CHAPTER 12

EXPLOSIVES

CHAPTER 12 OBJECTIVES

- CHEMICAL EXPLOSIVES
  - INTRODUCTION
  - DEVELOPMENT OF EXPLOSIVES
  - CLASSIFICATION OF EXPLOSIVES
  - CHEMISTRY OF EXPLOSIVES
- PROPELLANTS
  - GUN PROPELLANTS
  - ROCKET PROPELLANTS
- PYROTECHNICS

CHAPTER 12 OBJECTIVES

- MANUFACTURING OF EXPLOSIVES
  - TNT PRODUCTION
  - BLACK POWDER PRODUCTION
  - RDX AND HMX PRODUCTION
- CLASSIFICATION, TRANSPORTATION AND STORAGE OF EXPLOSIVES

CHEMICAL EXPLOSIVES INTRODUCTION

- Explosives are chemical compounds or their mixtures that rapidly produce a large volume of hot gases when properly initiated.
- Explosives are known to detonate at the rates of kilometers per seconds.
- Explosives are capable of exerting sudden high pressures and generate a loud noise and more or less destructive types of reactions that produce mechanical, chemical, or nuclear explosions.
- A mechanical explosive depends on a physical reaction such as overloading a container with compressed air.

CHEMICAL EXPLOSIVES INTRODUCTION

- A nuclear explosive is one in which a sustained nuclear reaction can be made rapidly, releasing large amounts of energy.
- Chemical explosives account for virtually all explosive applications.
- The destructive effects of explosives are much more spectacular than their peaceful uses. However, it appears that more explosives have been used in industry for peaceful purposes than in all the wars.
- Solid explosives are chemical compounds or mixtures of compounds that, when initiated by energy in the form of shock, impact, heat, friction or spark, undergo very fast chemical decomposition reactions.

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CHEMICAL EXPLOSIVES
DEVELOPMENT OF EXPLOSIVES

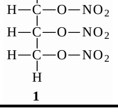
- Among the important explosive materials, ***black powder***, also known as ***gunpowder*** was most likely the first explosive discovered accidentally by Chinese alchemists.
- Black powder was formed during the process of separation of gold from silver at a low temperature.
- They added potassium nitrate, KNO_3, and sulfur to the gold ore in the furnace and they forgot to add charcoal to the mixture.
- However, they added the amount of charcoal at the last step of the reaction. As the result, a black powder was formed causing a strong explosion.

CHEMICAL EXPLOSIVES
DEVELOPMENT OF EXPLOSIVES

- Black powder was then introduced in the market as a mixture of potassium nitrate, charcoal, and sulfur. The composition and the order of addition determine the properties of this composite explosive.
- Black powder contains a fuel and oxidizer. The fuel is a powdered mixture of charcoal and sulfur. Potassium nitrate is the oxidizer.
- Black powder was successfully introduced for blasting in 1627. The use of black powder then spread fast for mining, road building, for recovering ore, in copper mines, and other important industrial applications.
- The limitations of black powder as a blasting explosive were apparent for difficult mining and tunneling operations.

CHEMICAL EXPLOSIVES
DEVELOPMENT OF EXPLOSIVES

- More efficient explosive were required. Liquid nitroglycerine [$C_3H_5O_3(NO_2)_3$], **1**.
- It was discovered by the Italian Professor Sobrero, was later studied and manufactured by the Swedish inventor, Immanuel Nobel in 1863.
- The major problem that the Nobel family faced was the transportation of liquid nitroglycerine that cause loss of life and property.
- The destruction of the Nobel factory in 1864 was one of many accidents caused by the explosion of nitroglycerine.



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CHEMICAL EXPLOSIVES
DEVELOPMENT OF EXPLOSIVES

- The discovery of mercury fulminate [$Hg(CNO)_2$] by Alfred Nobel in 1864 has improved the initiation process. This chemical complex replaced the black powder in the initiation of nitroglycerine in boreholes.
- In 1866, a major explosion had completely destroyed the nitroglycerine factory. Alfred Nobel had discovered the safety hazard of nitroglycerine during transportation.
- He reduced the sensitivity of nitroglycerine by mixing it with adsorbent clay known as "Kieselguhr".

CHEMICAL EXPLOSIVES
DEVELOPMENT OF EXPLOSIVES

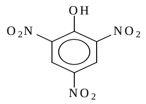
- Nitrocellulose, known as gun cotton, was produced by the direct nitration of cellulose.
- The synthesis of nitrocellulose was extremely difficult and many accidents took place such as the destruction of the manufacturing plants in France, England and Austria.
- The stability of nitrocellulose was improved by the process of pulping, boiling and washing. Wet nitrocellulose could be exploded by adding a small amount of dry nitrocellulose.
- An interesting discovery was made in 1875 by Alfred Nobel when an explosive gel was formed by mixing nitrocellulose and nitroglycerine.

CHEMICAL EXPLOSIVES
DEVELOPMENT OF EXPLOSIVES

- This gel was converted later in 1888 into gelatin dynamite and ballistile, known at first as smokeless powder. Ballistile was in fact a mixture of nitrocellulose, nitroglycerine, benzene and camphor.
- The explosive properties of dynamite were improved by the Swedish chemists Ohlsson and Norrbin by adding ammonium nitrate (NH_4NO_3).
- Ammonium nitrate was not considered to be hazardous and explosive until disastrous accidents took place in 1947 in the harbor of Texas City.

CHEMICAL EXPLOSIVES
DEVELOPMENT OF EXPLOSIVES

- The development of military explosives started almost with the discovery of black powder. In 1885, Turpin discovered picric acid or trinitrophenol, **2**, which was found to be a suitable replacement of black powder.



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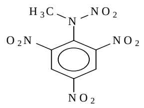
- Picric acid was adopted all over the world as the basic explosive for military uses.
- The major problems of picric acid are the corrosion of the shells in the presence of water, and the high sensitivity of its salts. Also, picric acid melts only at very high temperatures.

CHEMICAL EXPLOSIVES
DEVELOPMENT OF EXPLOSIVES

- Tetryl, **3**, was also discovered at the same time as picric acid. Tetryl was used for the first time as an explosive in 1906.



