

CHAPTER 10

THE MANUFACTURE OF EXPLOSIVE SUBSTANCES

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10 THE MANUFACTURE OF EXPLOSIVE SUBSTANCES

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10.1 AWARENESS SUMMARY

The manufacture of energetic substances is a wide-ranging subject of Materials Science, which encompasses the study of the relationships between the structure and the properties of an explosive material and how it is made; the aim is to develop new and/or common use energetics to meet engineering specifications and high performance.

All manufacturing processes require a knowledge of the hazardous nature of both the process and the materials used including: starting materials, intermediates, desired products and any side products that might be found as impurities in reaction mixtures or final products. Many of the production processes require the use of highly concentrated acids which are hazardous chemicals in their own right.

In this chapter, the basic chemical principles and technology of commonly encountered explosives are outlined. The chemistry and the manufacturing processes for primary and secondary explosives will be discussed in detail. There has been no attempt to include commercially manufactured starting materials which can be purchased.

10.1.1 Nitration Reactions

10.1.1.1 General considerations

The most commonly used military secondary explosive materials contain nitro groups (NO_2) in their chemical structure (Figure 10-1). Nitration reaction plays a fundamental role in the preparation of explosives and it is explained in the paragraphs below.

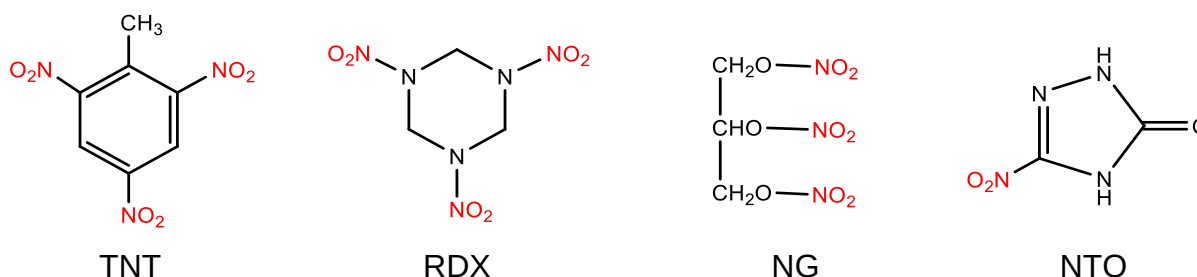


Figure 10-1 Chemical structures of commonly used secondary explosives; nitro groups in red

Secondary high explosives are manufactured by two differently operated systems; batch processing and continuous processing. A batch process requires starting materials to be loaded into the plant and all are processed together. This produces a 'batch' of product at the end of processing. The plant can then be cleaned and readied for the next batch of materials. A continuous process has starting materials fed into the system and product removed throughout the production process. The

daily throughput of a continuous plant tends to be larger than that of a batch plant of the same size. The continuous process normally gives a smaller unit risk than a batch process (whole material charge), and there are savings in, for example, the use and storage of acids.

10.1.1.2 The nitration reaction

There are several methods of nitration; the most common method of nitration for the manufacture of explosives is the use of mixed acids. These are normally nitric and sulphuric acids (HNO_3 and H_2SO_4) in varying concentrations depending on the difficulty and degree of the nitration process. In the manufacture of the N-nitro materials such as RDX and HMX by the Bachman process, the presence of the sulphuric acid would result in the degradation of the explosive product; an alternative material is used with nitric acid. This is ethanoic acid (acetic acid CH_3COOH) and the anhydride of the acid to remove the water liberated during the process.

In both processes the general reaction is:



The second acid is required to form the nitronium ion (NO_2^+), which is the nitrating species and is also a solvent for the reaction.

Nitration can take place on carbon, nitrogen and oxygen atoms in the fuel molecule generating C-nitro compounds such as trinitrotoluene (TNT), N-nitro compounds such as 1,3,5-triaza-1,3,5-trinitrocyclohexane (RDX), and O-nitro compounds such as nitroglycerine (NG), respectively (Figure 10-2). The process details are covered in later sections.

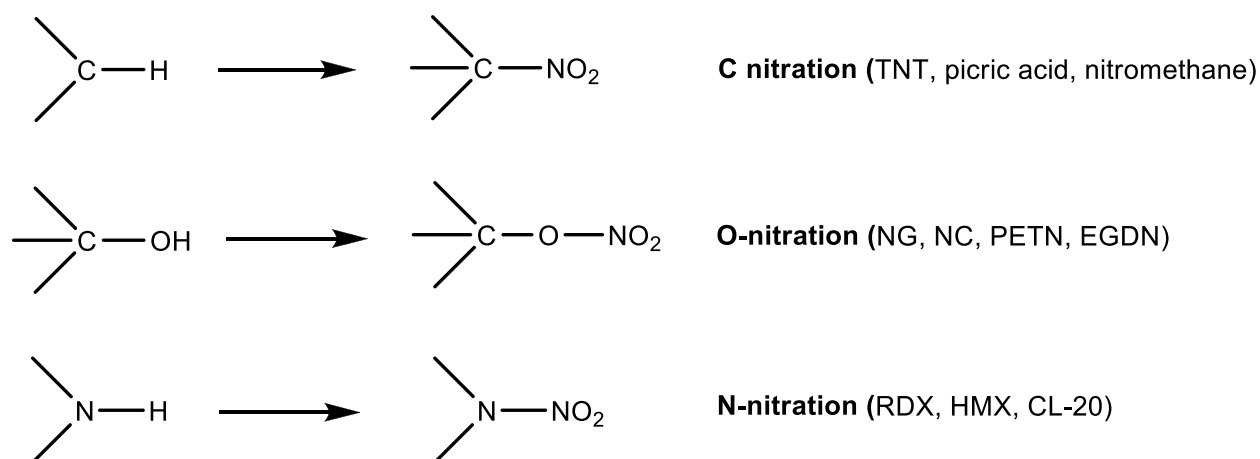


Figure 10-2 Types of nitration reaction

10.1.2 Primary Explosives

The sensitive primary explosives are produced in small batches due to their inherent hazards. Lead and silver azide employed in detonating explosive trains

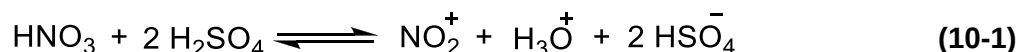
can be readily synthesised mixing water soluble lead or silver compounds with sodium azide, itself also water soluble. However, care must be taken when manufacturing lead azide as it can precipitate in different crystalline forms, some of which are more hazardous than others with the potential to spontaneously detonate even when present as a water slurry.

Lead styphnate and lead dinitroresorcinate (LDNR) employed in igniferous explosive trains are readily synthesised, however, control of the crystal types is of importance depending on the specific application.

10.2 NITRATION CHEMISTRY

10.2.1 Nitration Involving Nitric and Sulphuric Acids

The best studied and most common method of nitrating is the use of mixed nitric and sulphuric acids. These variable mixtures are known as 'mixed acids' or 'nitrating mixtures'. The key to the reaction is the formation of a positively charged nitronium ion, NO_2^+ , which will react with areas of high electron density in a molecule. The overall equation for its formation is given below in Equation (10-1).



In the nitration of benzene (I), for example, the initial reaction brings about the interaction of the benzene π -electrons, shown in Figure 10-3 as the double bonds, with the positive ion. This results in an unstable ion in which the benzene system is disrupted. Elimination of a proton yields the nitrated product, nitrobenzene (II).

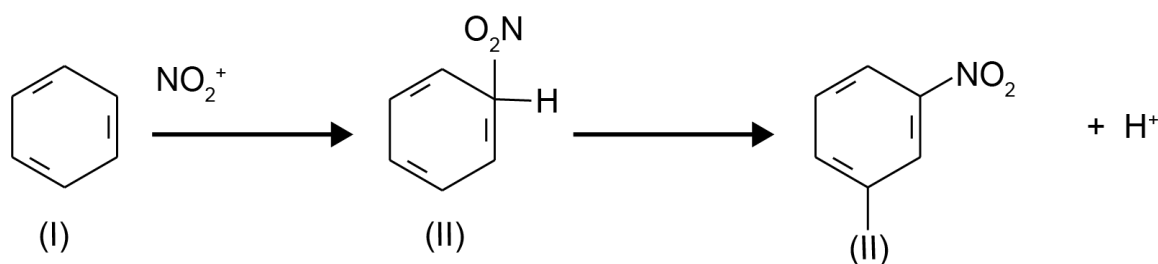


Figure 10-3 Schematic representation of nitration of benzene (I)

When toluene (methylbenzene) is used in place of benzene there are three different positions that may undergo nitration. These are the positions 2 and 6, 3 and 5, and 4 relative to the position of the methyl group. This is illustrated in Figure 10-4.

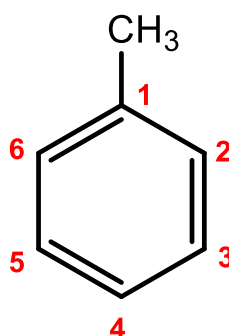


Figure 10-4 Chemical structure of toluene

The presence of the methyl group directs the positive nitronium ion into one of the 2-, 4-, or 6- positions by stabilizing an intermediate ion. Such stabilizing does not occur when nitration takes place in the 3- or 5- positions. This stabilizing is accounted for by the electron donating effect of the methyl group; that is to say, the methyl group pushes electron density towards the benzene ring. During the nitration, an unstable positive ion is formed as an intermediate step and this positive charge can 'move' around the ring. If this charge is capable of residing adjacent to the methyl group the electron donating effect will reduce the effective charge and stabilize the ion. This effect reduces the amount of methyl-3-nitrobenzene (3-nitrotoluene) to about 4 % compared with the 40 % expected on a purely statistical basis (2 locations in the 3 and 5 positions available for reaction) by providing a lower energy path to the 2-, 4-, and 6- positions. 2-nitrotoluene and 4-nitrotoluene then predominate in the product. Figure 10-5 illustrates the initial nitration steps for all three different isomeric nitromethylbenzenes (nitrotoluenes).

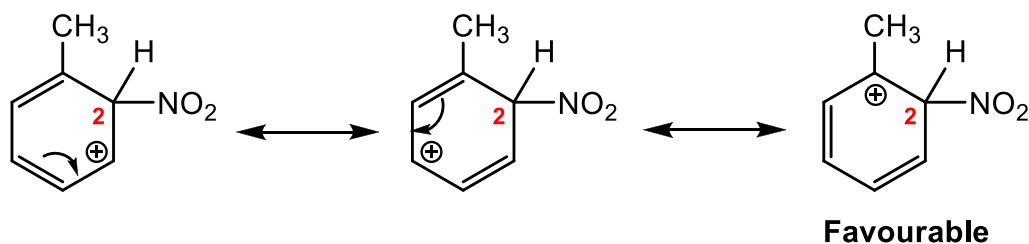
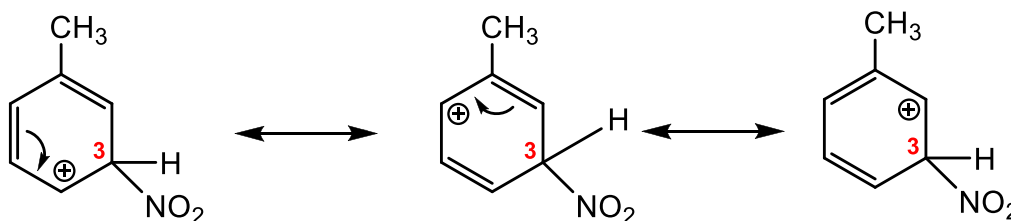
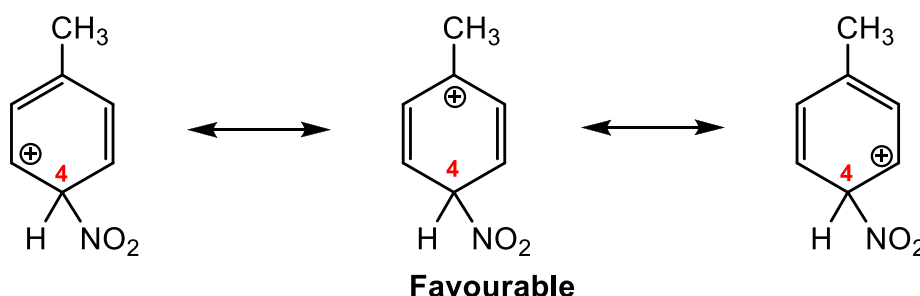
Nitration at position 2 (or 6)**Nitration at position 3 (or 5)****Nitration at position 4**

Figure 10-5 Schematic representation of nitration of toluene

10.2.2 Nitration using Nitrate Salts in Sulphuric Acid

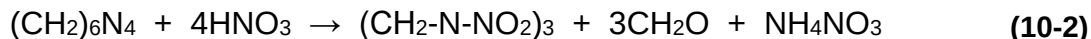
A mixture of a nitrate salt in sulphuric acid will behave similarly to the nitric acid/sulphuric acid mixtures. The amount of water present has been reduced by the replacement of a nitric acid solution with the solid nitrate salt. This advantage has been overtaken by the ready availability of 'anhydrous' nitric acid from modern plants so is now little used.

10.2.3 Nitration with Nitric Acid or Nitrate Salts in Other Acid Media

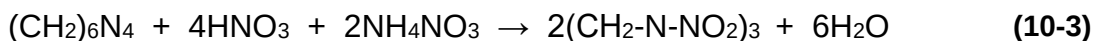
Sulphur dioxide, perchloric acid and certain fluorine compounds have all been cited as suitable materials to afford nitration using either nitric acid or one of its salts. The use of sulphur dioxide is discouraged due to its toxicity. Lewis acids (electron acceptors e.g., AlCl_3 and BF_3) in the presence of nitrate salts have also been cited as affording successful nitrating media.

10.2.4 Nitration with Nitric Acid

In the manufacture of RDX, the nitrating systems employed must not contain sulphuric acid. Traditionally, the nitration process was between hexamethylenetetramine (hexamine) and nitric acid on its own. The overall reaction known as the Woolwich Process is shown in Equation (10-2).



This reaction is said to proceed via a complicated sequence of reactions on the hexamine molecule. The poor utilisation of hexamine and consequent low yield of RDX, with the need for a large excess of nitric acid, 4 to 8 times of the theoretical quantity, results in an expensive process. Alternative systems have been tried, the inclusion of ammonium nitrate in the nitric acid is said to make the overall process more efficient in the use of hexamine. This gives an overall equation of:



10.2.5 Nitration in Ethanoic Acid

The sulphuric acid in a nitrating mixture can be replaced with ethanoic acid or mixtures of ethanoic acid and its anhydride (*Bachman Process*). It has been suggested that the mixture of nitric and ethanoic acids gives an addition compound of the formula $\text{HNO}_3 \cdot \text{CH}_3\text{COOH}$ which has a weaker HO-NO_2 bond. There is also some evidence of the presence of nitronium ions from spectroscopic measurements. Nitration of hexamine in the presence of ethanoic (acetic) acid and its anhydride, yields precursors to RDX and HMX which produce these materials on further treatment with nitric acid and ammonium nitrate. The result is a mixture of RDX and HMX. Equation (10-4) shows the formation of RDX.



