616	−172,4	−22,1	−19,8
2-Methyl-2-nitropropanediol	$C_4H_9O_4N$	135,12	548	4 057	974,7	131,7	135,8
Guanidine nitrate	$CH_6O_3N_4$	122,09	209,5	1 716	712,8	87,0	90,8
Urea nitrate	$CH_5O_4N_3$	123,07	131,9	1 071,7	1063	130,9	134,4
Nitroaminoguanidine	$CH_5O_2N_5$	119,09	268	2 250	−43,4	−5,2	−1,7
Nitroguanidine	$CH_4O_2N_4$	104,07	210,6	2 023	177,6	18,5	21,4
Nitroisobutylglycerol	$C_4H_9O_5N$	151,12	507,9	3 361	1138	172	176,4
Nitromethane	CH_3O_2N	61,04	175,9	2 881	318,3	19,4	21,1
Nitrourea	$CH_3O_3N_3$	105,06	130,8	1 245	613,7	64,5	67,1
2-Nitro-2-ethylpropanediol	$C_5H_{11}O_4N$	149,15	703,7	4 718	923,2	137,7	142,3
Pentaerythritol	$C_5H_{12}O_4$	136,15	661	4 855	1573	214,1	218,7
Stearic acid	$C_{18}H_{36}O_2$	284,47	2703	9 503	718	204,2	215,2
Toluene	C_7H_8	92,13	932,8	10 125	−50,0	−4,6	−2,3
Triethyleneglycol	$C_6H_{14}O_4$	150,17	851	5 667	1236	185,7	190,9
Urotropine	$C_6H_{12}N_4$	140,19	1004,6	7 166	−252,5	−35,4	−30,8
Phenol	C_6H_6O	94,11	730,7	7 764	382,7	36,0	38,0
Centralite 1	$C_{17}H_{20}ON_2$	268,35	2254	8 400	72,3	19,4	26,1
Centralite 2	$C_{15}H_{16}ON_2$	240,29	1942	8 081	36	8,7	14,2
Centralite 3	$C_{16}H_{18}ON_2$	254,32	2094	8 233	71,5	18,2	24,3
Erythritol	$C_4H_{10}O_4$	122,12	500,2	4 096	1748	213,4	217,5
Ethyleneglycol	$C_2H_6O_2$	62,07	285,2	4 594	1698	105,4	107,7
Ethyl alcohol	C_2H_6O	46,07	326,2	7 081	1396	64,3	66,3
Ethyl ether	$C_4H_{10}O$	74,12	650,5	8 776	851	63,1	66,3
Trimethylolethylmethane	$C_6H_{14}O_3$	134,17	863,5	6 436	1294	173,2	178,1

a) Formula; b) Molecular weight; c) Heat of combustion:(v = const); d) Heat of formation