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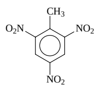
- In 1863, Wilbrand prepared for the first time trinitrotoluene (TNT), **4**. In 1902, TNT, **4**, was adopted for use by the German army and in 1912 by the U.S. army.



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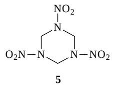
- The storage of TNT was made easier by the use of the mixture of TNT and ammonium nitrate, known as amatol.

CHEMICAL EXPLOSIVES
DEVELOPMENT OF EXPLOSIVES

- After World War I, the research in the area of explosives was concentrated on the development of new and more powerful explosive materials.
- For example, cyclotrimethylene trinitramine ($C_3H_6N_6O_6$), known as RDX, **5**, and pentaerythritol tetranitrate (PETN) ($C_5H_8N_4O_4$), **6**, were among the new discovered explosives.



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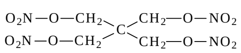
- PETN, **6**, was discovered in 1894 and obtained by the nitration of pentaerythritol. During World War II, RDX was utilized more than PETN.



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CHEMICAL EXPLOSIVES
DEVELOPMENT OF EXPLOSIVES

- The mixture of 50% PETN and 50% TNT was developed and used for foiling hand and anti-tank grenades, and detonators.
- Another class of explosives known as polymer bonded explosives (PBXs).
- They were developed to reduce the sensitivity of the explosive crystals by embedding then in a rubber-like polymer, such as polystyrene.
- PBXs based on RDX and RDX/PETN, and also on HMX were developed.
- Energetic plasticizers have also been developed for PBXs production.

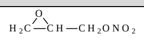
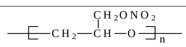
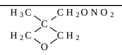
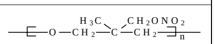
CHEMICAL EXPLOSIVES
DEVELOPMENT OF EXPLOSIVES

Table 12.1. Examples of PBX compositions.

HMX	–	Cyclotetramethylene tetranitramine (Octogen)
HNS	–	Hexanitrostilbene
PETN	–	Pentaerythritol tetranitrate
RDX	–	Cycltrimethylene trinitramine (Hexogen)
TATB	–	1,3,5- triamino-2,4,6-trinitrobenzene

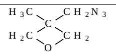
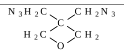
CHEMICAL EXPLOSIVES
DEVELOPMENT OF EXPLOSIVES

Table 12.2. Examples of energetic polymers.

Common name	Chemical name	Structure
GLYN (monomer)	Glycidyl nitrate	
PolyGLYN	Poly (glycidyl nitrate)	
NIMMO (monomer)	3-Nitratomethyl-3-methyl oxetane	
polyNIMMO	Poly (3-nitratomethyl-3-methyl oxetane)	

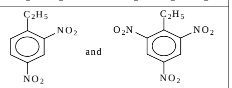
CHEMICAL EXPLOSIVES
DEVELOPMENT OF EXPLOSIVES

Table 12.2. Examples of energetic polymers.

Common name	Chemical name	Structure
GAP	Glycidyl azide polymer	$-[CH_2-CH(CH_2N_3)-O]_n-$
AMMO (monomer)	3-Azidomethyl-3-methyl oxetane	
PolyAMMO	Poly (3-azidomethyl-3-methyl oxetane)	$-[O-CH_2-C(H_3C)(CH_2N_3)-CH_2]_n-$
BAMO (monomer)	3,3-bis-azidomethyl oxetane	
PolyBAMO (monomer)	Poly(3,3-bis-azidomethyl oxetane)	$-[O-CH_2-C(N_3H_2C)(CH_2N_3)-CH_2]_n-$

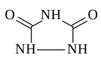
CHEMICAL EXPLOSIVES
DEVELOPMENT OF EXPLOSIVES

Table 12.3. Examples of energetic plasticizers.

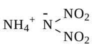
Common name	Chemical name	Structure
NENAs	Alkyl nitratoethyl nitramines	$R-N(NO_2)-CH_2-CH_2ONO_2$
EGDN	Ethylene glycol dinitrate	$O_2NOH_2C-CH_2ONO_2$
MTN	Metriol trinitrate	$H_3C-C(CH_2ONO_2)_3$
BTTN	Butane-1,2,4-triol trinitrate	$O_2NOH_2C-CH(ONO_2)-CH_2-CH_2ONO_2$
K10	Mixture of di-and tri-nitroethylbenzene	

CHEMICAL EXPLOSIVES
DEVELOPMENT OF EXPLOSIVES

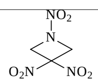
- Research and development is continuing in the chemistry of explosives in order to produce compounds, which are insensitive to accidental initiation but still highly efficient as explosives.
- NTO (**7**), ADN (**8**), and TNAZ (**9**) are good examples of explosive compounds under development and testing.



5-Nitro-1,2,4-triazol-3-one
NTO (**7**)



Ammonium dinitramide
ADN (**8**)



1,3,3-Trinitroazetidine
TNAZ (**9**)

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CLASSIFICATION OF EXPLOSIVES

- Explosives have been classified in relation to their chemical nature and to their performance. The explosives have been divided into three classes:
  - Primary explosives
  - Secondary explosives
  - Tertiary explosives or propellants
- These explosives are also divided into two other groups based on the chemical nature of the materials.
  - Pure compounds
  - Mixture of compounds.

CLASSIFICATION OF EXPLOSIVES

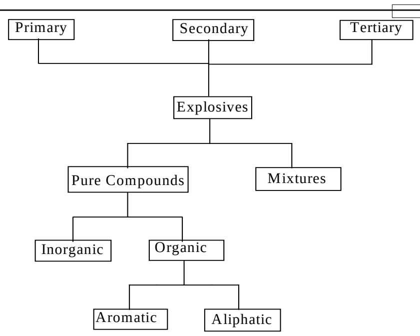


Figure 12.2. Types of explosives

CLASSIFICATION OF EXPLOSIVES

- These explosives are also divided into two other groups based on the Explosives are compounds that have functions of groups, which have explosive properties.
- The most common functional groups, both oxidizer and fuel types, are as follows:
  - \- Nitro NO_2
  - \- Nitrate NO_3
  - \- Nitroso NO
  - \- Azide N_3
  - \- Amine NH_2
  - \- Hydroxy OH

Primary Explosives

- Primary or initiator explosives are the most sensitive to heat, friction, impact and shock.
- Primary explosives are capable of transforming a low-energy into a high-intensity shock wave.
- Primary explosives are used to initiate the materials with increasing mass and decreasing sensitivity.
- They are used mainly in military detonators and commercial blasting caps.
- Primary explosives are characterized by their low detonation rates and less energy than secondary explosives.