10.2.6 Other Nitrating Systems

The use of oxides of nitrogen has been investigated as a method of nitrating organic materials. Of these, probably the most interest has been shown in the use of dinitrogen pentoxide, N_2O_5 , which is the anhydride of nitric acid:



Dinitrogen pentoxide was first used in the nitration of cellulose. It has been suggested that the oxide undergoes heterolysis to form ionic materials in solution:



This is demonstrated in Figure 10-6 below:

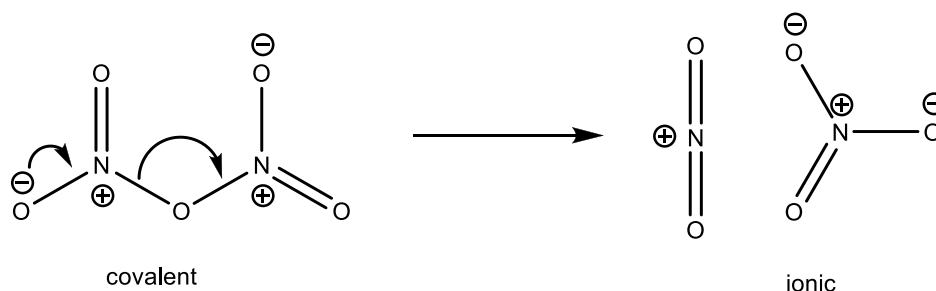


Figure 10-6 Heterolysis of dinitrogen pentoxide

The formation of the nitronium ion (NO_2^+) is the key to the nitrating properties of the material. Dinitrogen pentoxide can be produced by electrogeneration in a polar solvent. This method affords a non-aqueous reaction system which provides interesting alternative reaction pathways. An alternative method of generating dinitrogen pentoxide employs the use of a gas flow system. Recent advances in the ozonolysis of N_2O_4 to prepare dinitrogen pentoxide suggest that it may soon be readily available for the production of explosives and other nitrated materials.

Dinitrogen pentoxide is thermally unstable and it must be stored at $<-20^\circ\text{C}$ or used as generated. Its decomposition produces highly toxic nitrogen dioxide gas:



Dinitrogen pentoxide in HNO_3 may be used for the synthesis of nitramines while in dichloromethane (or chloroform) is used in the manufacture of PolyNIMMO and PolyGLYN, two common energetic binders. This nitrating medium allows the acid-sensitive substrates to be nitrated selectively. The resulting mono-nitrate esters, NIMMO and GLYN, are then polymerised.

There are a wide variety of other methods which will afford the introduction of a nitro-group into an organic molecule. Many of these are of little practical value due to the high relative cost of the materials. In practice, the utilization of mixed acids is currently the major method of nitration due to the relatively low cost of the readily available starting materials. As the use of HMX and RDX increases relative to that of TNT the mixed acids method of nitration is likely to diminish, and alternative clean and environmentally friendly nitrating systems based on dinitrogen pentoxide are likely to come to the fore.

10.3 MANUFACTURE OF COMMONLY ENCOUNTERED SECONDARY EXPLOSIVES

10.3.1 Nitration Process - General Considerations

There are two different methods of operation for a chemical plant. These are 'continuous' operation and 'batch' operation. A continuous operation is one where materials are fed in to the plant throughout the production sequence and the product is continually run off. Batch operation requires all the starting material to be loaded into the plant sequentially and the product is then recovered at the end of

the production run. The daily throughput of a continuous operation plant tends to be larger than that of a batch operation plant of the same size. The main difference in the two operations is the unit explosives risk: in a batch operation plant is the whole materials charge, while in a continuous operation plant the amount of explosive products in the reactor at any instant is relatively small, consequently the unit risk is considerably less. Both safety and economics are considered in deciding the relative merits of one method of operation against another. The more hazardous the process the greater the emphasis on 'unit risk' and hence the continuous operation method finds favour. With less hazardous materials the choice of batch operation or continuous operation could well be determined by economic factors. The production of primary explosives involves very hazardous operations; they are therefore generally manufactured in small batches. The high probability of damage to the plant makes the continuous operation method impossible.

For a process to be economically and environmental satisfactory, the spent nitrating acids must be recovered and recycled. The nitric and sulphuric acids must be re-concentrated. All organic waste must be destroyed and the water used for washing must be decontaminated before discharge. Any solvents used in the purification of the explosives must be collected and recycled.

The purification of explosives is done by re-crystallisation of the reaction product. The crude product needs to be separated from the reaction mixture (spent acids, by-products, etc.) and all traces of the reagents must be removed by washing and drying. The purification for the specific explosives is reported later in this Chapter.

Small batches (gram scale) of explosives can be made in the laboratory using batch or flow reactors. Pilot plant scale, batch or flow, is used for multi-Kg scale production and for the demonstration of a new technology or process.

All nitration reactions are exothermic and the temperature must be controlled during the manufacturing process. The heat release must be monitored to avoid "thermal runaway" or "fume off" due to the violent decomposition reactions even for small (<5 g) laboratory scale operations. Larger scale preparations require more efficient cooling in the reactor. External cooling jackets or cold baths are replaced by internal heat-exchange coils/pipes. On industrial scale processes, efficient stirring is vital for effective heat dissipation and avoid runaway. Dump-valves are still used in medium-to-large batch synthesis of nitrate esters.

Safe systems of work are indispensable to avoid any accidents during the manufacturing of all explosives. All the documents related to the process as manufacturing description, storage facilities availability, transportation and waste collection procedures must be clearly reported and authorised. Process assessments (i.e. General risk assessment, COSHH, DSEAR) need to be in place and REACH regulations (see 1.3.2.4.6) to be considered before starting the nitration process. Permission to work and continuous training of personnel guarantee the safest way to manufacture the explosives.

10.3.2 The Production of C-Nitro Explosives

10.3.2.1 Trinitrotoluene (TNT) production

Trinitrotoluene is generally manufactured by continuous production plants. The TNT is formed by the successive replacement of three hydrogen atoms from the benzene ring with nitro-groups using a mixture of concentrated nitric and sulphuric acids.



Figure 10-7 Conversion of toluene to trinitrotoluene

The introduction of nitro groups requires increasingly more vigorous conditions as the number of nitro groups increase. This is achieved in a modern continuous process by having many reactors, arranged in series, with the organic feed flowing in one direction and the mixed acid flowing in the opposite direction.

A typical TNT manufacturing plant operates as follows: the fresh nitrating mixture is introduced at one end of the plant and becomes less potent due to the production of H₂O as it flows towards the next reactor. DNT encounters fresh mixed acid, whilst toluene or MNT, which is more easily nitrated, encounter depleted mixed acid. Crude trinitrotoluene exits from the last reactor. In this way the acid concentration is lowest where the toluene is introduced, lowering the heat liberation and reducing the risk of fire.

In each nitrator the acids and organic materials are mixed together and partial nitration takes place. In the separators, the acids and organic material are immiscible and separate because of their density difference to facilitate their movement in opposite direction through the plant. Each nitrator is temperature controlled by either cooling to remove the heat liberated due to the mixing of the materials, or heating to accelerate the reaction. Typically some 8 to 15 nitrators and separators are placed in series in a TNT production plant. As the feed material passes along through a series of nitrators, the proportion of nitro-groups in the material increases.

In practice the production of TNT is in two stages: the formation of mononitrotoluene (MNT) and the subsequent conversion of MNT to trinitrotoluene (TNT). This method of production has been adopted due to the large amounts of heat liberated in the mixing of toluene with the mixed acids. Sufficient heat can be liberated by this process to ignite the toluene. By separating the two processes, any ignition is confined to the materials of the first reaction and is prevented from propagating through to the TNT, thus eliminating the risk of explosion.

Acids flow through the plant and are diluted by the production of water from the nitration reaction. Most of the nitric acid will have been used up by the time it has percolated to the end of the plant. The sulphuric acid, on the other hand, does not react; it is merely diluted and will be separated from the organic materials, purified and reused.

During the manufacturing process a small percentage of unwanted products are formed. These are materials nitrated in the 3-position or 5-position. These are not desired in the final product and must be removed. All of the nitration products are shown in Figure 10-8.

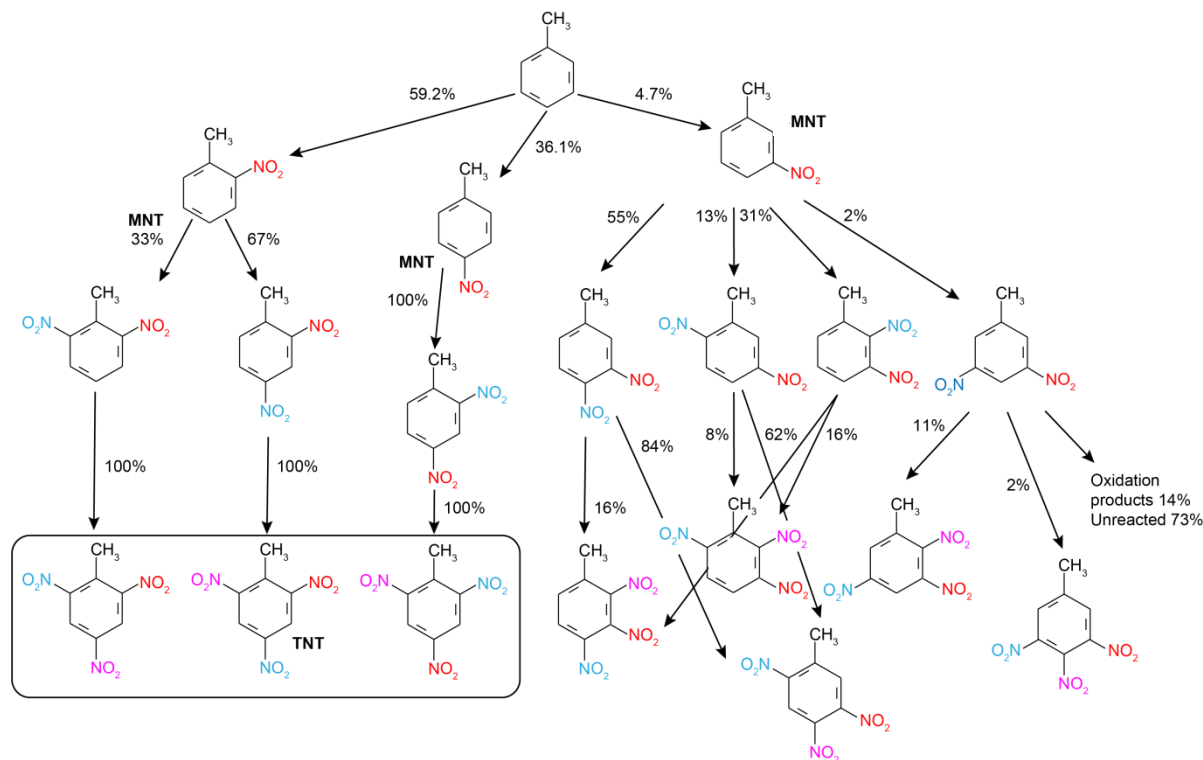
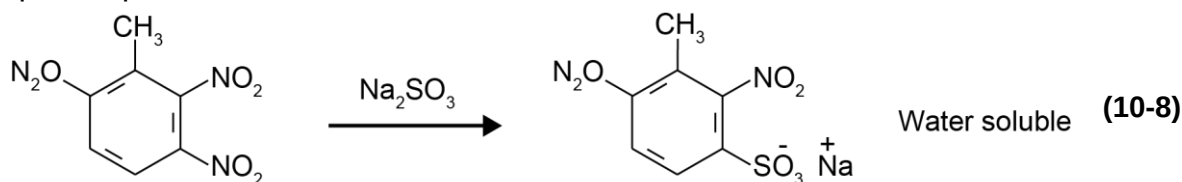


Figure 10-8 Nitration products of toluene during the three steps nitration reaction

The presence of oxidation products will generally afford increased sensitiveness (see 20.2.1), and the incorrectly nitrated materials lower the melting point of the TNT produced. The formation of oxidation products can be reduced by the careful control of the reaction temperature. In any production plant there will always be a small percentage of unwanted nitrated material formed, typically this is between 4-5 % w/w, which is removed by sulphite washing. The crude product from the plant is passed through a series of mixers and separators in counter current flow with a hot sodium sulphite solution which only reacts with NO_2 groups in the 3-position. The products form a water soluble sulphonate salt, which is then washed into the aqueous phase and removed from the TNT.



Final washing with water removes any salts or acid present and the TNT can be cooled to solidify and is then collected, often in the form of TNT flake when cooled on the surface of a rotating drum, then scraped off.

The washings from the TNT purification called “red water” have always been considered as a hazardous waste as they contain very toxic products of incomplete nitrate compounds as well as other complex by-products formed during nitration and purification stages in addition to DNT sulfonated compounds. They created concern related to environmental pollution and public health since most of them are toxic and mutagenic to humans and other animals even at low concentrations. Ground contamination may still exist in very old plants while common treatment methods for TNT waste water currently include activated carbon adsorption, evaporation to dryness (as the toxic components are not volatile), followed by incineration, biodegradation and other disposal methods.

The whole process is shown in Figure 10-9 below.

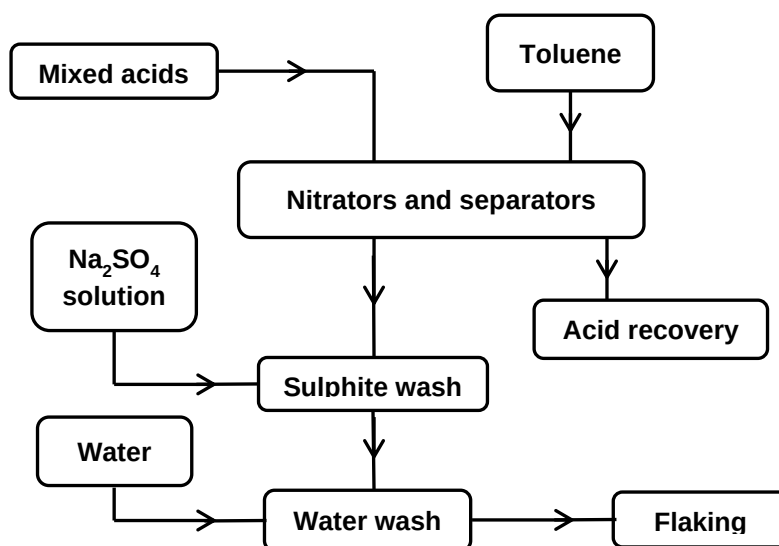


Figure 10-9 A flow diagram for the manufacture of TNT

10.3.2.2 Triaminotrinitrobenzene (TATB) production

TATB (1,3,5-triamino-2,4,6-trinitrobenzene) is an explosive with high temperature stability and low sensitiveness (see 20.2.1). It is manufactured, in a two-step process (Benziger process) in which 1,3,5-trichlorobenzene (TCB) is first nitrated to produce an intermediate compound, 1,3,5-trichloro-2,4,6-trinitrobenzene (TCTNB) as shown in Figure 10-10, which is then subsequently aminated to produce the final product.

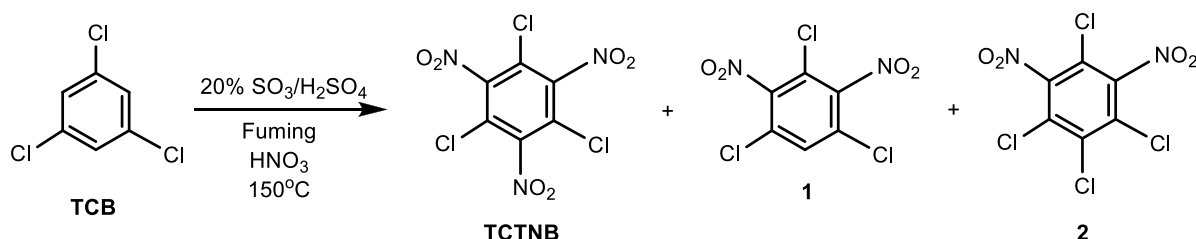


Figure 10-10 Conversion of trichlorobenzene to trichloro-trinitrobenzene

A mixture of 30 % v/v oleum and fuming nitric acid is used for the nitration of TCB at 90 °C. TCB reacts with the mixed acid exothermically to produce first the mono-nitrate and then the di-nitrate intermediate. This reaction proceeds adiabatically and the temperature within the nitration vessel increases to about 140 °C. However, this is not sufficient to drive the trinitration reaction; so towards the end of the reaction period, steam is passed into the jacket surrounding the vessel to raise the temperature to the required value. The trinitration reaction is kinetically slow and the whole nitration process takes about four hours to complete. At the end of this period, the contents are cooled and diluted and the intermediate product filtered off. The spent acid is returned to the acids section of the plant for re-concentration. The intermediate compound TCTNB is completely insensitive when wet, and even in the dry state has a very high Figure of Insensitiveness (169) (see 20.10.2.1). The unwanted by-products 1 and 2 are also insensitive.