APPENDIX 24

Heat of Formation and Combustion of Explosives

Explosives	a)	b)	c)		d)		
			q_{hc} kcal/mole	Q_{hc} kcal/kg	Q_v kcal/kg	q_v kcal/mole	q_p kcal/mole
Dinitroethane	$C_2H_4O_4N_2$	120	284,6	2370	320,6	38,5	41,4
Glycoldinitrate	$C_2H_4O_4N_2$	152	268	1764	360,4	54,8	58,3
Ethylenedinitroamine	$C_2H_6O_4N_4$	150	370	2465	133	20	24
Ethylenediamine dinitrate	$C_2H_{10}O_6N_4$	186	376	2020	803,6	149,6	155,4
Glycerol trinitrate	$C_3H_5O_9N_3$	227	368,6	1623	362,3	82,3	87,2
Cyclotrimethylenetrinitrosoamine	$C_3H_6O_3N_3$	174	557,3	3200	—417,4	—72,7	—68,3
Hexogen (cyclotrimethylenetrinitroamine)	$C_3H_6O_6N_6$	222	507	2282	—100,4	—22,3	—17,1
Dinitrodimethyloxamide	$C_4H_6O_6N_4$	206	512	2485	322,2	66,4	71,1
Nitroisobutylglycerol trinitrate	$C_4H_6O_{11}N_4$	286	530	1856	167,8	48,0	54,1
Erythritol tetranitrate	$C_4H_6O_{12}N_4$	302	467	1546	369,2	111,5	117,9
2-Methyl-2-nitropropanediol-dinitrate	$C_4H_7O_8N_3$	225	529	2349	371,2	83,6	88,8
Diglycol dinitrate	$C_4H_8O_7N_2$	196	549	2798	496,5	97,4	102,3
DINA	$C_4H_8O_8N_4$	240	578	2409	282,7	67,7	73,5
PETN (pentaerythritol tetranitrate)	$C_5H_8O_{12}N_4$	316	620	1962	379,5	120,0	127,0
Nitro-2-ethylpropanediol dinitrate	$C_5H_9O_8N_3$	239	694	2900	336,1	80,4	86,2
Trimethylenemethyl-methanetrinitrate	$C_5H_9O_9N_3$	255	674	2644	389,5	99,4	105,5
Trinitrochlorobenzene	$C_6H_2O_6N_3Cl$	247,6	646	2609	—36,2	—9,2	—5,5
Trinitrobenzene	$C_6H_3O_6N_3$	213	660	3099	23,5	5,0	8,5
Picric acid	$C_6H_3O_7N_3$	229	618	2696	208,9	47,8	51,5
Trinitroresorcinol	$C_6H_3O_8N_3$	245	566	2310	404,8	99,2	103,3
Tetranitroaniline	$C_6H_3O_8N_5$	273	659	2411	25,4	6,9	11,5
Dinitrobenzene	$C_6H_4O_4N_2$	168	696	4142	17,1	2,9	5,8
Trinitroaniline	$C_6H_4O_6N_4$	228	686	3008	57,5	13,1	17,2
Trinitrophenylhydrazine	$C_6H_5O_6N_5$	243	747	3074	—59,7	—14,5	—9,9
Ammonium picrate	$C_6H_6O_7N_3$	246	679	2760	354,8	87,3	91,9
NENO	$C_6H_8O_{12}N_6$	356	715	2007	335,1	119,4	126,9

a) Formula; b) Molecular weight; c) Heat of combustion (v = const); d) Heat of formation

Continued

Explosives	a)	b)	c)		d)		
			q_{kc} kcal/mole	Q_{hc} kcal/kg	Q_v kcal/kg	q_v kcal/mole	q_p kcal/mole
Mannitol hexanitrate	$C_6H_8O_{18}N_6$	452	684	1512	342,8	150,5	159,8
Trimethylene-ethylmethanetrinitrate	$C_6H_{11}O_9N_3$	269	829	3081	394,3	106,1	112,8
TNT	$C_7H_5O_6N_3$	227	817	3596	44,6	10,1	14,2
Trinitrocresol	$C_7H_5O_7N_3$	243	772	3175	226,7	55,1	59,5
Trinitroanisole	$C_7H_5O_7N_3$	243	795	3269	132,0	32,1	36,5
Tetryl	$C_7H_5O_8N_5$	287	840	2926	—46,2	—13,3	—8,0
Trinitrophenylglycol nitrate	$C_8H_6O_{10}N_4$	318	894	2811	189,8	60,4	66,2
Xylene	$C_8H_7O_6N_3$	241	971	4025	74,3	17,9	22,5
Trinitroethylbenzene	$C_8H_7O_6N_3$	241	977	4051	47,7	11,6	16,2
Trinitrophenetole	$C_8H_7O_7N_3$	257	946	3680	164,2	42,2	47,4
Trinitrophenylethylnitramine	$C_8H_7O_8N_5$	301	990	3289	—6,4	—1,9	3,9
Trinitromesitylene	$C_9H_9O_6N_3$	255	1126	4412	94,5	24,1	29,3
Trinitrophenyltrimethylnitramine	$C_9H_9O_{12}N_9$	435	1190	2734	—91,7	—39,9	—31,2
Tetranitronaphthalene	$C_{10}H_4O_8N_4$	308	1085	3522	—32,5	—10,0	—5,4
1,3,8-Trinitronaphthalene	$C_{10}H_5O_6N_3$	263	1121	4259	—44,7	—11,8	—7,7
1,4,5-Trinitronaphthalene		263	1124	4270	—55,5	—14,6	—10,1
1,5-Dinitronaphthalene	$C_{10}H_6O_4N_2$	218	1154,7	5293	—54,6	—11,9	—8,4
1,8-Dinitronaphthalene		215	1156,0	5299	—60,5	—13,2	—9,7
Dipentaerythritol hexanitrate	$C_{10}H_{16}O_{19}N_6$	524	1276	2434	389,5	204,2	216,1
Hexyl	$C_{12}H_5O_{12}N_7$	439	1315	2994	—41,2	—18,1	—11,1
Ditetryl	$C_{14}H_8O_{16}N_{10}$	572	1630	2849	—77,0	—44,1	—34,2