Primary Explosives

- Most primary explosives are powders with a good flow transfer and pressing characteristics to permit high-speed automatic loading of detonators, which are produced in very large quantities.
- Initiators are very sensitive to shock and are loaded into detonators in the production plant.
- The manufacture of detonators requires maximum precautions to prevent the accumulation of substantial masses of explosives, dusting, and accidental initiation.
- Most primary explosives are dense and inorganic compounds.

Primary Explosives
Mercury Fulminate

- Mercury fulminate or mercuric cyanate, **10**, is a grey-white powder obtained by reacting mercuric nitrate with alcohol in nitric acid

$Hg(CNO)_2$
10

- Mercury fulminate is the most sensitive of initiating agents to impact and friction, although its sensitivity decreases as the density of the pressed mass increases.
- The sensitivity decreases also by the addition of water but increases in the presence of sunlight.
- Mercury fulminate decomposes when stored at elevated temperatures.
- Mercury fulminate will easily detonate after initiation. It decomposes into stable products.

$$Hg(CNO)_2 \longrightarrow 2CO + N_2 + Hg$$

Primary Explosives
Lead Azide

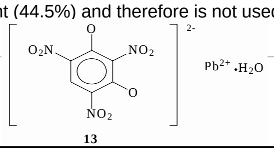
- Lead azide, **11**, is the primary explosive used in military detonators in the U.S.

$Pb(N_3)_2$
11

- Lead azide is a very stable compound at ambient and high temperatures, and has good flow characteristics. It is less sensitive to ignition then mercury fulminate.
- Lead styphnate, known to be readily ignitable material, is used as a cover charge to ensure initiation.

Primary Explosives
Lead Styphnate

- Lead styphnate, **13**, also known as 2,4,6-trinitro-soreinate, is an explosive compound used to start the ignition-to-detonation process in the explosive sequence.
- It is stable at elevated temperatures and non-corrosive.
- The addition of graphite enhances its electrical conductivity in systems designed for electrical initiation.
- Dry lead styphnate is the most sensitive of the primary explosives to electrostatic discharge.
- Lead styphnate is a weak primary explosive because of its high metal content (44.5%) and therefore is not used in the filling of detonators.



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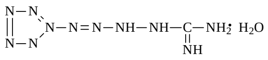
Primary Explosives

Tetrazene

- Tetrazene, **14**, is classified as a primary explosive that is a very hazardous material.
- An explosion can occur during the preparation, which is based on sodium nitrite and amino guanidine sulfate (**15**).



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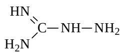

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- Tetrazene is hygroscopic and stable at ambient temperatures.
- The detonation property of tetrazene can detonate if it is not compacted. Tetrazene is not suitable for filling detonators.

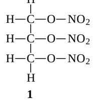
Secondary Explosives

- Secondary explosives are usually more difficult to detonate and they differ from primary explosives in three basic ways:
- Secondary explosives do not easily go from burning to detonation.
- Electrostatic ignition is difficult with secondary explosives.
- Secondary ignition requires large shocks.

Secondary Explosives

Nitroglycerine

- Nitroglycerine, **1**, is still one of the most widely produced nitrate ester. The first process for the manufacture of nitroglycerine was developed in France and in England in 1882.



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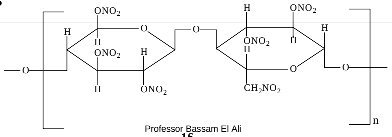
- Nitroglycerine is a very powerful secondary explosive with a high brisance, i.e., shattering effect. It is used in dynamite.
- Nitroglycerine is also thickened or gelatinized by an addition of a small percentage of nitrocellulose.
- It provides a source of high energy in propellant compositions.
- Nitroglycerine is insoluble in water but readily dissolves in most organic solvents.

Secondary Explosives
Nitrocellulose

- Nitrocellulose, **16**, is a generic term denoting a family of compounds.
- The composition is determined by the percentage by weight of nitrogen. The number of nitrogen groups present in nitrocellulose can be calculated by the following equation:

$$n = \frac{162N}{1400-45N}$$

- Where N is the percentage of nitrogen calculated from chemical analysis



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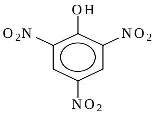
Secondary Explosives
Picric Acid

- Picric acid, **2**, also known as 2,4,6-trinitrophenol has been used in grenade and mine fillings and has a tendency to form impact-sensitive metal salts (picrates) with the metal walls of the shells.



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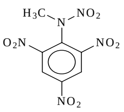
- Picric acid is a strong acid, very toxic, soluble in hot water, alcohol, ether, benzene and acetone.
- The explosive power of picric acid is superior to TNT with regard to the velocity of detonation.

Secondary Explosives
Tetryl

- Tetryl or 2,4,6-trinitrophenyl methylnitramine, **3**, was frequently used as a base charge in blasting caps, as the booster explosive in high-explosive shells, and as an ingredient of binary explosives.
- Tetryl is now replaced by PETN or RDX. Tetryl is a very toxic chemical.



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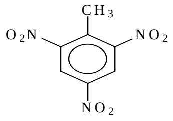
- Tetryl is moderately sensitive to initiation by friction and percussion. It is more sensitive than picric acid and TNT.

Secondary Explosives
TNT

- TNT, also known as trinitrotoluene, **4**, remains an important military explosive, particularly in mixtures with ammonium nitrate (NH_4NO_3).
- TNT has a low melting point (80°), which permits loading into bombs and shells in the molten state.



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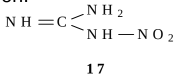
Secondary Explosives
TNT

- TNT has the advantages of low manufacturing costs and cheap raw materials, safe handling, a low sensitivity to impact and friction, high explosive power, and also has good chemical and thermal stability.
- TNT is widely used in commercial explosives and is much safer to produce and handle than nitroglycerine and picric acid.
- The important disadvantage of TNT is the exudation (leaching out) of the isomers of dinitrotoluenes and trinitrotoluenes.