At the beginning of the second stage of the process, the intermediate TCTNB is first washed and then dissolved in toluene before being charged into the amination vessel. Additional quantities of toluene and water are added, and the vessel is then sealed and heated. Gaseous ammonia is introduced and the amination reaction proceeds at 152 °C and 5 bar pressure for 4 to 6 hours.

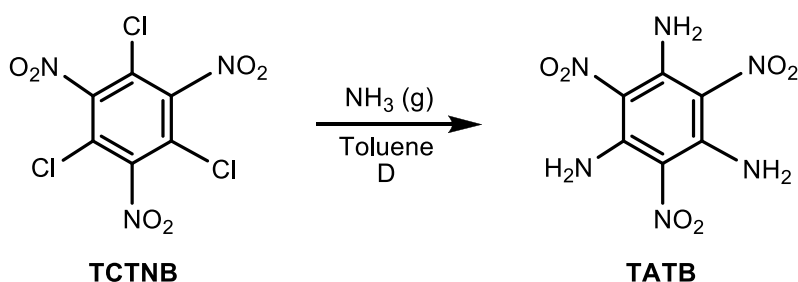


Figure 10-11 Conversion of trichloro-trinitrobenzene to triamino-trinitrobenzene

When the reaction as shown in Figure 10-11 is complete the contents are cooled and then diluted with water before being discharged to the filter press. The TATB cake is steamed in the press, washed, partly dried with compressed air, and then blended and packaged. The toluene in the filtrate is recovered by distillation.

An alternative, halogen free, synthetic route to TATB has been reported^(1,2) as shown below in Figure 10-12. The synthesis of TATB is carried out in three steps:

1. Nitration of 1,3,5-trihydroxybenzene to 1,3,5-trihydroxy-2,4,6-trinitrobenzene
2. Alkylation of the trihydroxytrinitrobenzene product to give the trialkoxy intermediate
3. Amination of the trialkoxy intermediate with NH_3 (gas or liq.) to yield TATB in an overall yield of 87 %.

The trialkoxy intermediate also can be synthesised by alkylation followed by nitration.

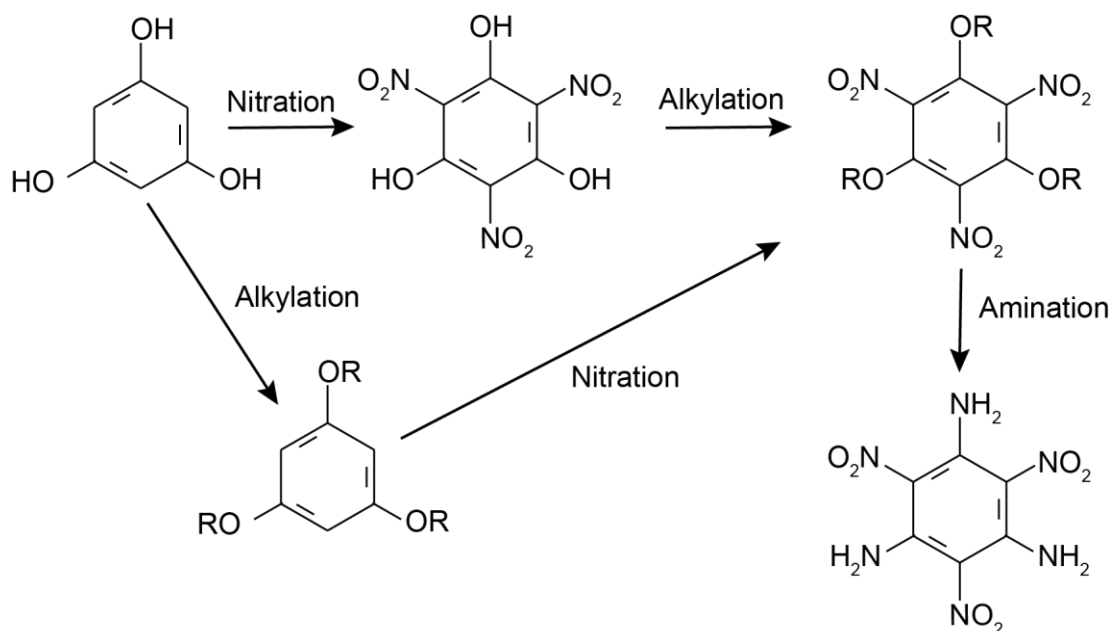


Figure 10-12 Halogen free synthetic route to triamino-trinitrobenzene

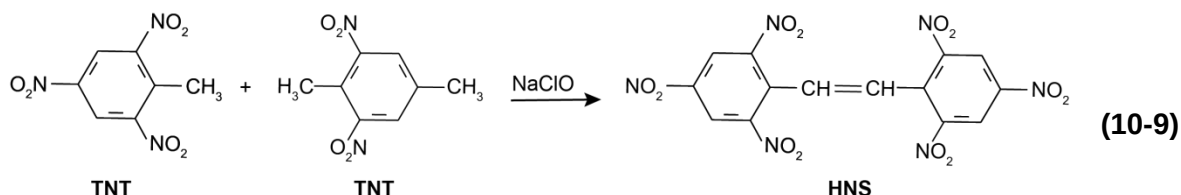
The nitration step is typically carried out with NaNO_2 in HNO_3 or with N_2O_5 in H_2SO_4 . The alkylation step is carried out with K_2CO_3 -dimethyl sulphate, or with a trialkylorthoformate alkylating agent, typically tri-methyl orthoformate or tri-ethyl orthoformate.

Finally, the amination is performed by NH_3 in a solvent. On a small scale, it is convenient to pass ammonia gas into a solution in an organic solvent at low temperature, but on a larger scale the use of liquid ammonia is preferred. The amination may be performed at the boiling point of liquid ammonia (-33°C), or at ambient temperature under pressure (0.8 - 0.9 MPa). The substrate may be added directly as a solid to the liquid ammonia, or it may be introduced as a solution in an organic solvent.

The type of TATB, i.e. particle size, crystalline surface characteristics, etc., produced depends on conditions used during the amination step⁽³⁾ and whether or not water and/or emulsifier is present during the reaction.

10.3.2.3 Hexanitrostilbene (HNS) production

HNS is relatively insensitive to impact and friction. It also is heat resistant with a melting point in the range 316-320 °C. It is manufactured by oxidative coupling of TNT using the Schipp process⁽⁴⁾ shown in Equation (10-9). This employs a solution of sodium hypochlorite as the oxidizing agent acting on a solution of TNT in methanol to produce HNS as shown below. The process does not produce pure HNS but contains up to 6 % w/w hexanitrobibenzyl and other traces of impurity.



Attempts to remove this impurity by multiple washing have resulted in recrystallized material of a new geometry and consequently larger particle size. The larger particle size is undesirable in many applications. The recrystallization process of HNS-I to produce HNS-II improves the bulk density of the material and could be performed using a single or binary system of solvents. Current manufactures produce all four types of HNS from type I to type IV:

- HNS Type I - for initiation (WS 5003F specification): more stable than stipulated in the MIL specification thanks to a special purification process.
- HNS Type II - for oil and gas drilling: a special quality of HNS, coated with a high temperature resistant polymer, is produced according to WS 5003F specification.
- HNS Type III - for nucleation of TNT, produced under German and US specifications.
- HNS type IV - for Exploding Foil Initiator (EFI) detonators, it is characterized by a higher sensitivity and thereby good reliability of initiation⁽⁵⁾.

10.3.3 The Production of N-Nitro Explosives

Nitramines, also known as nitroamines, are organic compounds containing a nitro group bonded to an amine group:

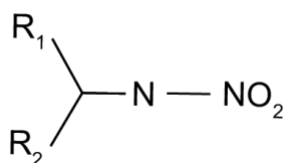


Figure 10-13 Nitramine structure

Nitration on a nitrogen atom, in general, gives a material with greater sensitiveness (see 20.2.1) than the C-nitro materials. N-nitro materials are, generally, more nearly oxygen balanced and have higher densities than C-nitro materials which gives an

increase in the performance of the explosive. Thus the introduction of the N-nitro explosives RDX and HMX during and after the Second World War, respectively, produced a range of higher performance military explosives for both power (see 9.2.2) and shock pressure (see 11.2). However, N-nitration is a more expensive process than C-nitration.

The most prominent members of this class are RDX; hexahydro-1,3,5-trinitro-1,3,5-triazine, (also known as trinitrotriazacyclohexane, hexogen and cyclonite); HMX; octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazine (also known as tetranitrotetrazacyclo-octane and octogen), nitroguanidine also known as Picrite and NQ), and tetryl; 2,4,6-trinitrophenylmethylnitramine (also known as tetranitroaniline and CE – Composition Exploding).

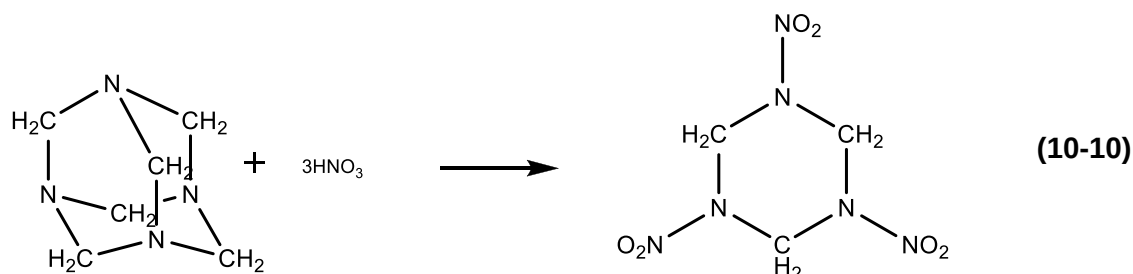
10.3.3.1 Trinitrotriazacyclohexane (RDX) production

RDX is the most commonly used member of the nitramines family. It is produced in large industrial quantities and used in military and civilian applications. There are several types of RDX depending on the method of manufacture, purity and crystal size (Table 10-1)^(6,7).

RDX has been produced from hexamethylenetetramine (hexamine) in several ways; using fuming nitric acid (Woolwich method, (10-10)), nitric acid and ammonium nitrate or nitric acid, ammonium nitrate, glacial acetic acid, and acetic anhydride (Bachmann process).

Table 10-1 Types of RDX

Manufacture method		Purity (w/w)		Particle morphology
Type A	Type B	Type I	Type II	RS (reduced sensitivity) or I (Insensitive)
Direct HNO ₃ nitrolysis process	Bachmann process	<5 % HMX content	4-17 % HMX content	RDX based on mean particle size, shape and impurity content that result in PBX formulations less sensitive to shock.



A continuous production plant will typically feed hexamine and nitric acid into a series of nitrators using co-current flow. The complex reaction taking place produces both ammonia and formaldehyde as by-products. These are both toxic gases and their removal is required on health and safety grounds. These by-products can be recycled as the hexamine is itself manufactured from them. Some

of the ammonia reacts with additional nitric acid to form ammonium nitrate. The process is inefficient in the utilization of the hexamine which adds to the costs of manufacture. In the manufacture, if there is evolution of excess oxides of nitrogen or a thermal run away, drowning of the reaction mixture may become necessary. The drowning is achieved by use of a release valve dumping the reaction mixture into a solution of urea.

After nitration, the RDX and other products of the reaction are passed into further tanks where the acid concentration is reduced by dilution with less concentrated nitric acid. At this stage the materials are heated to about 75 °C to decompose the more unstable impurities as the RDX precipitates as a white solid.

Filtration and washing with water complete the production process. Occluded acidity in the crystals is removed by grinding the damp RDX to a fine powder and boiling in water or by recrystallisation from cyclohexanone solution. The process is illustrated in Figure 10-14.

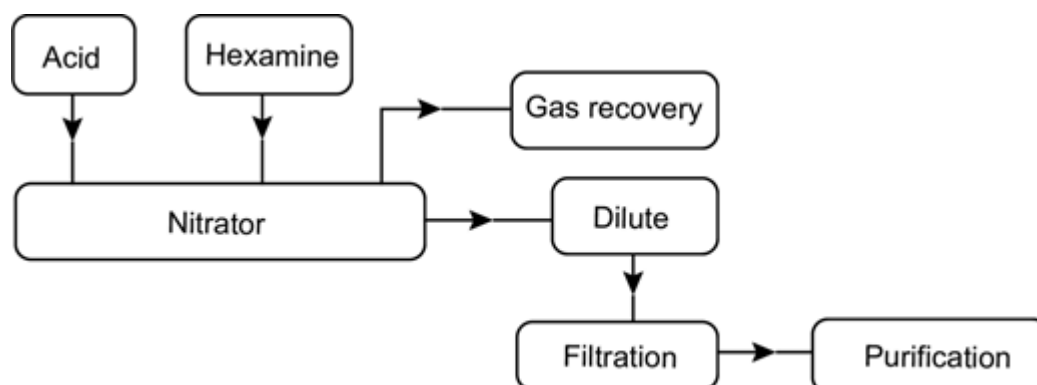
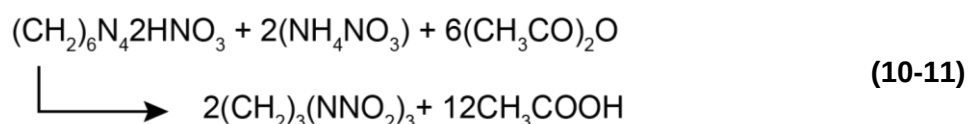


Figure 10-14 A flow diagram for the production of RDX

Alternative methods of production include the treatment of hexamine with ammonium nitrate and nitric acid, the reaction of sulphamic acid with methanal (formaldehyde) and nitric acid, and the treatment of hexamethylenediamine dinitrate with ammonium dinitrate in the anhydride of ethanoic acid (acetic anhydride). This is basically the manufacturing process widely used today as the reaction shown in Equation (10-11), although there are still manufacturers that use the Woolwich process.



10.3.3.2 Tetranitrotetrazacyclo-octane (HMX) production

HMX, also called octogen, is the highest performance explosive produced in industrial quantities. There are several types of HMX depending on the method of manufacture, purity and crystal size (Table 10-2).

Table 10-2 Types of HMX

Purity (w/w)		Particle morphology
Grade B	High purity	RS (reduced sensitivity)
<2 % RDX content	<0.2 % RDX content	Recrystallisation techniques provide particle shapes that reduce sensitivity for Insensitive Munitions (IM) purposes.

HMX is formed as a by-product of RDX manufacture using the Bachmann Process. By adjusting the reaction conditions it is possible to improve the HMX yield, although not normally higher than 65 % and reduce the amount of RDX produced. The nitrolysis of hexamine using a nitric acid/ammonium nitrate system containing paraformaldehyde with ethanoic acid/ethanoic acid anhydride (acetic acid/acetic anhydride) as solvent will give an HMX-rich product. RDX can be removed from the product by dissolution in hot water. The product can be purified to Military Grade of the correct crystal form (β - least sensitive to impact, Table 10-3) by recrystallisation from cyclohexanone.

Table 10-3 Types of HMX and Their Relative Stability

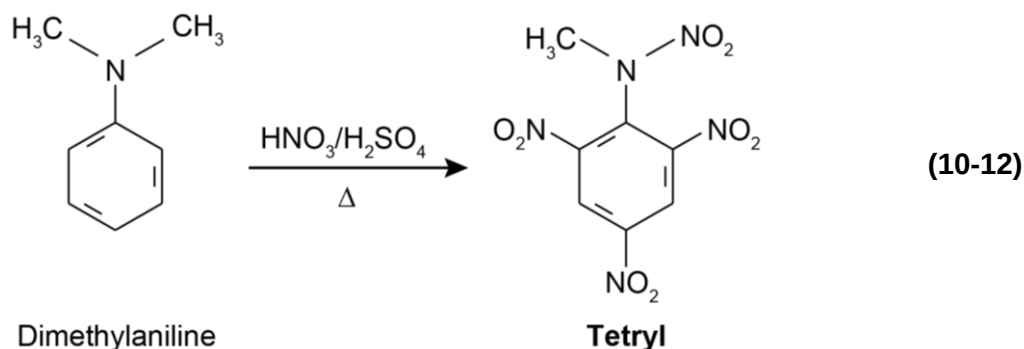
Properties	Form			
	α	β	γ	δ
Specific gravity ⁽⁸⁾	1.87	1.96	1.82	1.78
Stability of crystalline form	Metastable	Stable	Metastable	Labile

Due to the larger quantities of acetic anhydride used to obtain HMX, and the need to free the product of RDX as the latter would reduce the performance of the HMX, the cost of HMX is considerably higher (~3×) than that of RDX.