a) Formula; b) Molecular weight; c) Heat of combustion (v = const);

d) Heat of formation

APPENDIX 25

Physical Chemical Constants of Brisant Explosives, as well as of Initial Products and Intermediate Synthesis Thereof

The numerical values of the constants are rounded off and carried as far as necessary for use under ordinary technological conditions of computaion. The figures in parentheses indicate the temperatures for which the data are valid.

Name	a)	b)	c)	d)	e)	f)
Benzene	C_6H_6	73,1	5,58	80,1	0,879	0,451
Toluene	$CH_3 \cdot C_6H_5$	92,1	−95,0	110,6	0,867	0,408
Ortho-xylene	$(CH_3)_2 \cdot C_6H_4$	106,1	−25	144	0,881	0,423
Meta-xylene	$(CH_3)_2 \cdot C_6H_4$	106,1	−47,4	139,3	0,867	0,413
Para-xylene	$(CH_3)_2 \cdot C_6H_4$	106,1	−13,2	138,5	0,861	0,414
Ethylbenzene	$C_2H_5 \cdot C_6H_5$	106,1	−94,4	136,2	0,864	—
Naphthalene	$C_{10}H_8$	128,1	80,2	217,9 sublimates	1,152	0,308
Diphenyl	$C_6H_5 \cdot C_6H_5$	154,2	69,5	254,9	0,992 (73)	0,306
Methyl alcohol	$OH \cdot CH_3$	32,0	−97,8	64,7	0,792	0,609
Ethyl alcohol	$OH \cdot C_2H_5$	46,1	−112	78,4	0,789	0,579
Glycol	$OH \cdot CH_2 \cdot CH_2 \cdot OH$	62,0	−15,6	197,4	1,113 (10°)	—
Glycerin	$OH \cdot CH_2 \cdot$ $\cdot CH(OH) \cdot CH_2 \cdot OH$	92,1	17,9	290	1,261	0,525
Phenol	$OH \cdot C_6H_5$	94,1	42,5	181,4	1,071	0,561
Chlorobenzene	$Cl \cdot C_6H_5$	112,5	−45,2	132,1	1,107	0,311
Urea	$NH_2 \cdot CO \cdot NH_2$	60,0	132,7	decomposes	1,335	0,371
Aniline	$NH_2 \cdot C_6H_5$	93,1	−6,2	184,4	1,022	0,512
Nitrobenzene	$NO_2 \cdot C_6H_5$	123,1	5,7	210,9	1,204	0,360 (0°)
Ortho-dinitrobenzene	$(NO_2)_2 \cdot C_6H_4$	168,1	116,5	319	1,59 (18°)	—
Meta-dinitrobenzene	$(NO_2)_2 \cdot C_6H_4$	168,1	89,7	302	1,575	—
Para-dinitrobenzene	$(NO_2)_2 \cdot C_6H_4$	168,1	172,1	309	1,625	—
1,3,5-Trinitrobenzene	$(NO_2)_3 \cdot C_6H_3$	213,1	123,25	decomposes	1,688	—
Ortho-nitrotoluene	$NO_2 \cdot C_6H_4 \cdot CH_3$	137,1	−10,6 (α) −4,1 (β)	222	1,163 (20°)	—
Meta-nitrotoluene	$NO_2 \cdot C_6H_4 \cdot CH_3$	137,1	15,5	231	1,160 (18°)	—
Para-nitrotoluene	$NO_2 \cdot C_6H_4 \cdot CH_3$	137,1	51,9	237,7	1,139 (55°)	—
2,4-Dinitrotoluene	$(NO_2)_2 \cdot C_6H_3 \cdot CH_3$	182,1	69,95	boils and decomposes at 300°	1,32 (71°)	0,33
2,6-Dinitrotoluene	$(NO_2)_2 \cdot C_6H_3 \cdot CH_3$	182,1	65,1		1,28 (111°)	—
3,4-Dinitrotoluene	$(NO_2)_2 \cdot C_6H_3 \cdot CH_3$	182,1	58,5		1,259 (111°)	—
2,3-Dinitrotoluene	$(NO_2)_2 \cdot C_6H_3 \cdot CH_3$	182,1	59,23		1,263 (111°)	—
3,6(2,5)-Dinitrotoluene	$(NO_2)_2 \cdot C_6H_3 \cdot CH_3$	182,1	59,5		1,282 (111°)	—