Secondary Explosives
Nitroguanidine

- Nitroguanidine, **17**, also known as picrite ($CH_4N_4O_2$), has been used as an industrial explosive but not as a military explosive because of its relatively low energy content and difficulty of initiation.

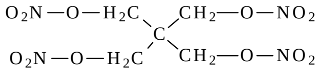


17

- Nitroguanidine can be also used in flashes and propellants due to the low heat and temperature of explosion.
- Nitroguanidine combined with nitrocellulose, nitroglycerine and nitroglycerine and nitrodiethyleneglycol forms a colloidal gel, which is the basis of these propellants.

Secondary Explosives
PETN

- Pentaerythritol tetranitrate (PETN), **6**, is known as one of the most sensitive of the military high explosives.

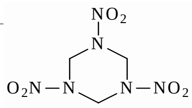


6

- It has a great shattering effect. PETN is not used in its pure form due to its high sensitivity to friction and impact.
- Pentolite is a military explosive composed of 20-50% PETN and TNT. However, PETN has been largely replaced by RDX in military applications.

Secondary Explosives
RDX

- RDX, cyclonite or cyclotrimethylene trinitramine, **5**, is one of the most powerful explosives.
- Pure RDX is very sensitive to initiation by impact and friction.
- However, the polymer bonded explosive (PBX) is less sensitive due to embedding the RDX crystals in a polymeric matrix.
- RDX - a very high explosive power compared with TNT and picric acid.
- RDX has a high melting point, which makes it difficult to use in casting.



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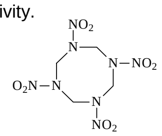
Secondary Explosives
HMX

- HMX, octogen, or cyclotetramethylene tetranitramine, **18**, is present in four different crystalline forms in their density and sensitivity.



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Crystal density	($20^oC/g.cm^{-3}$)
α-form	1.87
β-form	1.96
γ-form	1.82
δ-form	1.78

- HMX has similar properties of RDX with respect to the chemical reactivity and solubility in organic solvent.
- HMX is superior to RDX as an explosive due to its high ignition temperature and chemical stability.
- The disadvantage of HMX compared to RDX is reflected in its lower explosive power.

Secondary Explosives
Tertiary Explosives or Propellants

- Tertiary explosives or propellants are combustible materials that contain, in addition to their components, the oxygen needed for their combustion. Propellants produce large amounts of gas upon combustion.
- Propellants only burn and do not explode.
- However, burning proceeds violently and is accompanied by a flame or sparks.
- Propellants can be initiated by a flame or spark, and change from a solid to a gaseous state relatively slowly.
- Examples of these propellants include black powder, smokeless propellants, blasting explosives and ammonium nitrate.

CHAPTER 12 OBJECTIVES

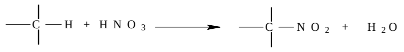
- CHEMICAL EXPLOSIVES
  - INTRODUCTION
  - DEVELOPMENT OF EXPLOSIVES
  - CLASSIFICATION OF EXPLOSIVES
  - CHEMISTRY OF EXPLOSIVES
- PROPELLANTS
  - GUN PROPELLANTS
  - ROCKET PROPELLANTS
- PYROTECHNICS

CHEMISTRY OF EXPLOSIVES

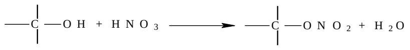
- Nitration represents a major chemical reaction that plays an essential role in the production of most explosives.
- A variety of nitrocompounds ranging from C-nitrocompounds such as TNT to N-nitrocompounds such as RDX and HMX to O-nitrocompounds such as trinitroglycerol are considered among the most energetic compounds.
- Nitration is an electrophilic reaction of addition of a nitro group to an organic compound with a nitrating agent.
- The introduction of the nitro group can take place onto a carbon atom (C-nitration) or oxygen atom (O-nitration) or nitrogen atom (N-nitration).

CHEMISTRY OF EXPLOSIVES

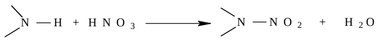
C-Nitration



O-Nitration



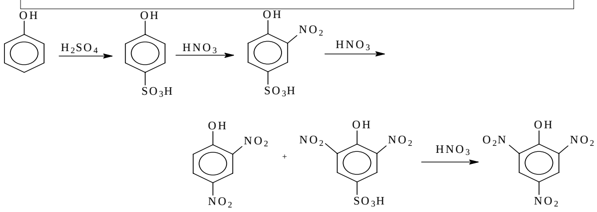
N-Nitration



- The nitrating agents for the manufacture of explosives via C-nitration, O-nitration, or N-nitration are mixtures of nitric and sulfuric acids.
- Except for RDX and HMX where a mixture of nitric acid and ammonium nitrate is used.

CHEMISTRY OF EXPLOSIVES C-Nitration

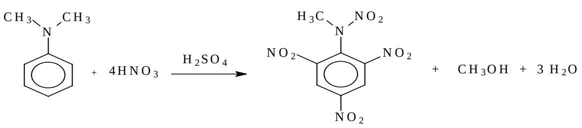
- Picric acid, **2**, can be synthesized by reacting phenol in sulfuric acid and then adding nitric acid.



2

CHEMISTRY OF EXPLOSIVES C-Nitration

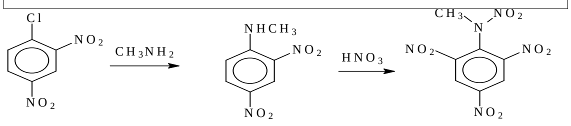
- Tetryl, **3**, can be prepared by reacting dimethylaniline [$C_6H_5N(CH_3)_2$] with sulfuric acid followed by the addition of a mixture of nitric acid and sulfuric acid .