Nitration with dinitrogen pentoxide is currently being investigated as a possibly cheaper and more efficient method of producing HMX. Hexamine is first converted to a non-energetic intermediate, 1,3,5,7-tetraacetyl-1,3,5,7-tetraazacyclooctane (TAT), which is cleanly nitrolysed by N_2O_5 to give HMX. High yields (>80 % w/w) and high purity HMX can be obtained. This is an ideal laboratory process but not exploited industrially in practice.

10.3.3.3 Tetranitroaniline (Tetryl, CE) production

The basic process of nitration to manufacture tetryl starts from N,N-dimethylaniline which is readily nitrated with conventional nitrating mixtures. The replacement of three hydrogen atoms on the ring and the displacement of a methyl group by nitro-groups produces tetryl. The overall reaction is shown in Equation (10-12) below.



A typical continuous nitrating plant would contain two heated nitrating vessels and a cooled diluter to precipitate the product. A block diagram for the process is shown in Figure 10-5. The crude product is washed to remove acid and recrystallized either from benzene or propanone to produce the final product.

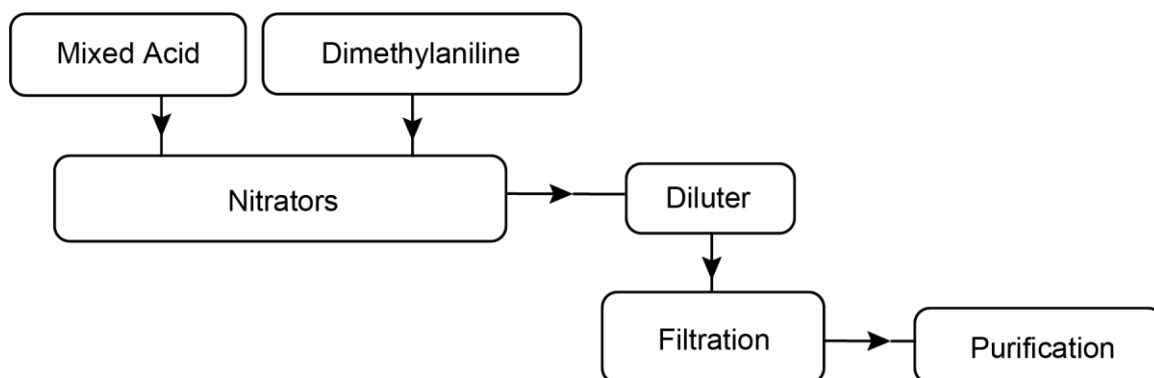
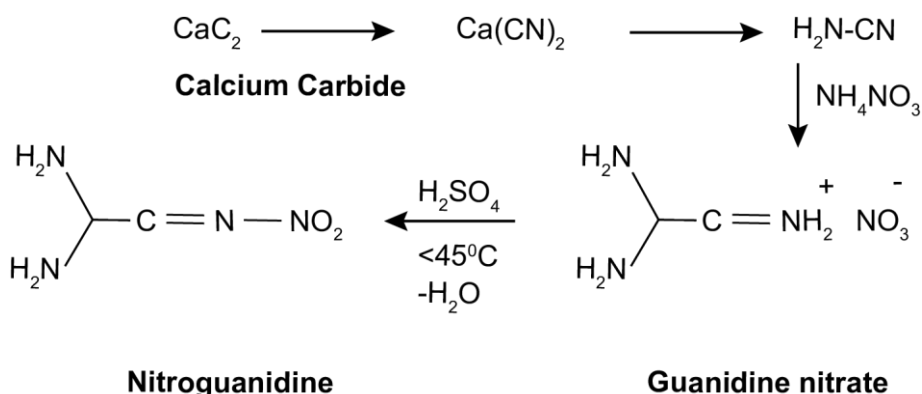


Figure 10-15 Flow diagram for the production of Tetryl

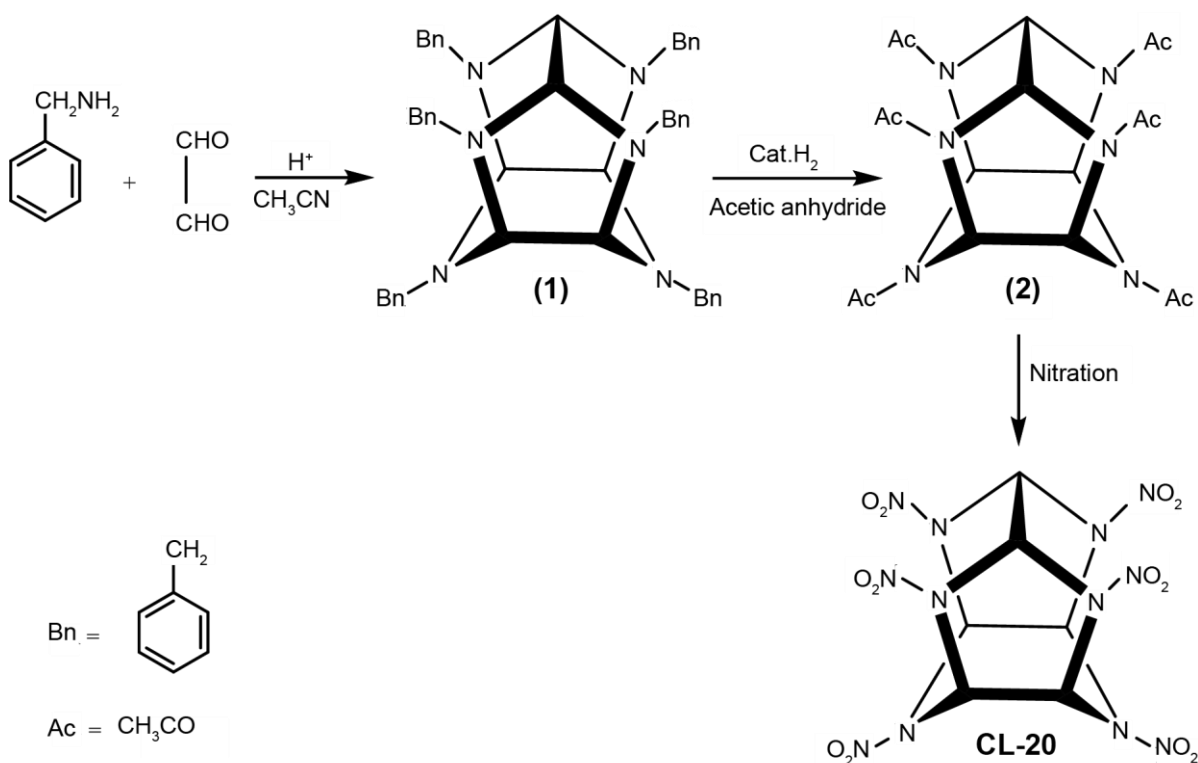
10.3.3.4 Nitroguanidine (Picrite, NQ) production

Nitroguanidine is mainly used in the preparation of triple-base propellants. The material is readily prepared by treatment of guanidine nitrate with sulphuric acid. Guanidine nitrate is a readily available starting material, it can be manufactured by heating calcium carbide in a stream of nitrogen, acidifying the product and then fusing with ammonium nitrate. The guanidine nitrate is added to a nitrator containing sulphuric acid with the temperature maintained at about 45 °C by cooling. The reaction is rapid and nitroguanidine is recovered in high yield (>90 %) by passing the nitration mixture into water to precipitate the product. The crude product, after washing to remove acid, is recrystallized from water. The reaction sequence is shown in Figure 10-16.

Another route to synthesise nitroguanidine starts with the fusing of ammonium nitrate with dicyandiamide to form guanidine nitrate. Concentrated sulphuric acid then converts this to nitroguanidine.

**Figure 10-16 Synthesis route to manufacture nitroguanidine****10.3.3.5 Hexanitrohexaazaisowurtzitane (CL-20) production**

CL-20 can be synthesised on a laboratory scale accordingly to the reaction scheme shown in Figure 10-17.

**Figure 10-17 Synthesis route to manufacture hexanitro-hexa-azaisowurtzitane (CL-20)**

2,4,6,8,10,12-hexabenzyl-2,4,6,8,10,12-hexaazaisowurtzitane (Compound 1) can be synthesised by reaction of benzylamine with aqueous glyoxal (40 % v/v) in aqueous acetonitrile in the presence of a catalytic amount of formic acid. Reductive acetylation of compound 1 with palladium hydroxide on carbon in acetic anhydride in the presence of catalytic amount of bromobenzene yields the tetra-acetate compound 2. Treatment of 2 with 3 mole equivalents of nitronium tetrafluoroborate in sulfolane followed by 12 mole equivalents of nitronium

tetrafluoroborate in the same vessel, produces CL-20 in 90 % yield⁽⁹⁾. CL-20 exists in four crystalline forms, stable at different temperatures. Only the ϵ and the β form are used currently.

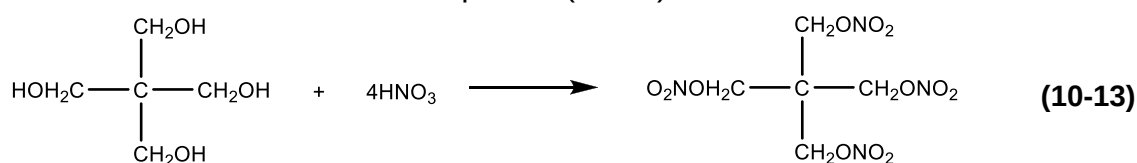
10.3.4 The Production of O-Nitro Explosives

Nitration on an oxygen atom produces more nearly oxygen balanced explosives (see 4.3.1) than the C-nitro or N-nitro explosives. Due to the higher oxygen balance of these materials they tend to have high heats of explosion (see 4.4.2), however, they tend to be less stable and to have a higher sensitiveness (see 20.2.1) than other explosives. The chemical stability of O-nitro compounds, or nitrate esters as they are also known, is relatively low, due to the ease of hydrolysis of the O-NO₂ bond. Further, the hydrolysis is catalysed by the presence of acid or alkali. In this context it is the presence of acid from the manufacturing process or as a degradation product that is generally of concern.

O-nitration readily takes place using conventional nitric acid/sulphuric acid mixtures. The production of nitroglycerine (a member of the O-NO₂ family) is probably the most dangerous explosive preparation performed on large scale.

10.3.4.1 Pentaerythritol tetranitrate (PETN) production

The nitration of pentaerythritol is achieved by the use of 98-99 % v/v nitric acid and is the only nitrate ester to be produced using only nitric acid. A typical continuous nitrator would require cooled nitrators for the mixing of nitric acid with pentaerythritol due to the exothermic reaction of the materials on mixing. After nitration the reaction mixture is diluted to ease separation of the precipitated pentaerythritol tetranitrate and recovery of the spent acid, which contains about 80 % v/v HNO₃. The acid is diluted to 30 % v/v HNO₃ with water, not only to reduce the PETN solubility but also to stabilise the mixture. Spent acid containing 75-80 % v/v HNO₃ is dangerously unstable due to the hydrolysis of PETN to its lower nitrates. The overall reaction is shown below in Equation (10-13).

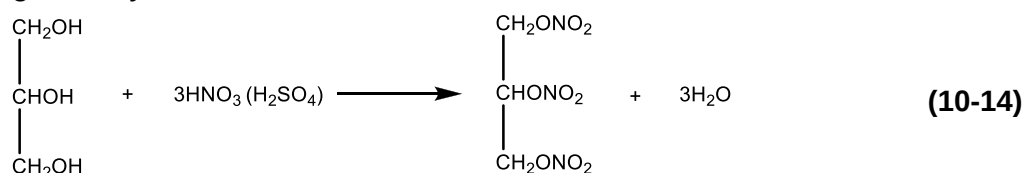


The product requires washing to remove acid residues and crystallization from aqueous acetone, with ammonia added to neutralise traces of acids, producing the required material. A second recrystallisation and precipitation is often carried out as a particle size adjustment process to produce a powder with the desired specific surface area. Resulting crystals have irregular faces in the size range 5-16 microns. The preferred shape for use in detonators is a tetragonal rod. Crystal morphology can be controlled by recrystallization using acetone/water mixtures where solvent addition, stirring rate and temperature are all critical conditions.

10.3.4.2 1,2,3-Trinitroxypropane (nitroglycerine, glyceryl trinitrate or NG) production

The explosive commonly known as nitroglycerine (NG) is probably the most sensitive explosive manufactured on a large scale. It has a low Figure of insensitiveness (see 20.10.2.1) and is susceptible to accidental initiation. Production methods take account of the dangers of NG production and traditional methods utilize gravity feed to move the material rather than any form of pumping. Due to this, the plant is normally raised on small, natural or man-made, hills. Modern plants may pressurize the starting materials to achieve movement through the plant.

There are three main types of continuous nitration plant in operation, these are based on: the Biazzi Process, the Nilssen and Brunnberg (NAB) Injector Process and, less common, the Hercules Tubular Process. In all the production processes, nitration takes place with 'mixed acids' in the reaction shown in Equation (10-14). The main differences occur in the method used to mix the acids and glycerine, and the size and geometry of the nitrator.



In a Biazzi Process, mixed acids and glycerine are metered and introduced into a nitrating vessel where they are stirred at high speed (Figure 10-18). The vessel is cooled to maintain a temperature in the range of 10 °C to 15 °C. The nitrated product overflows into the separator which is a larger vessel where the NG/acid emulsion slowly rotates affording time for separation. Nitroglycerine is removed from near the top of the separator and spent acid from the bottom. A large Biazzi plant can produce over 2000 kg h⁻¹ but only 80 kg is at risk at any specific time. The overall process is shown in Figure 10-19.

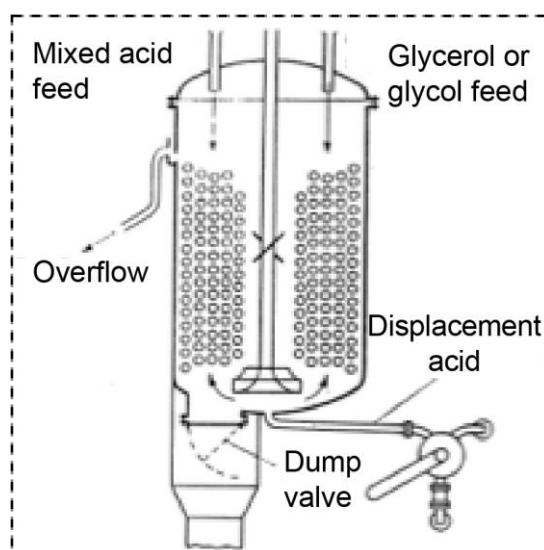


Figure 10-18 The Biazzi process reactor

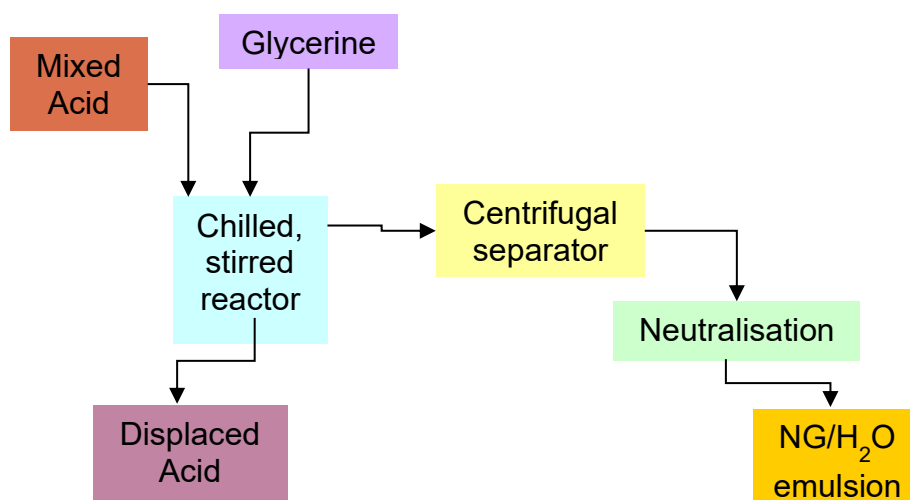


Figure 10-19 Schematic of the Biazzi process for NG production

The Nilssen and Brunnberg (NAB) Injector Process utilizes the flow of mixed acid through a small nozzle to 'suck' glycerine into the nitrator. The process allows the reaction mixture to achieve about 45 °C for half a second. This is followed by rapid cooling. Separation is achieved by a similar process to that carried out in the Biazzi Process. The unit explosion risk is reduced to 3.5 kg of NG. Mixed acids and glycerine, under pressure, are mixed at a T-piece before entering a tubular nitrator in the Hercules Process. After flowing through an uncooled portion of tube the reaction mixture enters a cooled portion of tube before separation. Again similar methods are used for the separation process.