a) Chemical formula; b) Molecular weight; c) Melting point, °C; d) Boiling point at p = 760 mm, °C; e) Specific gravity or density; f) Specific heat at 25°, kcal/kg (°C); g) (sublimates); h) Decomposes; i) Boils and decomposes at 300°

Name	a)	b)	c)	d)	e)	f)
3,5-Dinitrotoluene	$(NO_2)_2\cdot C_6H_3\cdot CH_3$	182,1	92,1	g)	1,277 (111°)	—
2,4,6-Trinitrotoluene	$(NO_2)_3\cdot C_6H_2\cdot CH_3$	227,1	80,85	h)	1,663 1,467 (82°)	0,328
2,4,5(3,4,6)-Trinitrotoluene	$(NO_2)_3\cdot C_6H_2\cdot CH_3$	227,1	102,3	i)	1,620	—
2,3,4-Trinitrotoluene	$(NO_2)_3\cdot C_6H_2\cdot CH_3$	227,1	110,3	—	1,620	—
2,3,6-Trinitrotoluene	$(NO_2)_3\cdot C_6H_2\cdot CH_3$	227,1	109,8	—	1,620	—
2,3,5-Trinitrotoluene	$(NO_2)_3\cdot C_6H_2\cdot CH_3$	227,1	92,5	—	1,620	—
3,4,5-Trinitrotoluene	$(NO_2)_3\cdot C_6H_2\cdot CH_3$	227,1	132,0	j)	1,620	—
2-Nitro-m-xylene	$NO_2\cdot C_6H_3\cdot CH_3$	151,1	13	225	1,112 (16°)	—
4-Nitro-m-xylene	$NO_2\cdot C_6H_3\cdot CH_3$	151,1	2	244	1,135 (15°)	—
5-Nitro-m-xylene	$NO_2\cdot C_6H_3\cdot CH_3$	151,1	74	273	—	—
2-Nitro-n-xylene	$NO_2\cdot C_6H_3\cdot CH_3$	151,1	—	239	1,132	—
3-Nitro-o-xylene	$NO_2\cdot C_6H_3\cdot CH_3$	151,1	15	240	—	—
4-Nitro-o-xylene	$NO_2\cdot C_6H_3\cdot CH_3$	151,1	30	259	—	—
Ortho-nitroethylbenzene	$NO_2\cdot C_6H_4\cdot C_2H_5$	151,1	—23	228	1,126	—
Para-nitroethylbenzene	$NO_2\cdot C_6H_4\cdot C_2H_5$	151,1	—32	245	1,124	—
Meta-nitroethylbenzene	$NO_2\cdot C_6H_4\cdot C_2H_5$	151,1	—37	246	—	—
2,4-Dinitro-m-xylene	$(NO_2)_2\cdot C_6H_2\cdot(CH_3)_2$	196,1	83—4	—	—	—
2,5-Dinitro-m-xylene	$(NO_2)_2\cdot C_6H_2\cdot(CH_3)_2$	196,1	101	—	—	—
4,6-Dinitro-m-xylene	$(NO_2)_2\cdot C_6H_2\cdot(CH_3)_2$	196,1	93	—	—	—
4,5-Dinitro-m-xylene	$(NO_2)_2\cdot C_6H_2\cdot(CH_3)_2$	196,1	132	—	—	—
2,6-Dinitro-n-xylene	$(NO_2)_2\cdot C_6H_2\cdot(CH_3)_2$	196,1	123.5	—	—	—
2,3-Dinitro-n-xylene	$(NO_2)_2\cdot C_6H_2\cdot(CH_3)_2$	196,1	93	—	—	—
2,5-Dinitro-n-xylene	$(NO_2)_2\cdot C_6H_2\cdot(CH_3)_2$	196,1	118	—	—	—
3,4-Dinitro-o-xylene	$(NO_2)_2\cdot C_6H_2\cdot(CH_3)_2$	196,1	82	k)	—	—

a) Chemical formula; b) Molecular weight; c) Melting point, °C; d) Boiling point at p = 760 mm, °C; e) Specific gravity or density; f) Specific heat at 25°, kcal/kg (°C); g) Boils and decomposes at 300°; h) Explodes at 280°; i) Explodes at 290°; j) Decomposes at 313°; k) Explodes at 13°