3

CHEMISTRY OF EXPLOSIVES
C-Nitration

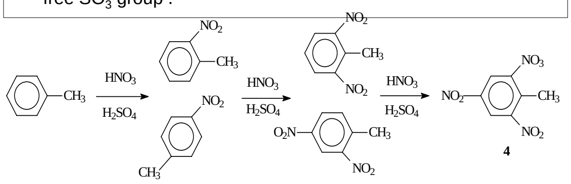
- In this reaction, one methyl group is oxidized and the benzene ring undergoes an electrophilic nitration in the 2-,4- and 6-positions.
- Another method for the synthesis of tetryl is the treatment of methylamine with 2,4-or 2,4-dinitrochlorobenzene to give dinitrophenylmethylamine. This later is then treated with nitric acid to tetryl.



3

CHEMISTRY OF EXPLOSIVES
C-Nitration

- TNT, 4, is produced by the nitration of toluene with a mixture of nitric and sulfuric acids.
- Toluene is first mononitrated and then dinitrated and finally crude trinitrotoluene (TNT) is produced by the trinitration step.
- This step requires a high concentration of mixed acids with a free SO_3 group .



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CHEMISTRY OF EXPLOSIVES
O-Nitration

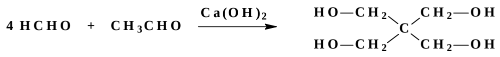
- Nitroglycerine, **1**, is an explosive prepared in a batch reactor or continuous process by mixing pure glycerine with a mixture of highly-concentrated sulfuric acids at a controlled temperature.

$$\begin{array}{l} CH_2\text{—}OH \\ CH\text{—}OH \\ CH_2\text{—}OH \end{array} + 3\,HNO_3 \xrightarrow{H_2SO_4} \begin{array}{l} CH_2\text{—}ONO_2 \\ CH\text{—}ONO_2 \\ CH_2\text{—}ONO_2 \end{array} + 3\,H_2O$$

1

CHEMISTRY OF EXPLOSIVES
O-Nitration

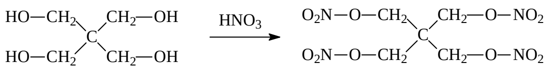
- PETN (Pentaerythritol tetranitrate), **6**, is an old explosive made from acetaldehyde and formaldehyde, which reacts by condensation under basic catalysis followed by a crossed Cannizaro reaction to produce pentaerythritol



Pentaerythritol

CHEMISTRY OF EXPLOSIVES
O-Nitration

- The nitration of pentaerythritol takes place by adding concentrated nitric acid at 25-30°C to produce PETN.
- PETN is not very soluble in nitric acid or water and is easily filtered from solution.
- PETN has been largely replaced by RDX, which is thermally more stable.



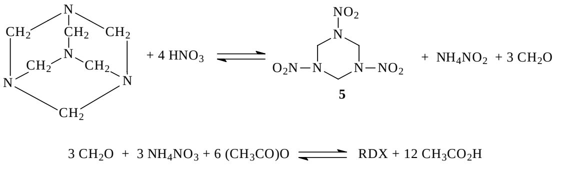
PETN, **6**

CHEMISTRY OF EXPLOSIVES
N-Nitration

- RDX, **5**, is a cyclic nitramine obtained by the nitration of hexamethylene tetramine (HMT) in the presence of an excess of concentrated nitric acid.
- RDX is formed by the nitration of the three outside nitrogen atoms of HMT with removal of the internal nitrogen and methylene ($-CH_2-$) groups.
- RDX is produced along with ammonium nitrate (NH_4NO_3) and formaldehyde (HCHO) as by-products. .

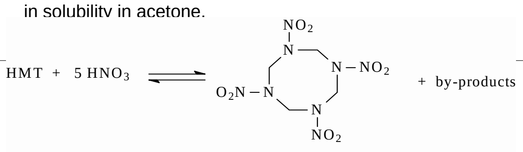
CHEMISTRY OF EXPLOSIVES
N-Nitration

- However, another molecule of RDX can be produced by adding NH_4NO_3, HCHO and acetic acid.



CHEMISTRY OF EXPLOSIVES
N-Nitration

- HMX, **18**, was identified as an impurity of the reaction of the production of RDX. HMX is an eight-membered ring which can be formed by adjusting the reaction conditions.
- The nitration of all four nitrogen atoms in HMT and the removal of two methylene groups.
- RDX, which is formed as a product of the reaction of formation of HMX, must be removed by alkaline hydrolysis or by a difference in solubility in acetone.



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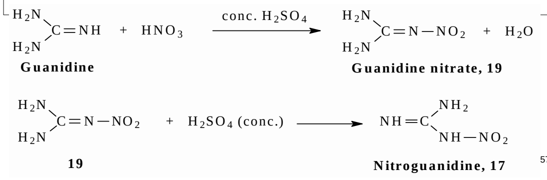
CHEMISTRY OF EXPLOSIVES
N-Nitration

- Nitroguanidine, **17**, is another aliphatic nitramine that is used as a major constituent in triple-base propellants.
- It exists in two crystalline forms, the a- and b-forms.
- The a -form of nitroguanidine, **17,** can be prepared by reacting guanidine nitrate in concentrated sulfuric acid followed by the addition of an excess of water from which guanidine nitrate, **19**, is crystallized.



CHAPTER 12
OBJECTIVES

- CHEMICAL EXPLOSIVES
  - INTRODUCTION
  - DEVELOPMENT OF EXPLOSIVES
  - CLASSIFICATION OF EXPLOSIVES
  - CHEMISTRY OF EXPLOSIVES
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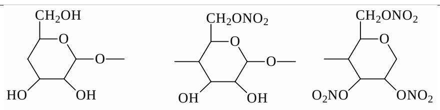
  - GUN PROPELLANTS
  - ROCKET PROPELLANTS
- PYROTECHNICS

PROPELLANTS
GUN PROPELLANTS

- Gun propellants, chemically similar to explosives, can burn but do not detonate.
- Propellants are not pure substances but mixtures of chemical compounds capable of producing large volumes of gas and they give off heat.
- They are mainly used in launching projectiles from guns, rockets, and missile systems. Propellants are divided into four different categories:
  - Single base
  - Double base
  - Triple base
  - Composite

PROPELLANTS
SINGLE-BASE PROPELLANTS

- Single-base propellants are essentially formed from pure nitrocellulose, which are produced from a cellulose monomer, **25**.
- Cellulose is produced industrially from cotton and wood pulp.
- The hydroxyl groups (-OH) in the cellulose are nitrated by a reaction with a mixture of nitric and sulfuric acids.
- The control of the degree of nitration of the single hydroxyl group on the side may produce mono nitrocellulose, **26**, or all hydroxyl groups forming nitrocellulose, **27**.