Both processes will work with a range of acid compositions and nitration mixture to glycerine ratios. As the processes are hazardous, methods of quenching the system are required in case the reaction becomes uncontrolled. The Biazzi Process has built in dump facilities, the materials being deposited in water to dilute the acids in the event of excess temperature in the nitrator or separator. Automatic shut-down of the feed is also incorporated. The NAB Injector Process has a fail-safe shut-down operated by the closing off or reduction in the pressure of the mixed acids at the injector, which stops or greatly reduces the amount of glycerine 'sucked' in to the nitrator. Table 10-4 summarises the reaction conditions for the manufacture of nitroglycerine in Biazzi and NAB processes. Both procedures give very similar high yields.

Table 10-4 Reaction Conditions for Glycerine Nitration

Process	HNO ₃	H ₂ SO ₄	H ₂ O	(HNO ₃ + H ₂ SO ₄)/glycerine	Yield (%)
Biazzi	51	49	0	4.85	96
N.A.B.	27	63	10	12.1	94

In all production plants, washing of the product is required to remove acid from the nitroglycerine. This is commonly achieved by washing with sodium carbonate solution which neutralizes the residual acid. Storage of the final product can cause

problems and many manufacturing processes use the NG to manufacture propellant or commercial explosives directly without intermediate storage. Figure 10-20 gives a general flow diagram for the production of nitroglycerine.

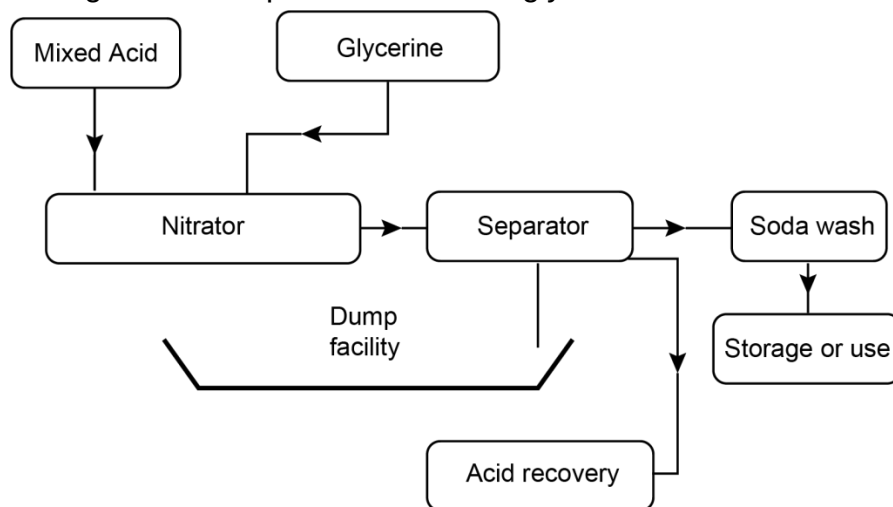
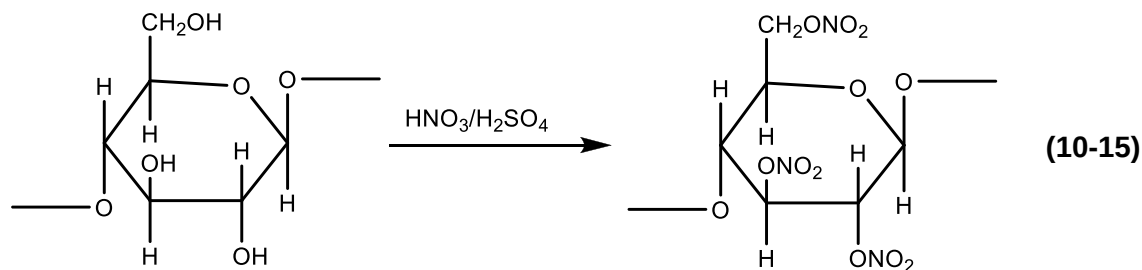


Figure 10-20 Flow diagram for nitroglycerine manufacture

10.3.4.3 Nitrocellulose (cellulose nitrate or NC) production

Cellulose is a polymeric material containing large numbers of glucose molecules joined together through an ether (-O-) link. The cellulose contains many thousands of glucose molecules. Nitrocellulose (NC) is readily formed by the treatment of cellulose with a variety of nitrating materials. However, the production of evenly and efficiently nitrated cellulose limits the practical nitration methods. Complete nitration of all hydroxyl groups (3 per glucose unit) gives a weight percentage for nitrogen content of 14.15 %. The percentage nitration (% N) determines many of the properties of the nitrocellulose including solubility, explosives properties and stability. In practice, nitration with $\text{HNO}_3/\text{H}_2\text{SO}_4$ gives at most 13.5 % N while products with higher levels of N are unstable; $\text{HNO}_3/\text{H}_3\text{PO}_4$ gives 14.04 % N and gaseous N_2O_5 gives 14.12 % N. The % N from an $\text{HNO}_3/\text{H}_2\text{SO}_4$ nitration is determined by the composition of the mixed acid and the contact time. The nitration reaction is shown below in Equation (10-15).



All methods of forming nitrocellulose require purified cellulose. This is available from natural or naturally based materials such as wood, cotton fibre or paper. The purification of the starting materials is essential to obtain a consistent product. Probably the richest source of cellulose is cotton fibre. This plant produces two types of fibre, a long fibre used in the manufacture of threads and hence fabric and

a shorter fibre, called linters, which is used in the manufacture of nitrocellulose. This fibre is collected and shipped to the manufacturer where it requires much pre-treatment before nitration.

The initial step in purification is the removal of unwanted 'foreign bodies', which will consist of parts of the cotton seed, stalks and even insects. The cotton linters are combed with mechanical combs to remove these unwanted materials. Autoclaving in dilute sodium hydroxide solutions is employed to chemically treat the cotton and remove some of the non-cellulose matter present with the cellulose. The final chemical treatment is that of bleaching with a chlorine bleach or chlorine itself. After this treatment the material requires thorough washing and some drying before nitration can take place.

The nitration of cellulose is carried out on a large-scale batch process. Nitrators capable of holding about 1 tonne of material (acids and cellulose together) are often grouped together to feed separators within a single large plant. Batches of material progress through the plant giving a semi-continuous operation. The degree of nitration, as measured by the percentage nitrogen in the product, will vary depending on the reaction conditions. The concentrations of nitric acid and sulphuric acid, the temperature and duration of nitration all play a part in the degree of nitration and quality of the product. In a typical production plant a ratio of between 1:40 to 1:60 of cellulose to mixed acids is employed. The composition of the acid varies but typical values of 20 % v/v nitric acid and 60 % v/v sulphuric acid are used.

Once the nitrator is loaded with acid, the cellulose is added and submerged. After nitrating for approximately 20 minutes, the acid and nitrocellulose are separated centrifugally to remove the bulk of the acid. Due to the absorbent nature of the cellulose fibre there will be a large amount of residual acid present within the fibre. This residual acid requires removal if the final product is not to spontaneously ignite. A process of washing and boiling is employed to remove this acid. Typically the product of a number of nitrators is boiled several times with fresh loads of water at elevated temperatures in an autoclave.

After stabilization the material is dried before it can be used in the manufacture of propellants. Dry NC is susceptible to initiation by friction and impact and in general the NC is handled with a controlled water content to reduce the risk. The overall process is illustrated in the flow diagram (Figure 10-21).

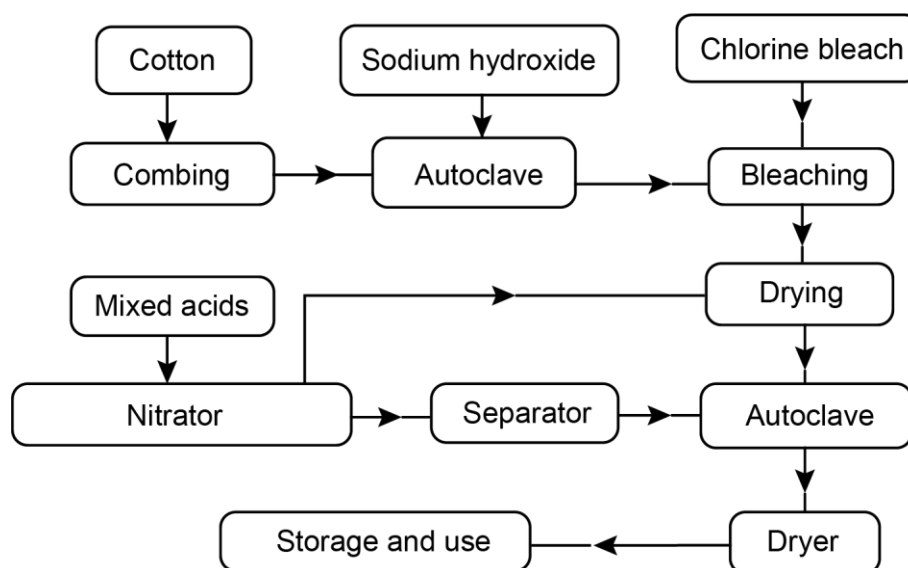


Figure 10-21 A flow diagram for nitrocellulose manufacture

10.3.5 Recent Developments

10.3.5.1 3-Nitro-1,2,4-triazol-5-one (NTO) production

The synthesis pathway for NTO shown in

Figure 10-22 involves two simple reactions, the reaction of semicarbazide hydrochloride with formic acid followed by a nitration with 99 % v/v nitric acid. Formic acid is added to solid semicarbazide hydrochloride at ambient temperature and the resulting solution is then heated to 65 °C and stirred to give the intermediate 1,2,4-triazol-5-one. The reaction mixture is cooled to ambient temperature and HNO₃ added. After 3 hours the mixture is filtered and the resulting solid is washed with cold water. Recrystallisation from hot water gives NTO as a white crystalline solid. The current manufacturing technique prevents full recovery of NTO.

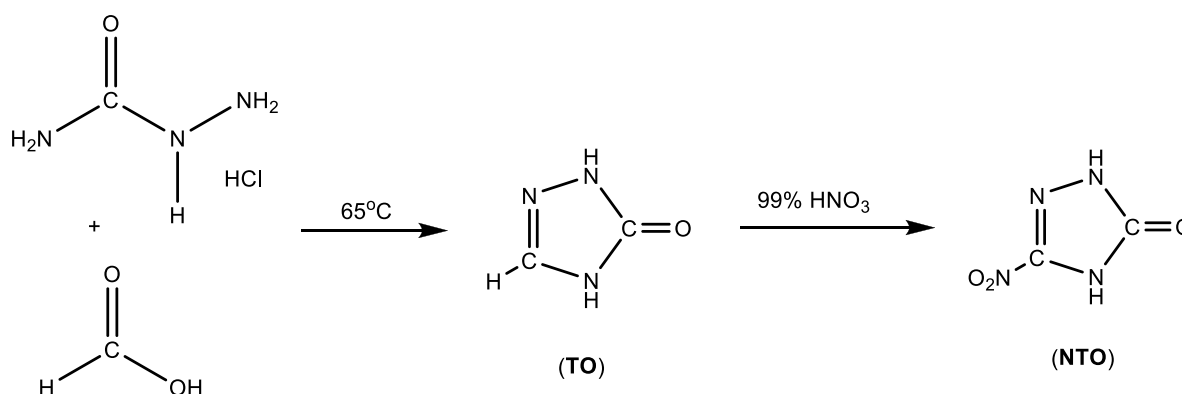


Figure 10-22 The synthesis pathway for NTO manufacture

10.3.5.2 1,1-Diamino-2,2-dinitroethene (FOX-7) production

The synthesis of FOX-7 is relatively easy and it can be synthesised in a single-step process⁽¹⁰⁾. The nitration using a mixture of concentrated nitric and sulphuric acid of the 2-methyl-4,6-dihydroxypyrimidine gives an intermediate, 2-dinitromethylene-5,5-dinitropyrimidine-4,6(1H,5H)-dione (Figure 10-23) which then is hydrolysed in water to produce FOX-7 after several hours at ambient temperature.

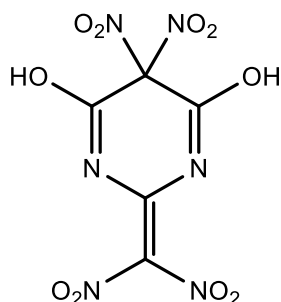
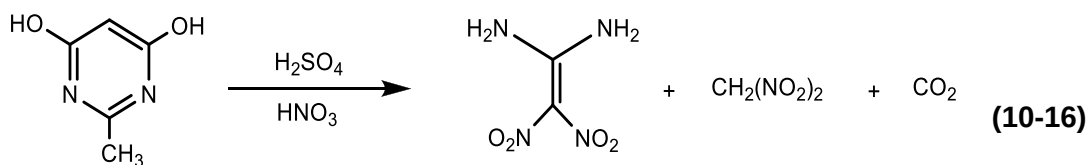


Figure 10-23 Structure of 2-dinitromethylene-5,5-dinitropyrimidine-4,6(1H,5H)-dione

The product separates out as it is formed and is finally filtered off and washed with water. Two by-products also are formed during the hydrolysis, dinitromethane and carbon dioxide, as shown in Equation (10-16) below.



2-Methyl-4,6-dihydroxypyrimidine

FOX-7

FOX-7 exists as a canary-yellow solid and may be recrystallized from a variety of solvents, dimethylsulphoxide-water, *N*-methylpyrrolidin-2-one-water and dilute HCl being commonly employed. Figure 10-24 shows a schematic representation of a FOX-7 plant.