Continued

Name	a)	b)	c)	d)	e)	f)
3,6-Dinitro-o-xylene	$(NO_2)_2\cdot C_6H_2\cdot(CH_3)_2$	196,1	56	—	—	—
3,5(3,4)-Dinitro-o-xylene	$(NO_2)_2\cdot C_6H_2\cdot(CH_3)_2$	196,1	75	g)	—	—
4,5-Dinitro-o-xylene	$(NO_2)_2\cdot C_6H_2\cdot(CH_3)_2$	196,1	115,6	—	—	—
2,4-Dinitroethylbenzene	$(NO_2)_2\cdot C_6H_3\cdot C_2H_5$	196,1	4	—	—	—
2,4,6-Trinitro-m-xylene	$(NO_2)_3\cdot C_6H\cdot(CH_3)_2$	241,1	182	—	1,604 (18°)	—
2,4,5-Trinitro-m-xylene	$(NO_2)_3\cdot C_6H\cdot(CH_3)_2$	241,1	90	—	—	—
4,5,6-Trinitro-m-xylene	$(NO_2)_3\cdot C_6H\cdot(CH_3)_2$	241,1	125	—	1,494	—
2,3,6-Trinitro-n-xylene	$(NO_2)_3\cdot C_6H\cdot(CH_3)_2$	241,1	137	h)	1,159	—
3,4,6-Trinitro-o-xylene	$(NO_2)_3\cdot C_6H\cdot(CH_3)_2$	241,1	115	—	—	—
3,4,5-Trinitro-o-xylene	$(NO_2)_3\cdot C_6H.\cdot(CH_3)_2$	241,1	72	—	—	—
2,4,5-Trinitroethylbenzene	$(NO_2)_3\cdot C_6H_2\cdot C_2H_5$	241,1	37	—	—	—
α-Nitronaphthalene	$NO_2\cdot C_{10}H_7$	173,1	60	304	1,223 (61°)	—
1,5-Dinitronaphthalene	$(NO_2)_2\cdot C_{10}H_6$	218,1	216	i)	—	—
1,8-Dinitronaphthalene	$(NO_2)_2\cdot C_{10}H_6$	218,1	173,5	j)	—	—
1,3-Dinitronaphthalene	$(NO_2)_2\cdot C_{10}H_6$	218,1	144	i)	—	—
1,3,8-Trinitronaphthalene	$(NO_2)_3\cdot C_{10}H_5$	263,1	218	—	—	—
1,4,5-Trinitronaphthalene	$(NO_2)_3\cdot C_{10}H_5$	263,1	146	—	—	—
1,2,5-Trinitronaphthalene	$(NO_2)_3\cdot C_{10}H_5$	263,1	112	—	—	—
1,3,6,8-Tetranitronaphthalene	$(NO_2)_4\cdot C_{10}H_4$	308,1	202	—	—	—
1,2,5,8-Tetranitronaphthalene	$(NO_2)_4\cdot C_{10}H_4$	308,1	270°		k)	
1,3,5,8-Tetranitronaphthalene	$(NO_2)_4\cdot C_{10}H_4$	308,1	194	—	—	—
1,4,5,8-Tetranitronaphthalene	$(NO_2)_4\cdot C_{10}H_4$	308,1	300°		k)	
Ortho-nitrochlorobenzene	$NO_2\cdot C_6H_4\cdot Cl$	157,5	32,5	245	—	—

a) Chemical formula; b) Molecular weight; c) Melting point, °C; d) Boiling point at p = 760 mm, °C; e) Specific gravity or density; f) Specific heat at 25°, kcal/kg (°C); g) Explodes at 438°; h) Explodes at 463°; i) Sublimates; j) Decomposes; k) Decomposes without melting