25 **26** **27**

PROPELLANTS
DOUBLE-BASE PROPELLANTS

- Double-base propellants are made of gelatinized or plasticized nitrocellulose with another liquid propellant or explosive.
- This second type of propellant is nitroglycerine. Other nitrate esters may be also used in place of nitroglycerine.
- Also, dinitrotoluene is used as the second component.
- The second propellant is intimately bonded to nitrocellulose and does not separate.
- The function of the second component is also to adjust the oxygen balance which affects the energy output and reaction temperature.
- The oxygen balance is also adjusted by the addition of inorganic oxidizers such as nitrates, perchlorates, or sulfates.

PROPELLANTS
TRIPLE-BASE PROPELLANTS

- A third energetic material such as nitroguanidine is added in the double-base propellants to reduce the muzzle flash, which is the result of a fuel-air explosion of the combustion products.
- The triple-base propellant is now formed of nitrocellulose, nitroglycerine and nitroguanidine.
- The nitroguanidine is added in 50% to the propellant composition in order to adjust the gas output, energy, temperature, and burning rate.
- Triple-base propellants are used in tank guns and large caliber guns.

PROPELLANTS
COMPOSITE PROPELLANTS

- A composite propellant represents a group of propellants in which the composites, the fuels, and the oxidizers are separated materials.
- This type of propellant has replaced the sensitive propellants, which suffer from the possibility of accidental initiation from fire, impact, electric spark and others.
- The composite propellants are used for rockets and for gas generators. The typical composite is a blend of a crystalline oxidizer and are amorphous or plastic fuel.

PROPELLANTS
COMPOSITE PROPELLANTS

- The typical composite propellant oxidizers are as follows:
  - Sodium nitrate $NaNO_3$
  - Potassium nitrate KNO_3
  - Ammonium nitrate NH_4NO_3
  - Ammonium perchlorate NH_4ClO_4
  - Potassium perchlorate $KClO_4$
  - Lithium perchlorate $LiClO_4$
- The fuel acts both as fuel and binder and it provides the mechanical strength and structural properties to the composite propellant.

PROPELLANTS
COMPOSITE PROPELLANTS

- The typical composite propellant fuels are as follows:
  - Asphalt Amorphous
  - Polyisobutylene Polymer, amorphous
  - Polysulfide rubber Polymer, thermosetting
  - Polyurethane rubber Polymer, thermosetting
  - Polybutadiene-acrylicco-polymer Polymer, thermosetting
  - Polyvinyl chloride Polymer, thermoplastic
  - Cellulose acetate Polymer, thermoplastic
- The oldest of the composite propellants is black powder, which is produced by mixing the ingredients wet and then wheel-milling them.

PROPELLANTS
COMPOSITE PROPELLANTS

Table 12.7. Example of additives used in gun propellants

Function	Additive	Action
Stabilizer	Carbamite (diphenyl diethyl urea), methyl centralite (diphenyl dimethyl urea), chalk and diphenylamine	Increase shelf life of propellant
Plasticizer	Dibutyl phthalate, carbamite and methyl centralite	Gelation of nitrocellulose
Coolant	Dibutyl phthalate, carbamite, methyl centralite and dinitrotoluene	Reduce the flame temperature
Surface moderant	Dibutyl phthalate, carbamite, methyl centralite and dinitrotoluene	Reduce burning rate of the grain surface

PROPELLANTS
COMPOSITE PROPELLANTS

Table 12.7. Example of additives used in gun propellants

Function	Additive	Action
Surface lubricant	Graphite	Improve flow characteristics
Flash inhibitor	Potassium sulfate, potassium nitrate, potassium aluminum fluoride and sodium cryolite	Reduce muzzle flash
Decoppering agent	Lead or tin foil, compounds containing lead or tin	Remove deposits of copper left by the driving band
Anti-wear	Titanium dioxide	Reduce erosion of gun barrel

CHAPTER 12 OBJECTIVES

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  - GUN PROPELLANTS
  - ROCKET PROPELLANTS
- PYROTECHNICS

PYROTECHNICS
SOUND PRODUCERS

- Sound-producing pyrotechnics are primarily used in the fireworks industry and in military simulators.
- There are two types of sound producers: a composition that produces a loud, short-duration sound, like a bomb or grenade, and a composition that produces a shrill whistle of long duration.
- The short loud bang producers are sometimes made of black powder that is heavily confined in a cardboard tube.

PYROTECHNICS
LIGHT PRODUCERS

- There are two subdivisions of light-producing pyrotechnics: flash powders and flares.
- The main difference in their performance is in the bulk burning rates. Flash powders burn very rapidly, some almost bordering on detonation velocities.
- The flash powders are generally loaded as loose or lightly pressed mixed dry powder. They are sometimes initiated by an ignitron and in some application by a detonator.
- In military tactical use, they are employed as lighting for night reconnaissance photography.

PYROTECHNICS
LIGHT PRODUCERS

- The majority of photoflash mixes use magnesium and/or aluminum as the fuel and barium nitrate and/or potassium perchlorate as the oxidizers.

  $$8\ Al + 3\ KClO_4 \rightarrow 4\ Al_2O_3 + 3\ KCl$$

  $$4\ Al + 3\ BaNO_3 \rightarrow 2\ Al_2O_3 + 3\ BaO + 1.5\ N_2$$

- Typical fuels are magnesium (sometimes mixed with aluminum), manganese, and silicon.
- Typical oxidizers include the nitrates of barium, sodium, potassium, and strontium.
- The chlorine and fluorine from the Teflon are the oxidizers in this mix. Magnesium/Teflon flares burn several hundred degrees (^oC) hotter than metal/salt flares and radiate very strongly in the infrared spectrum.