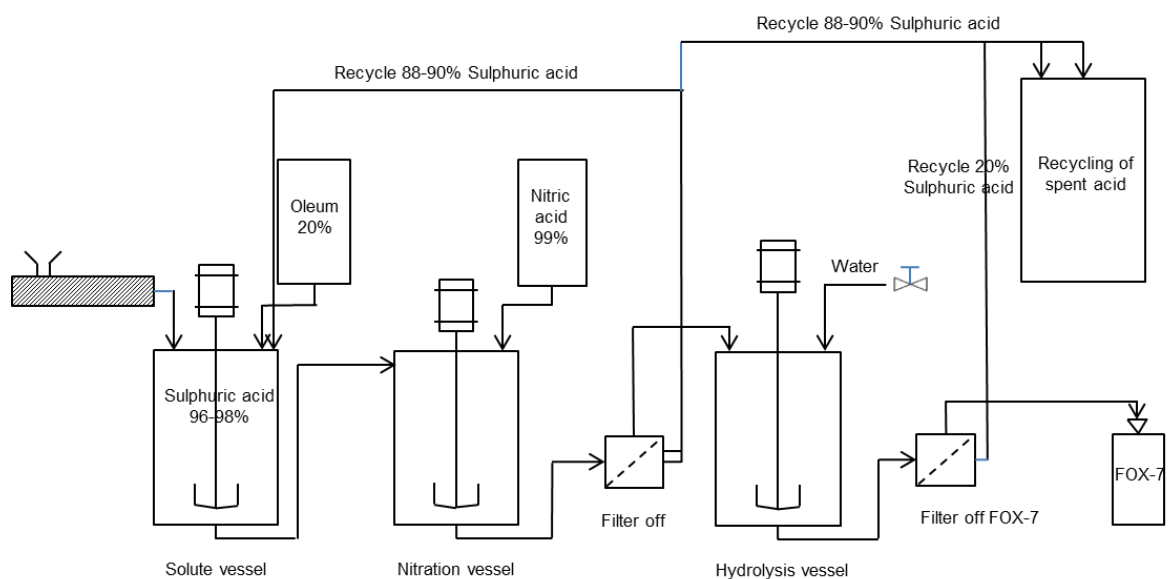
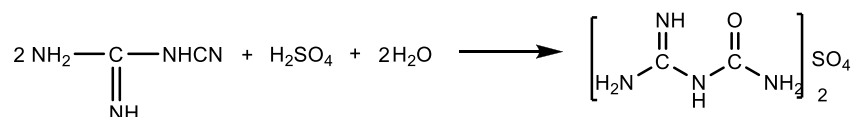


Figure 10-24 FOX-7 plant schematic

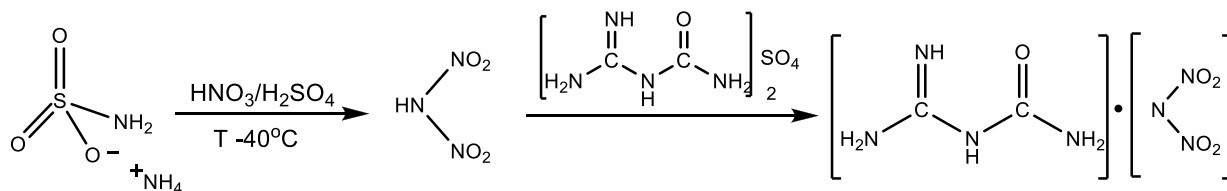
10.3.5.3 N-Guanylurea dinitramide (GUDN, FOX-12) production

GUDN is a low sensitiveness (see 20.2.1) explosive with good thermal stability and potential candidate for Insensitive Munition filling. It is also an important precursor for the synthesis of the solid oxidiser ammonium dinitramide (ADN) via potassium dinitramide⁽¹¹⁾.

GUDN is synthesised in a two steps process as shown in Figure 10-25; 1) synthesis of guanylurea sulphate from dicyandiamide and 2) nitration of ammonium sulphamate which reacts with guanylurea sulfate to give GUDN as a white crystalline solid.



STEP 1



STEP 2

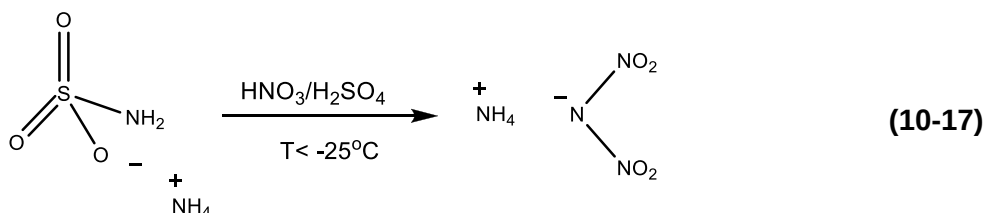
Figure 10-25 Schematic for synthesis of FOX-12

GUDN is more thermally stable compared to ADN. It exhibits a layered packing with intermolecular hydrogen bonds within the layers and van der Waals interactions

between the layers⁽¹²⁾. Low impact and friction sensitiveness, absence of melting point and low water solubility are attributed to the special molecular packing.

10.3.5.4 Ammonium dinitramide (ADN) production

ADN can be synthesized from standard industrial chemicals by direct nitration of salts of sulfamic acid by mixed nitric and sulphuric acids (Equation (10-17)), followed by neutralization and separation of the ADN formed. Sulphamic acid is, for instance, used to produce sweeteners and as an ingredient in cleaning agents.



10.4 MANUFACTURE OF COMMONLY ENCOUNTERED PRIMARY EXPLOSIVES

10.4.1 General

Primary explosives are very much more readily initiated than the majority of high explosives. Their manufacture must take suitable precautions to account for this added danger. In general, the manufacture of primary explosives is carried out on a small scale, often in a very similar way to an ordinary laboratory scale preparation. The manufacture of several commonly encountered primary explosives is detailed in the following sections.

10.4.2 Lead Styphnate

Lead styphnate (lead 2,4,6-trinitroresorcinate) is particularly sensitive to initiation by electric spark. It is also a very weak explosive and as such is not normally used on its own.

10.4.2.1 General Manufacture of Lead Styphnate⁽¹³⁾

Styphnic acid (2,4,6-trinitroresorcinol) and magnesium oxide (or carbonate) are mixed in water to give a solution of magnesium styphnate. Lead styphnate is precipitated from solution by the addition of an aqueous lead nitrate or lead acetate solution. Filtering and drying are required and stringent safety precautions are employed during the manufacture, handling and storage of lead styphnate. The manufacture of RD1303, RD1346, RD1349 and RD1367, the various forms of lead styphnate, are detailed below.

10.4.2.2 RD1303

The RD1303 manufacturing processes⁽¹⁴⁾ involve the preparation of stock solutions of magnesium styphnate prepared from styphnic acid and magnesium carbonate,

lead acetate and dilute nitric acid. For the precipitation, lead acetate solution is added to magnesium styphnate solution which is maintained at a suitable temperature and controlled rate of stirring. Basic lead styphnate is precipitated and then converted to the normal salt by the controlled addition of nitric acid. The reaction sequence is shown in:



Figure 10-26 Reaction sequence to manufacture normal lead styphnate

The process gives rise to single crystals of lead styphnate that are rhombic varying from granular to prism form with a tendency to widely varying aggregation according to the conditions of its formation. Broadly the conditions tending towards aggregation are:

- Too rapid addition of acid
- Insufficient acidity and direct precipitation of the normal salt.
- Incomplete conversion of the basic salt due to inefficient stirring or reduced time gives rise to a powdery product.

Figure 10-27 shows normal lead styphnate (single rhombic crystals) and for comparative purposes basic lead styphnate (needle like crystals) are shown in Figure 10-28⁽¹⁵⁾. RD1303, Figure 10-29⁽¹⁵⁾, is a free flowing powder consisting of bright yellow predominantly tabular crystals having an average particle size of approximately 0.03 mm.

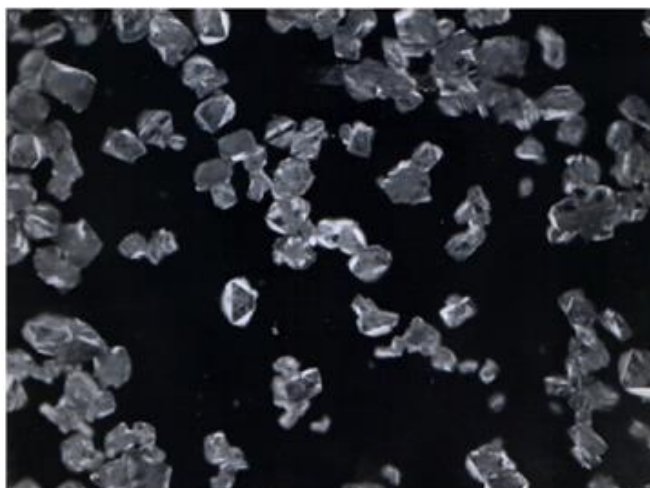


Figure 10-27 Normal lead styphnate (×80 magnification)



Figure 10-28 Basic lead styphnate (×80 magnification)

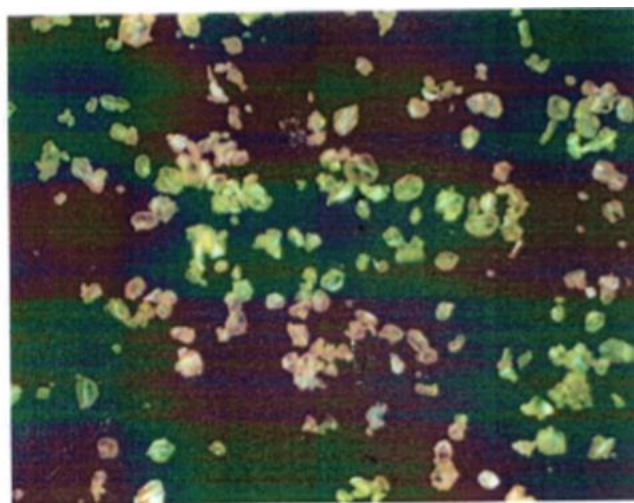
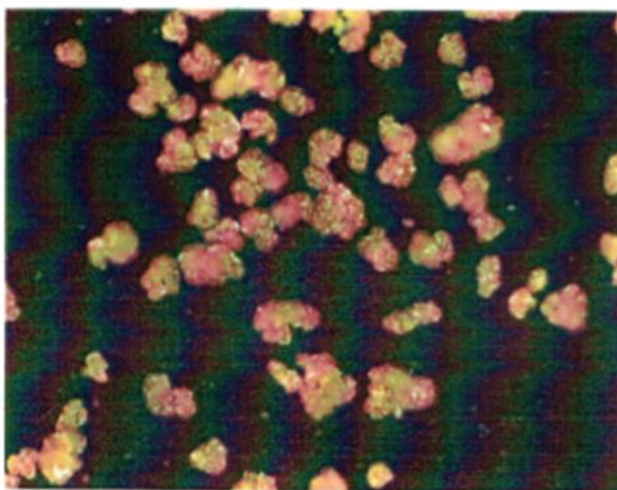


Figure 10-29 Lead styphnate, RD1303 (×100 magnification)**10.4.2.3 Manufacture of RD1346 and RD1349**

Because of its water of recrystallisation normal lead styphnate monohydrate is not suitable for use in munitions which may be subjected to high temperatures (>130 °C) in use. For this purpose, mono basic lead styphnates have been found to be suitable. Two compositions based upon the β -form (obtained by careful precipitation) namely RD1346 and RD1349 are used in UK service. Both are granular in form and free flowing. The RD1346 has a higher bulk density than the RD1349 and is recommended for use in dry loading applications such as an ingredient for priming and bridgewire compositions. RD1349 is especially suitable for making fuseheads without cavitations.

10.4.2.3.1 RD1346

RD1346 is prepared⁽¹⁶⁾ by reacting an aqueous solution of lead nitrate with an aqueous solution containing sodium styphnate, sodium hydroxide and 2-nitroresorcinol at a suitable temperature and rate of stirring. The product, Figure 10-30⁽¹⁵⁾, is a free flowing powder consisting of orange, rounded granules, approximately 0.07 mm².

**Figure 10-30 Lead styphnate, RD1346 (×100 magnification)****10.4.2.3.2 RD1349**

RD1349 is prepared⁽¹⁶⁾ by reacting an aqueous solution of styphnic acid and ammonium hydroxide with ammonium 2-nitroresorcinol solution with a mixed solution of lead acetate/ammonium hydroxide at a suitable temperature and rate of stirring. The product, Figure 10-31⁽¹⁵⁾, is a free flowing powder consisting of small, brown single crystals with a distinctive 'cigar-shape'. The approximate size of individual crystals is 0.06 mm × 0.01 mm.

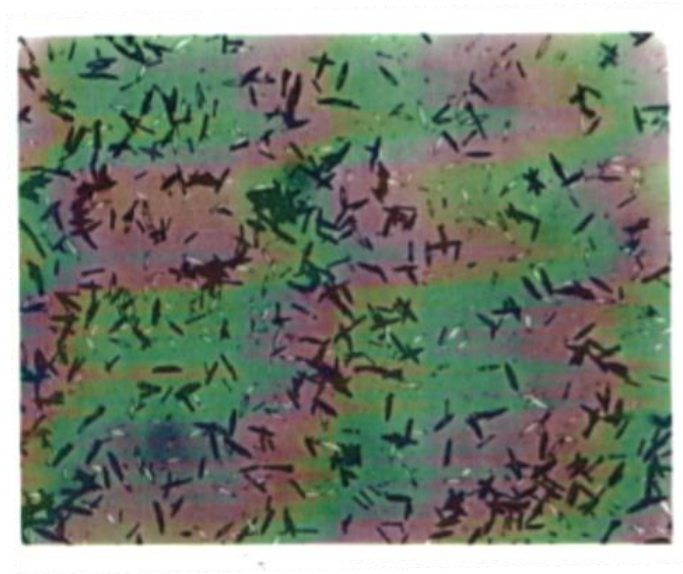


Figure 10-31 Lead styphnate, RD1349 (×100 magnification)

10.4.2.4 Manufacture of RD1367

The RD1367 process was introduced to provide a more economic method for the manufacture of lead styphnate. Although the RD1303 process is efficient with respect to the quality of the products it had fairly stringent requirements on the quality of the styphnic acid employed and yields were not high. The common process for preparing normal lead styphnate (commercial and RD1367) consists of the addition of lead nitrate solution to heated and stirred magnesium styphnate solution, prepared from styphnic acid and magnesium carbonate, at a set pH and concentration. The use of lead nitrate to make RD1367 rather than lead acetate which is used to manufacture RD1303 yields a more uniform crystalline product. The product, Figure 10-32⁽¹⁵⁾, consists of a free flowing powder consisting of yellow/orange, single, equant crystals. The approximate size of individual crystals is 0.10 mm × 0.08 mm.

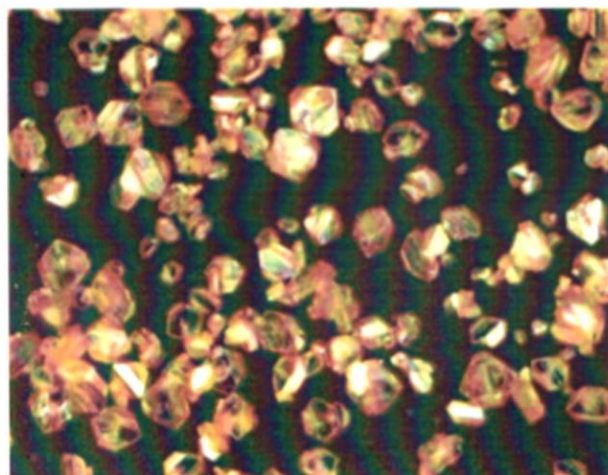


Figure 10-32 Lead styphnate, RD1367 (×100 magnification)

10.4.2.5 Eleyprime process

The Eleyprime process is based on the fact that the main explosive ingredient of VH2 and VH4 compositions, lead styphnate, can be formed after filling into the percussion cap by reaction between styphnic acid (2,4,6-trinitroresorcinol), which is not highly explosive or very sensitive, and lead dioxide. This reaction takes place only in the presence of water, which is not added until the insensitive reactants are filled into the percussion cap. Those ingredients of the mixture which are insoluble in water, namely the lead dioxide and antimony sulphide, are first mixed with wet tetrazene and dried (Mix A). The soluble or abrasive ingredients, comprising styphnic acid, barium nitrate and calcium silicide, are then added to Mix A and mixed in the dry state to produce a 'premix'. The resulting 'premix' at this stage behaves as a pyrotechnic and is relatively safe to handle and store. A measured quantity of the 'premix' is lightly pressed into the percussion cap and a drop of water added. The water causes the reaction to take place and after about 15 minutes the formation of lead styphnate is complete after which drying and final pressing takes place.

10.4.3 Barium Styphnate

Barium styphnate is a relatively insensitive primary explosive which is difficult to ignite by electric spark. When ignition is achieved, propagation is poor. It is less sensitive to impact and friction than lead azide or lead styphnate.

10.4.3.1 RD1320

RD1320 is prepared⁽¹⁷⁾ by reacting an aqueous solution of barium acetate and an aqueous solution of magnesium styphnate at a suitable temperature and rate of stirring. A trihydrate salt is formed which is converted to the monohydrate by the addition of nitric acid. The product, Figure 10-33⁽¹⁵⁾, is a free flowing yellow powder consisting of individual equant crystals approximately 0.15 mm × 0.10 mm with slight aggregation due to the small crystals.