Continued

Name	a)	b)	c)	d)	e)	f)
Meta-nitrochlorobenzene	$NO_2\cdot C_6H_4\cdot Cl$	157,5	46,0	235	—	—
Para-nitrochlorobenzene	$NO_2\cdot C_6H_4\cdot Cl$	157,5	83,0	242	—	—
2,4-Dinitrochlorobenzene	$(NO_2)_2\cdot C_6H_4\cdot Cl$	202,5	53,4	—	—	—
2,6-Dinitrochlorobenzene	$(NO_2)_2\cdot C_6H_4\cdot Cl$	202,5	43,2	—	—	—
3,5-Dinitrochlorobenzene	$(NO_2)_2\cdot C_6H_4\cdot Cl$	202,5	27,0	—	—	—
Ortho-nitrophenol	$NO_2\cdot C_6H_4\cdot OH$	139,1	45	214,5	1,295 (45°)	—
Meta-nitrophenol	$NO_2\cdot C_6H_4\cdot OH$	130,1	96	194 (70 mm)	1,485	—
Para-nitrophenol	$NO_2\cdot C_6H_4\cdot OH$	139,1	113,4	sublimates	1,48	—
2,4-Dinitrophenol	$(NO_2)_2\cdot C_6H_3\cdot OH$	184,1	112,5	sublimates	1,683	—
2,6-Dinitrophenol	$(NO_2)_2\cdot C_6H_3\cdot OH$	184,1	62,5	—	—	—
2,4,6-Trinitrophenol	$(NO_2)_3\cdot C_6H_2\cdot OH$	229	122,5	—	1,763	0,234 (0°)
Tetryl	$(NO_2)_3\cdot C_6H_2\cdot \cdot NCH_3\cdot NO_2$	282	129,4	—	1,73	0,217
Ammonium nitrate	$(NO_2)_3\cdot C_6H_2\cdot \cdot ONH_4$	232	265—270	—	1,717	—
Hexyl	$(NO_2)_3\cdot C_6H_2\cdot \cdot C_6H_2(NO_2)_3$	439	243—244	—	1,653	—
Hexogen	$(CH_2\cdot N\cdot NO_2)_3$	222	204,1	—	1,816	0,30
Octogen	$(CH_2\cdot N\cdot NO_2)_4$	296	276—277	—	1,87	—
Nitroglycol	$NO_2O\cdot CH_2\cdot CH_2\cdot \cdot ONO_2$	152,0	—22,8	—	1,489	—
Nitroglycerin	$NO_2O\cdot CH_2\cdot CH\cdot \cdot (ONO_2)\cdot CH_2ONO_2$	227,1	13,2 (2,0)	explodes at 270°	1,596	—
Diethyleneglycol dinitrate	$NO_2OCH_2\cdot CH_2O\cdot CH_2\cdot CH_2ONO_2$	196	2 (—10,9)	—	1,385	—
PETN	$C(CH_2ONO_2)_4$	316	141,3	—	1,77	0,4
Dipentaerythritol hexanitrate	$(CH_2ONO_2)_3C\cdot \cdot CH_2\cdot OCH_2\cdot \cdot C(CH_2ONO_2)_3$	512	73,6	—	1,630 (15°)	—

a) Chemical formula; b) Molecular weight; c) Melting point, °C; d) Boiling point at p = 760 mm, °C; e) Specific gravity or density; f) Specific heat at 25°, kcal/kg (°C); g) Sublimates; h) Explodes at 270°

APPENDIX 26

Characteristics of Major Brisant Explosives

Explosives	a)	b)	c)	d)	e)	f)
TNT	82	290	1000	1,6	7000	285
Trinitrophenol	122,5	310	1050	1,6	7200	310
Tetryl	131	190	1100	1,6	7500	340
PETN	141	215	1400	1,7	8350	490
RDX	204	230	1300	1,7	8400	470

a) Melting point, °C; b) Deflagration point, °C; c) Heat of explosion, kcal/kg; d) Density, gm/cm^3; e) Velocity of detonation, m/sec; f) Work performed, due to Trauzl, ml

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INDEX

TABLE OF CONTENTS

Part I NITRO COMPOUNDS

TABLE OF CONTENTS (CONT'D)

TABLE OF CONTENTS (CONT'D)

Part II NITROAMINES

Part III NITRIC ESTERS

TABLE OF CONTENTS (CONT'D)