PYROTECHNICS
HEAT PRODUCERS

- Heat-producing pyrotechnics are used for ignition mixtures, thermites, sparks, and incendiaries and heat pellets for thermally activated batteries.
- The first ignition mixes are generally either metal/salt or metal/metal oxide mixes with no binders.
- The metal/salt mixtures are very sensitive to impact, flame (or a concentrated heat source such as a glowing hot wire), and sparks.
- The metal/metal oxide mixtures are not sensitive to impact, flame, or spark.

PYROTECHNICS
HEAT PRODUCERS

- Both types of mixtures are used as the “first fire” or the ignition element in a pyrotechnic train.
- Typical fuels are aluminum, zirconium, titanium, and titanium hydrides, and magnesium, boron, and in former times, beryllium.
- Typical oxidizers include the various nitrates already mentioned with the light producers, as well as calcium chromate, lead nitrate, iron oxides, copper oxide, and the perchlorates of sodium, potassium, and ammonia.

PYROTECHNICS
HEAT PRODUCERS

- A typical reaction of the metal/metal oxide type is the reduction/oxidation of aluminum mixed with copper oxide.

  $$2\ Al + 3\ CuO \rightarrow Al_2O_3 + 3\ Cu$$
- This reaction, where an oxide of one metal is reduced and the other metal is then oxidized, is the same reaction as in the thermites.
- These materials, generally a mixture of aluminum and iron oxide, produce molten iron as one of the products.

  $$2\ Al + Fe_2O_3 \rightarrow Al_2O_3 + 2\ Fe$$

  The molten iron is then the heat transfer medium that is used to perform the specific task of the thermite device, usually welding.
- Other fuels include nickel, and other oxidizers include Fe_3O_4 and Cu_2O.

PYROTECHNICS
SMOKE PRODUCERS

- These pyrotechnics are also subdivided into organic and inorganic types and can be made in a variety of colors and optical densities.
- The earliest organic smokes were droplets of kerosene that condensed from vapors produced smokes from boiling the kerosene.
- This smoke has the obvious drawback of being extremely flammable. The other organic smokes are quite different.
- They are aerosol droplets of condensed organic dyes that are vaporized out of a relatively low-temperature smoke.

PYROTECHNICS
SMOKE PRODUCERS

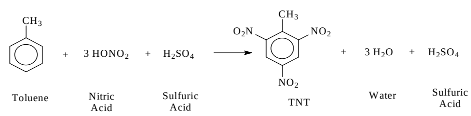
- The inorganic smokes are from reactions that produce zinc chloride as the major obscurant.
- These mixtures, called HC smokes, are a blend of aluminum powder, zinc oxide, hexachlorethane (HC), and sometimes a pinch or two of magnesium and ammonium perchlorate.
- At low percentages of aluminum, the major smoke products are Al_2O_3 and $ZnCl_2$ with CO.
- At higher aluminum concentrations the products form a grey, instead of white, smoke that consists of Al_2O_3, $ZnCl_2$ and carbon.

CHAPTER 12 OBJECTIVES

- MANUFACTURING OF EXPLOSIVES
  - TNT PRODUCTION
  - BLACK POWDER PRODUCTION
  - RDX AND HMX PRODUCTION
- CLASSIFICATION, TRANSPORTATION AND STORAGE OF EXPLOSIVES

MANUFACTURING OF EXPLOSIVES
TNT PRODUCTION

- TNT may be prepared by either a continuous or a batch process, using toluene, nitric acid (HNO_3) and sulfuric acid as raw materials.
- The production of TNT by nitration of toluene is a 3-stage process is performed in a series of reactors (Figure 12.6).



Equation 12.18

- The fresh 60% HNO_3 solution and the spent acid are fed into the first reactor along with toluene.

MANUFACTURING OF EXPLOSIVES
TNT PRODUCTION

- The organic layer is subjected to further nitration in the second reactor with fresh 60% HNO_3 and spent acid.
- The product obtained from the second reactor, is a mixture of all possible isomers including dinitrotoluene (DNT) as a major one.
- DNT is pumped into the third reactor and treated with a fresh feed of 97% HNO_3 and oleum (a solution of sulfur trioxide, **SO_3**, in anhydrous sulfuric acid).
- The resulting products from the third reactor include mainly 2,4,6-trinitritoluene (TNT). The crude TNT is purified by washing it with water to remove free acid.
- The TNT is then neutralized with soda ash and treated with a 16 percent aqueous sodium sulfite (Sellite) solution to remove contaminating isomers.

MANUFACTURING OF EXPLOSIVES
TNT PRODUCTION

- The wash water (yellow water) is recycled to the early nitration stages and the Sellite waste solution (red water), which is obtained from the purification process, is discharged directly as a liquid waste stream and then collected and sold or concentrated to a slurry and incinerated.
- The final TNT crystals are melted and passed through hot air dryers, where most of the water is evaporated.
- The dehydrated product is solidified, and the TNT flakes packaged for transfer to storage or loading area.

MANUFACTURING OF EXPLOSIVES
TNT PRODUCTION

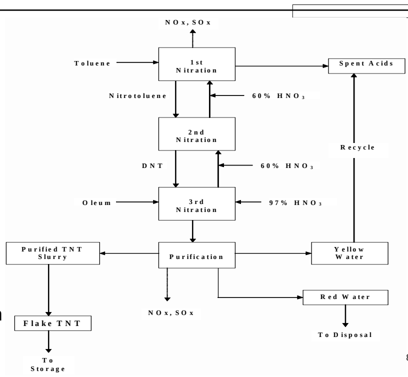


Figure 12.6: Nitration of toluene to form trinitrotoluene (TNT).

MANUFACTURING OF EXPLOSIVES
BLACK POWDER PRODUCTION

- Black powder is mainly used as an igniter for nitrocellulose gun propellants and to some extent in safety blasting fuses, delay fuses and in firecrackers.
- Potassium nitrate black powder (74 wt % plus 15.6 wt % carbon, 10.4 wt % sulfur) is used for military applications.
- The slower-burning, less costly, and more hygroscopic sodium nitrate black powder (71.0 wt % plus 16.5 wt % carbon, 12.5 wt % sulfur) is used industrially.