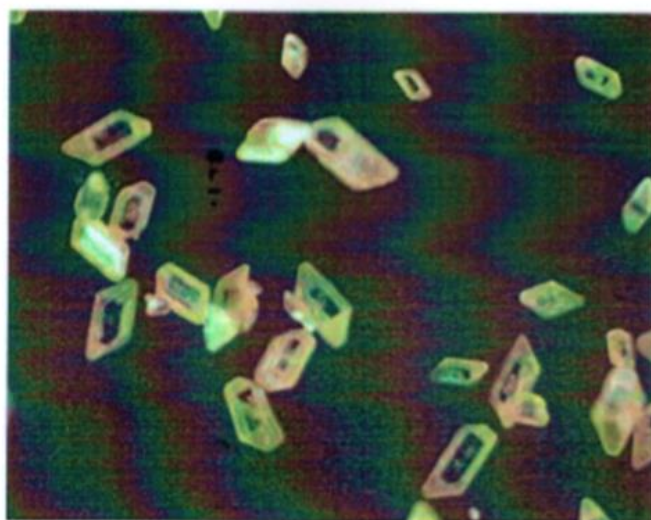


Figure 10-33 Barium styphnate, RD1320 (×100 magnification)

10.4.3.2 RD1320A

RD1320A is prepared⁽¹⁷⁾ by reacting an aqueous solution of barium chloride and an aqueous solution of magnesium styphnate at a suitable temperature and rate of stirring. The product, Figure 10-34⁽¹⁵⁾ consists of yellow free flowing columnar crystals approximately 0.15 mm × 0.10 mm with slight aggregation due to the small crystals.

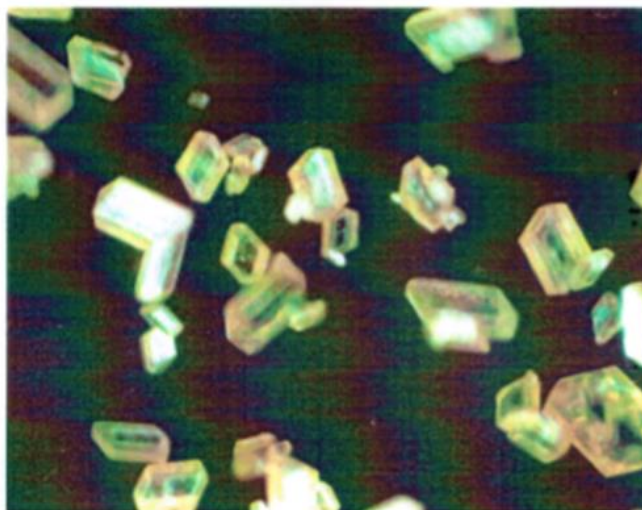


Figure 10-34 Barium styphnate, RD1320A (×100 magnification)

10.4.3.3 RD1320B

RD1320B is prepared⁽¹⁸⁾ by reacting an aqueous solution of barium chloride and an aqueous solution of magnesium styphnate solution containing sodium carboxymethyl cellulose at a suitable temperature and rate of stirring. The product, Figure 10-35⁽¹⁵⁾, consists of granular opaque rounded free flowing granules. Granules are approximately 0.3 mm × 0.15 mm.

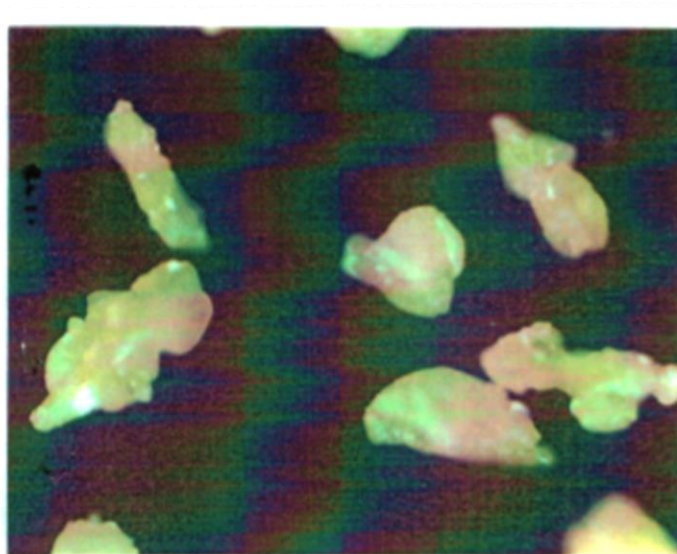


Figure 10-35 Barium styphnate, RD1320B (×100 magnification)

10.4.3.4 RD1340

RD1340 is prepared⁽¹⁹⁾ by reacting an aqueous solution of barium acetate containing a non-ionic surfactant with an aqueous solution of magnesium styphnate at a suitable temperature and rate of stirring. Following this, nitric acid solution is added over a pre-determined time. The product shown in Figure 10-36⁽¹⁵⁾, consists of a free flowing powder composed of yellow, plate-like crystals approximately 0.25 mm × 0.08 mm together with a number of smaller crystals approximately 0.07 mm × 0.04 mm. The small plates form a non-segregating mixture with potassium chlorate and antimony sulphide. This is due to the smaller particle size and low bulk density as compared with RD1320. The particle size of the product is controlled by the rate of addition of the nitric acid with slower addition producing larger crystals.

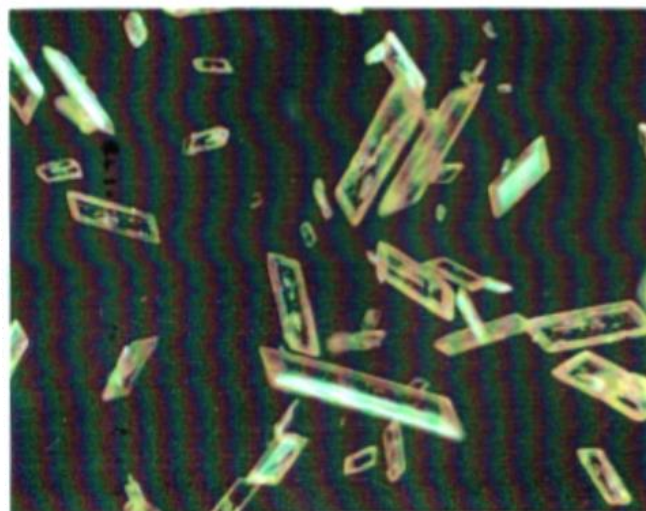


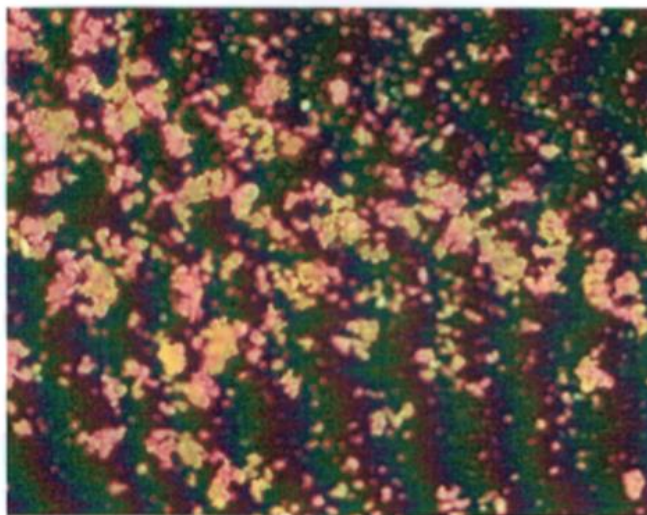
Figure 10-36 Barium styphnate, RD1340 (×100 magnification)

10.4.4 Lead Dinitroresorcinate

Lead dinitroresorcinate is an igniferous primary explosive which is sensitive to flash, impact or stab but is less violent than lead styphnate.

10.4.4.1 RD1308

RD1308 (4,6-lead dinitroresorcinate) is prepared⁽²⁰⁾ by reacting an aqueous solution of lead hydroxide, prepared by reacting an aqueous solution of sodium hydroxide, with an aqueous solution of lead acetate, an aqueous solution of sodium carboxymethyl cellulose and a suspension of 4,6-dinitroresorcinol at a suitable temperature and rate of stirring. The product, Figure 10-37⁽¹⁵⁾, is a free flowing powder, consisting of orange, irregular, granules approximately 0.03 mm².

**Figure 10-37 Lead dinitroresorcinate, RD1308 (×100 magnification)**

10.4.4.2 RD1337

RD1337 (2,4-lead dinitroresorcinate) is prepared⁽²¹⁾ by reacting an aqueous solution of sodium 2,4-dinitroresorcinate and an aqueous solution of lead acetate at a suitable temperature and rate of stirring. The product, Figure 10-38⁽¹⁵⁾, consists of a free flowing powder consisting of individual orange/red granules approximately 0.10 mm² and some granular aggregates

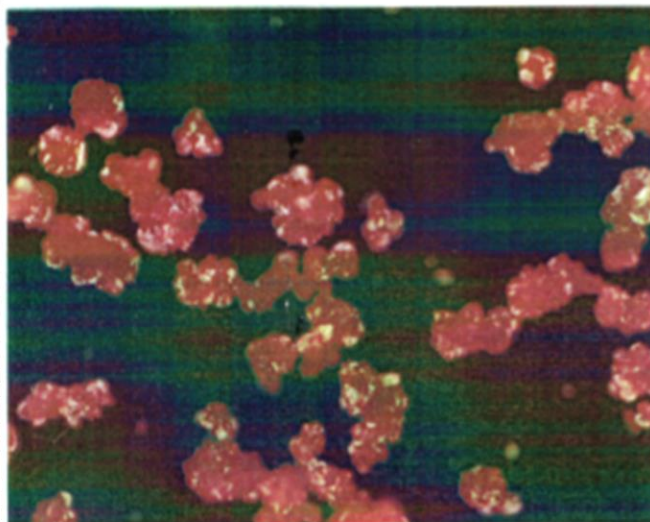


Figure 10-38 Lead dinitroresorcinate, RD1337 (×100 magnification)

10.4.5 Lead Azide

In the manufacture of lead azides and silver azide, safety is of primary importance to all concerned. The risks associated with the sensitiveness (see 20.2.1) of the azides cannot be overstressed. Lead azide is sensitive to shock, friction and low energy electrical discharge and it should be emphasised that wetting of the explosive does not appreciably reduce its sensitivity to shock and friction and in fact may increase the sensitiveness due to the formation of large crystals. As a result, precautions required to overcome dangers from electrostatic charges during the drying, sieving, weighing and pressing of the material are stringent and care must be taken to ensure that all apparatus is at earth electrical potential and that operatives do not build up an electrostatic charge whilst working with the material.

10.4.5.1 General manufacture of lead azide

The chemistry involved in the preparation of lead azide is relatively straightforward, however control of the reaction is critical as secondary growth of the lead azide crystals can occur and dangerous products can be formed. Lead azide is a white crystalline substance that is almost insoluble in water and can be prepared by mixing two solutions of a soluble and a relatively inert salt, lead acetate and sodium azide as shown below.

Sodium azide solution + lead acetate solution $\longrightarrow$ lead azide + sodium acetate

The insoluble lead azide is precipitated out and washed with distilled water to remove the excess ingredients and the other water soluble product, sodium acetate. If this mixing is done incorrectly or in a haphazard manner, the correct α -form of crystal will not always be obtained and one of the other crystal forms (β or γ) may result. This could cause the material to spontaneously detonate even though the material is suspended in a large volume of water. In order that the correct α -form

crystals are produced, the lead azide crystals are grown on a seed of lead carbonate crystal that has been formed by the addition of lead acetate and sodium carbonate to the distilled water in the precipitating pan.

10.4.5.2 Service lead azide (SLA)

The essential feature of British military detonator design was established in the early 1930s by the decision to use pure lead azide of a high output with its advantage of output/volume ratio compared with mercury fulminate. This decision led to the development of the Service lead azide process in which compact free flowing crystals were built up on nuclei of basic lead carbonate.

Service lead azide (SLA) is prepared by initially reacting an aqueous solution of lead acetate and an aqueous solution of lead carbonate. Small crystal of lead carbonate are formed which seed the lead azide as it is formed and ensure the preferred crystal type (α -form) is produced. Aqueous solutions of sodium azide and lead acetate are added at a controlled rate to the lead acetate/lead carbonate solution, maintained at a suitable temperature and rate of stirring. The lead azide is precipitated in the form of fine white crystals. A small amount of acetic acid is added to destroy any excess carbonate. The product, Figure 10-39⁽¹⁵⁾, consists of free flowing white, short, thick rhombic crystals of high bulk density. The size of individual crystals is approximately 0.10 mm $\times$ 0.03 mm.

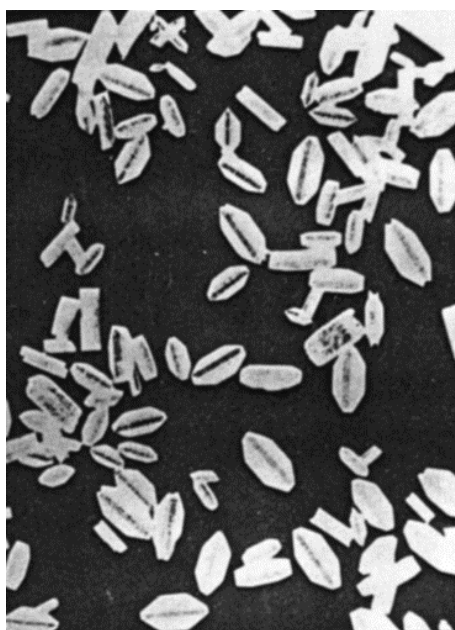


Figure 10-39 Service lead azide ($\times 50$ magnification)

10.4.5.3 Pure lead azide, RD1339

RD1339 is prepared⁽²²⁾ by reacting an aqueous solution of sodium azide containing a non-ionic surfactant with aqueous solutions of lead acetate and sodium azide at a suitable temperature and rate of stirring. The product, Figure 10-40⁽¹⁵⁾, consists of a

free flowing powder consisting of aggregates of small, white crystals approximately 0.03 mm².

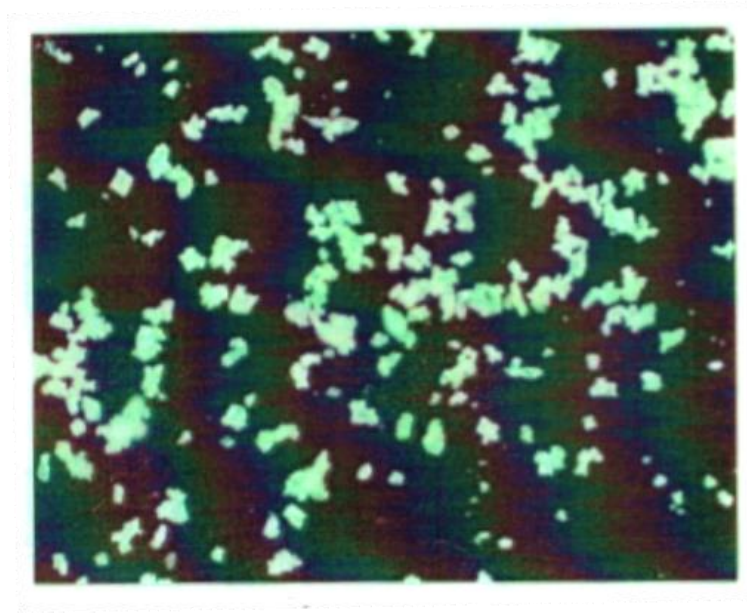


Figure 10-40 Pure lead azide, RD1339 (×100 magnification)

10.4.5.4 Colloidal co-precipitated lead azide, RD1343

RD1343 is prepared⁽²³⁾ by reacting an aqueous solution of sodium carboxymethyl-cellulose containing a non-ionic surfactant with an aqueous solution of lead acetate and a mixed aqueous solution of sodium azide and sodium hydroxide at a suitable temperature and rate of stirring. The product, Figure 10-41⁽¹⁵⁾, consists of free flowing white irregular granules with no aggregation of individual granules. The size of the granules is approximately 0.15 mm × 0.08 mm.