MANUFACTURING OF EXPLOSIVES
BLACK POWDER PRODUCTION

Component	Wt%
Gases	
Carbon dioxide	49
Carbon monoxide	12
Nitrogen	33
Hydrogen Sulfide	2.5
Methane	0.5
Water	1
Hydrogen	2
Total	**44**
Solids	
Potassium carbonate	61
Potassium sulfate	15
Potassium sulfide	14.3
Potassium thiocyanate	0.2
Potassium nitrate	0.3
Ammonium carbonate	0.1
Sulfur	9
Carbon	0.1
Total	**56**

Table 12.8. Approximate composition of reaction products of black powder.

MANUFACTURING OF EXPLOSIVES
RDX AND HMX PRODUCTION

- Both RDX and HMX are white, stable, crystalline solids. Both are much less toxic than TNT and may be handled with no physiological effect if appropriate precautions are taken to assure cleanliness of operations.
- Both RDX and HMX detonate to form mostly gaseous, low molecular weight products with little intermediate formation of solids.
- RDX has been stored for as long as ten months at 85ºC without perceptible deterioration.

MANUFACTURING OF EXPLOSIVES
RDX AND HMX PRODUCTION

- HMX is the highest energy solid explosive produced on a large scale, primarily for military use.
- It exists in four polymorphic forms of which the beta form is the least sensitive and most stable and the type required for military use.
- Both RDX and HMX are substantially desensitized by mixing with TNT to form cyclotols (with RDX) and octols (with HMX) or by coating with waxes, synthetic polymers, and elastomeric binders.

MANUFACTURING OF EXPLOSIVES
RDX AND HMX PRODUCTION

- The two most common processes for making RDX and HMX use hexamethylenetetramine (hexamine) as starting material.
- The Bachmann process, now used exclusively in the United States, is a simplification of a series of complex reactions.

$$C_6H_{12}N_4 + 4\,HNO_3 + 2\,NH_4NO_3 + 6\,(CH_3CO)_2O \longrightarrow 2\,RDX + 12\,CH_3COOH$$

MANUFACTURING OF EXPLOSIVES
RDX AND HMX PRODUCTION

- In the Bachmann process, the reactants are mixed, and the slurry aged to complete the reaction and increase the yield.
- The RDX-acetic acid slurry is filtered and water-washed and the spent acetic acid is processed for recovery. The RDX is recrystallized from cyclohexanone.
- In the Bachmann process an 80-84% yield is obtained, ca 10% of which is cyclotetramethylenetetranitramine (HMX).
- A modification of the Bachmann process used to make RDX with the same starting materials and in similar equipment is employed for the manufacture of HMX.

MANUFACTURING OF EXPLOSIVES
RDX AND HMX PRODUCTION

- The reaction temperature is lower (44 $\pm$ 1°C as compared to 68oC for RDX) and the raw materials are mixed in a two-step process.
- The yield of HMX per mole of hexamine is about 55-60%, as compared to 80-85% in the manufacture of RDX.
- A typical HMX batch process starts with a reactor which contains a heel of acetic acid. The proper amounts of hexamine in glacial acetic acid, ammonium nitrate in nitric acid, and acetic anhydride are added in stages.
- The HMX slurry is transferred to the aging tanks, held for 30 min at 44°C, and pumped to a simmer tank where sufficient dilution liquor is added to reduce the concentration to 80% acetic acid.

MANUFACTURING OF EXPLOSIVES
RDX AND HMX PRODUCTION

- After dilution the temperature is raised to 110°C, to decompose undesirable by-products and to improve the filtering characteristics of the HMX.
- The slurry is filtered at about 60oC to retain RDX in solution. The filtered product is almost 99% HMX.
- The crystals are washed with cold water and crystallized from acetone, cyclohexanone, or both, depending on the particle distribution desired.
- Recrystallization also converts the more sensitive alpha crystals to the higher density beta form and reduces occluded acid to less than 0.02%. The RDX is recovered from the spent acid which is reclaimed.

CHAPTER 12
OBJECTIVES

- MANUFACTURING OF EXPLOSIVES
  - TNT PRODUCTION
  - BLACK POWDER PRODUCTION
  - RDX AND HMX PRODUCTION
- THERMOCHEMISTRY OF EXPLOSIVES
  - OXYGEN BALANCE
  - HEAT OF FORMATION
  - HEAT OF EXPLOSION
  - EXPLOSIVE POWER AND POWER INDEX
- CLASSIFICATION, TRANSPORTATION AND STORAGE OF EXPLOSIVES

CLASSIFICATION, TRANSPORTATION AND STORAGE OF EXPLOSIVES

- The transportation of dangerous materials is regulated in order to prevent accidents to personnel and property.
- However, the regulations are designed so as not to impede the movement of dangerous materials other than those that are too dangerous to be accepted for transportation.
- The regulations are addressed to all modes of transport.
- It should be noted that the numerical order of the classes does not necessarily indicate the degree of danger the recommended definitions of hazard classes.

CLASSIFICATION, TRANSPORTATION AND STORAGE OF EXPLOSIVES

- The United Nations system (UNO) divides hazardous materials into nine classes for the purpose of determining the degree of risk in shipping and transport. The order and number of the class are not meant to imply the degree of risk or danger. These classes are as follows:
  - Class 1 – Explosives
  - Class 2 – Gasses
  - Class 3 – Flammable liquids
  - Class 4 – Flammable solids
  - Class 5 – Oxidizing substances, organic peroxides
  - Class 6 – Toxic and infectious substances
  - Class 7 – Radioactive materials
  - Class 8 – Corrosive substances
  - Class 9 – Miscellaneous dangerous substances and articles

CHAPTER 12 OBJECTIVES

- CHEMICAL EXPLOSIVES
  - INTRODUCTION
  - DEVELOPMENT OF EXPLOSIVES
  - CLASSIFICATION OF EXPLOSIVES
  - CHEMISTRY OF EXPLOSIVES
- PROPELLANTS
  - GUN PROPELLANTS
  - ROCKET PROPELLANTS
- PYROTECHNICS

CHAPTER 12
OBJECTIVES

- MANUFACTURING OF EXPLOSIVES
  - TNT PRODUCTION
  - BLACK POWDER PRODUCTION
  - RDX AND HMX PRODUCTION
- CLASSIFICATION, TRANSPORTATION AND STORAGE OF EXPLOSIVES