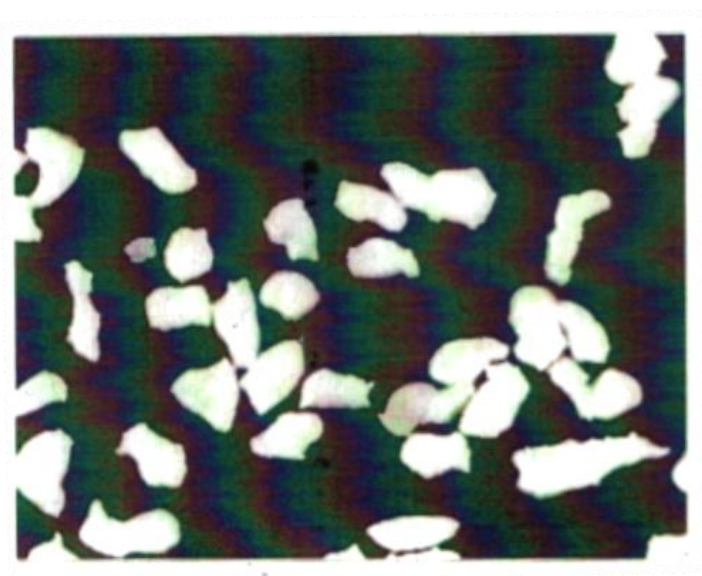


Figure 10-41 Colloidal co-precipitated lead azide, RD1343 (×100 magnification)

10.4.5.5 Dextrinated lead azide, RD1352

RD1352 is prepared⁽²⁴⁾ by reacting an aqueous solution of a non-ionic surfactant and an aqueous solution of dextrin with a mixed aqueous solution containing sodium azide, sodium hydroxide and Rochelle salt (potassium sodium tartrate) and aqueous solutions of sodium acetate and lead nitrate at a suitable temperature and rate of stirring. The product (lead azide coated and interspersed with dextrin granules), Figure 10-42⁽¹⁵⁾, consists of free flowing white rounded granules which are less irregular than those of RD1333 giving a composition of increased bulk density. Some 'dumb-bell' formation is evident. The approximate size of individual crystals is 0.09 mm × 0.07 mm.

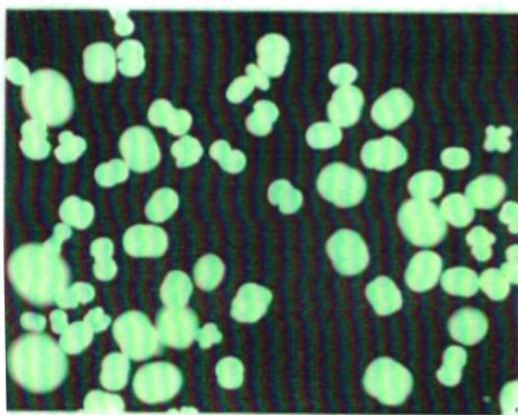


Figure 10-42 Dextrinated lead azide, RD1352 (×100 magnification)

10.4.5.6 Lead azide GAM

Gelatin, azide, molybdenum disulphide (GAM) form of lead azide was developed and introduced during 1967. It is manufactured by the precipitation of lead azide from a solution containing gelatin and a suspension of molybdenum disulphide which is incorporated in the crystal agglomerate to obtain the desired combination of cohesion and electrical properties. The electrical properties of the modified product are excellent, however, in comparison to dextrinated lead azide (bulk density 2.2 g cm^{-3} the bulk density of GAM ($1.3 - 1.5 \text{ g cm}^{-3}$) is lower. The power of lead azide GAM is also lower than that of dextrinated lead azide. The product, Figure 10-43⁽¹⁵⁾, consists of a free flowing powder consisting of grey/black rounded granules forming aggregates of approximately 0.08 mm^2 .

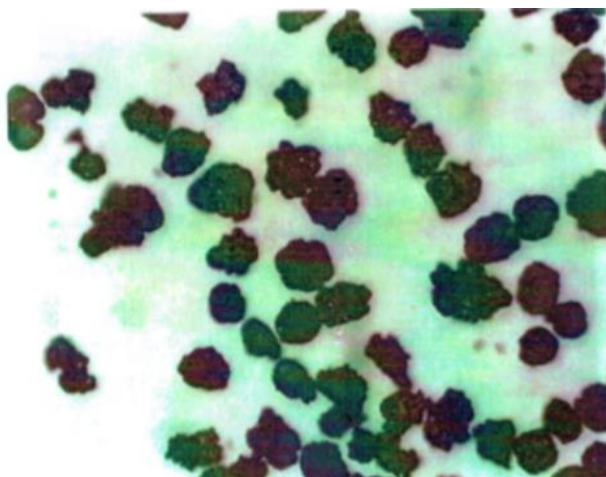


Figure 10-43 Lead azide, GAM (×100 magnification)

10.4.5.7 Basic Lead Azide

Basic lead azide is prepared by reacting aqueous solution of lead acetate containing Cepol DV and glycerine with a mixed aqueous solution of sodium

hydroxide and sodium azide containing trinitrophenol (TNP) at a suitable temperature and rate of stirring. The process for the preparation of basic lead azide has been reported in the literature⁽²⁵⁾ and has been successfully established on a pilot plant scale (2.5 kg/batch). Basic lead azide is a crystalline, free flowing, non-hygroscopic material. It has a bulk density of $2.0 \pm 0.2 \text{ g cm}^{-3}$ and detonates high explosives efficiently. It also has a better thermal and hydrolytic stability and its compatibility with copper is better than Service lead azide (SLA)

10.4.6 Silver Azide

10.4.6.1 General manufacture of silver azide

The chemistry involved in the preparation of silver azide is relatively straightforward and it can be prepared by the mixing two solutions of a soluble and a relatively inert salt, silver nitrate and sodium azide as shown below.

Sodium azide solution + silver nitrate solution $\longrightarrow$ silver azide + sodium nitrate

The insoluble silver azide is precipitated out and washed with distilled water to remove excess ingredients and the other product, sodium nitrate. There are two manufactured forms of silver azide RD1336 and a modified form of this salt, designated RD1374.

10.4.6.2 RD1336

RD1336 is prepared⁽²⁶⁾ by reacting ammonium hydroxide solution with aqueous solutions of sodium azide, silver nitrate and nitric acid at a suitable temperature and rate of stirring. The product, Figure 10-44⁽¹⁵⁾, consists of a free flowing powder comprising of irregular aggregates of small white crystals with the crystals having a uniform aggregate size of approximately 0.05 mm^2 . The difficulties in applying this material to automated detonator filling, "fortress filling" resulted in the development of a modified silver azide, designated RD1374.

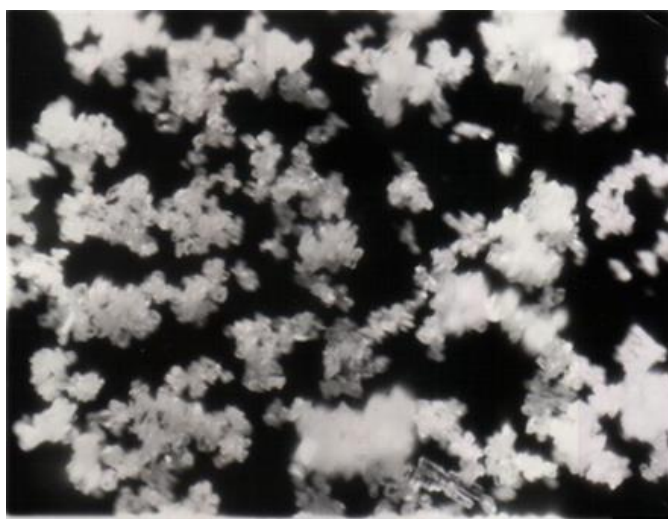


Figure 10-44 Silver azide, RD1336 ($\times 100$ magnification)

10.4.6.3 RD1374

RD1374 is prepared⁽²⁷⁾ by reacting aqueous solutions of sodium azide, potassium bromide, ammonia and silver nitrate at a suitable temperature and rate of stirring. The product, Figure 10-45⁽¹⁵⁾, consists of a free flowing powder which unlike RD1336 consists of small single crystals approximately 0.20 mm × 0.15 mm in size.

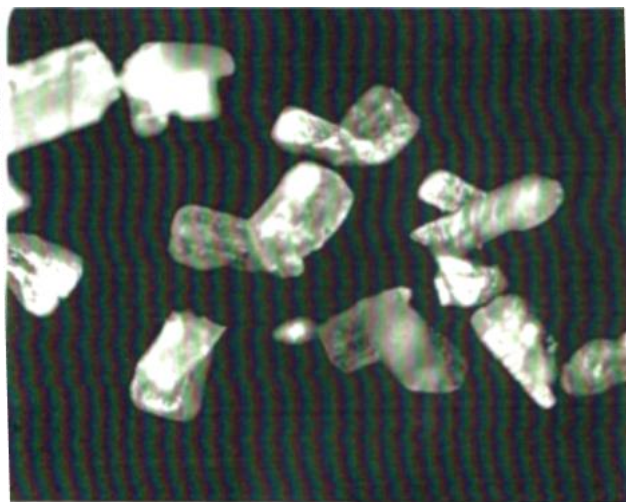


Figure 10-45 Silver azide, RD1374 (×100 magnification)

10.4.7 Tetrazene, RD1357A

RD1357A⁽²⁸⁾ is manufactured by the action of sodium nitrite on a heated solution of aminoguanidine sulphate in dilute ethanoic (acetic) acid. The reaction involves the formation of two diazonium links, one to form a ring structure, the other to increase the molecular mass. The basic process is carried out in a similar manner to the manufacture of lead azide and lead styphnate, i.e. small scale. The product, Figure 10-46⁽¹⁵⁾, consists of a fine crystalline powder of rosette like aggregates with an approximate size of 0.07 mm², which when dried are free from agglomerates and are free flowing.

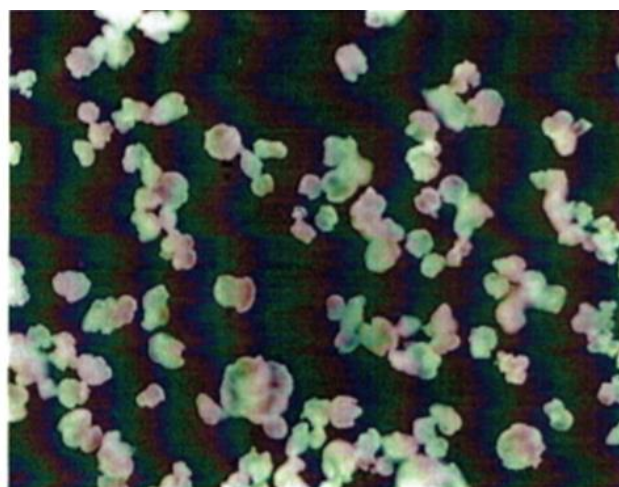


Figure 10-46 Tetrazene, RD1357A (×100 magnification)

10.4.8 Lead Free Primary Explosives

In recent years there has been a move to reduce the toxicity of primary explosives as mostly they contain lead. The term 'green explosives' is now often used to describe this development⁽²⁹⁾.

10.4.8.1 2-diazo-4,6-dinitrophenol (DDNP)

2-diazo-4,6-dinitrophenol (DDNP) was first prepared in the early 1800s by reaction of nitric oxide with 2-amino-4,6-dinitrophenol (picramic acid). More recent methods involve diazotisation of 2-amino-4,6-dinitrophenol or its sodium salt with sodium nitrite/hydrochloric acid. Depending on reaction conditions and the addition of crystal modifying substances, a free flowing form of DDNP can be obtained.

10.4.8.2 Potassium 4,6-dinitrobenzofuroxan (KDNBF), RD1372

The manufacture of KDNBF firstly involves the preparation of the precursor starting material 4,6-dinitrobenzofuroxan (DNBF). The method used involves the oxidation of ortho-nitroaniline in alkaline solution to benzofuroxan. The benzofuroxan is isolated and nitrated in a mixture of nitric acid and sulphuric acid to give 4,6-dinitrobenzofuroxan (DNBF), which is then recrystallised from nitric acid to give the compound in a pure form.

The KDNBF is prepared⁽³⁰⁾ by conversion of the DNBF to the soluble sodium salt by the addition of sodium bicarbonate to an aqueous suspension of DNBF at 70-75 °C and then slowly adding a solution of potassium nitrate. The formation of the KDNBF is carried out in the presence of a flocculant, which acts as a crystal habit modifier. Slow cooling of the solution results in the precipitation of the KDNBF. The product, Figure 10-47⁽¹⁵⁾, consists of a free flowing powder consisting of rounded orange/red granules with an approximate size of 0.10 mm² with some aggregation of granules.

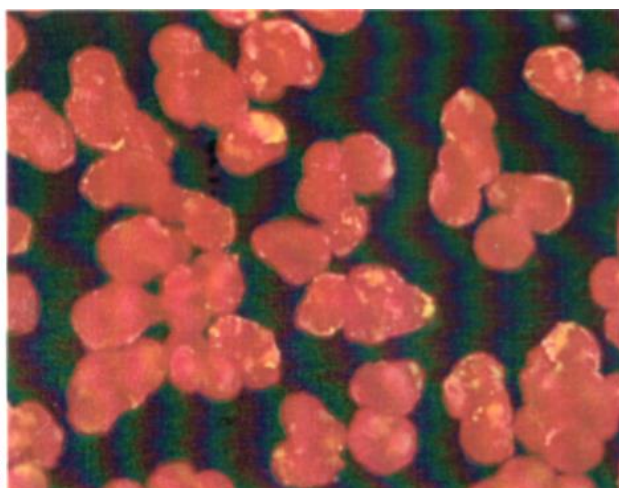


Figure 10-47 KDNBF, RD 1372 (×100 magnification)

10.4.8.3 Copper (I) salt of 5-nitrotetrazole, DBX-1

The traditional synthetic procedure for making DBX-1 is exposure of 5-aminotetrazole to a modified Sandmeyer reaction resulting in the formation of a copper acid salt, which is converted to the sodium salt of 5-nitrotetrazole (NaNT) upon exposure to sodium hydroxide (NaOH). Subsequently, copper (II) chloride (CuCl_2) is treated with sodium ascorbate ($\text{C}_6\text{H}_7\text{NaO}_6$) to generate the copper (I) species in situ, which reacts with NaNT to yield DBX-1. However, it should be noted that there were several safety issues associated with this procedure which were a major drawback and limited practical application for the material. However, there have been a number of modifications made to the procedure to increase process safety and interest in DBX-1 continues⁽³¹⁾.

10.4.8.4 Potassium salt of 7-hydroxy-4,6-dinitrobenzofuroxan (KDNP)

The potassium salt of 7-hydroxy-4, 6-dinitrobenzofuroxan (KDNP) was originally produced from the nitration and rearrangement of commercially available 5-chlorobenzofuroxan, however this process produced a very friction sensitive material due to occluded water from the recrystallisation process. Although other solvents could be used, this process was deemed unsuitable for larger scale production. An alternative 2 step process starting from commercially available 3-bromo-anisole has been reported⁽³²⁾. Nitration, azidation and ring closure gave a crude product which could be crystallised to give control of particle size and tailoring for specific use (e.g. bridgewire vs primer). The main advantage of this process is that 3-bromo-2,4,6-trinitroanisole is an intermediate in the synthesis of dipicramide (DIPAM), a well-known insensitive high explosive. Dipicramide was produced on a large scale in the 1960s and therefore the nitration chemistry is well understood. The KDNP produced by this route is in the anhydrous form unlike the monohydrate produced by the original method.

Performance studies^(33,34) carried out on a range of applications demonstrated the advantages of this material and it was qualified by US Naval Sea Systems Command as a primary explosive in accordance with the requirements of US NAVSEAINST 8020.5C and identified it as safe and suitable for service use for weapons development.

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