

## DEVELOPMENT OF EXPLOSIVES

### Development of Black powder

- Black powder also known as gun powder was most likely the 1st explosive composition.
- Black powder was not introduced in Europe until the 13<sup>th</sup> century. By the end of 13<sup>th</sup> century, many countries were using Black powder as military aid to breach walls of castles and cities.
- Black powder contains fuels and oxidizer, the fuel is powder mixture of charcoal and Sulphur which is mixed with KNO<sub>3</sub> oxidizer.
- Corned Black powder gradually came into use for small guns and hand grenades during 15<sup>th</sup> century. For big guns from 16<sup>th</sup> century.
- 1<sup>st</sup> recording to Black powder being used in civil engineering was during 1548-1572 for dredging the river Nieman.
- In England 1<sup>st</sup> use of Black powder was for blasting in Cornish copper mines in 1670.

### Development of Nitroglycerine

- In 1846 - the Italian professor Ascanio Sobrero discovered liquid Nitroglycerine  $C_3H_5O_3(N_2)_3$
- Swedish inventor Immanuel Nobel developed process for manufacturing nitroglycerine.
- In 1863 nitroglycerine was manufactured by mixing glycerol with mixture of nitric acid and sulphuric acid in strong jugs. The mixture was then stirred by hand and kept in ice water for cooling. After the reaction had gone to completion, the mixture was poured into excess of water.
- Alfred Nobel in 1864 invented the metal blasting cap detonator which greatly influenced the initiating power of black powder.
- The detonator contains mercury fulminate and was able to replace black powder for initiation of nitroglycerine in bore holes. The mercury fulminate in the blasting cap in an initial state which was transferred to separate container of Nitroglycerine via a fuse initiating the nitroglycerine.
- To reduce the sensitivity of nitroglycerine, Alfred mixed nitroglycerine with absorbent clay Kieselgur. This mixture was patented in 1867 and known as ghr dynamite.
- Nitroglycerine has got greater advantage as it contains both fuel and oxidizer in the same molecule.

### Development of Mercury fulminate

- Mercury fulminate was prepared in 17<sup>th</sup> century by a Swedish German alchemist Johann Kunckel von Löwenstern.
- Mercury fulminate is prepared by treating mercury with nitric acid and alcohol.
- Edward Howard between 1799 and 1860.
- Howard examined the property of mercury fulminate and proposed its use as a percussion initiator of black powder
- *Scottish Alexander Forsyth patented mercury fulminate percussion in 1807.*

### Development of nitrocellulose

- In 1833 French chemist Henri Braconnot held nitrated starch. In 1838 he also nitrated paper, cotton & various other materials. But he did not realize that he had prepared nitrocellulose.
- Nitrocellulose was not used in military and commercial explosives until 1868. When, with the assistance of E.A. Brown, discovered dry compressed highly nitrated nitrocellulose could be detonated using mercury fulminate detonator. And wet compressed nitrocellulose could be exploded by a small quantity of dry nitrocellulose. Thus large blocks of wet nitrocellulose could be used with comparative safety.

### Development of dynamite

- In 1875 Alfred Nobel discovered that on mixing nitroglycerine with nitrocellulose resulted in the formation of gel. This gel was developed to produce blasting gelatin. Gelatin dynamite and later in 1888 smokeless powder (ballistite) is basically a mixture of nitrocellulose, nitroglycerine and camphor benzene. Later in 1889 a similar composition to ballistite was patented by the British government as cordite.
- In 1867 Swedish chemist Ahlström and Morbihan found that explosive property of dynamite is enhanced by the addition of ammonium nitrate.

### Development of Ammonium nitrate

- First prepared in 1659 by Johann Rudolf Glauber in explosive property reports.

### Development of commercial explosives and permitted explosive

- Until 1870 black powder was only explosive used in coal mining and many attempts were made to modify black powder by mixing it with cooling agent such as starch, paraffin.
- When nitroglycerine and nitrocellulose were invented attempts were made to use these in coal mines instead of black powder but they were not found to be suitable in gaseous coal mines. Dynamite and blasting gelatin (nitroglycerine based explosive) began to dominate commercial blasting and mining industries.
- A testing was conducted in 1880 at Jaisén Kurchen in Germany in order to test the newly developed explosives. After explosion with various explosives the use of several explosive materials was recommended, mostly based on ammonium nitrate. Explosive which passed the test work all permitted explosives.

### Development of ANFO explosive

- In year 1913 92% of explosives used were ammonium nitrate (British). In order to reduce the cost, the composition of explosives were changed by adding cheaper compositions. Ammonium nitrate to the formulation which had side effect of reducing the explosive water proofness and this was significant problems because mines and quarries were often wet and holes drilled to take the explosive regularly filled with water the problem was over. Ammonium nitrate with various composition with dynamite and by improving the packaging of explosive with water in gases.

- Dupont begin adding point grade 'A' and monomethylamine nitrate. This formulation which could detonate easily in recent development. Emulsion explosive which contains droplet of solution in ammonium nitrate in oil.
- This emulsion are waterproof in continuous phase is mixed with which cause readily detonate since the ammonium nitrate and oil are in close contact.
- Safer than dynamite simple and cheap to manufacture.

#### Development of military explosive

- Picric acid (2,4,6-trinitrophenol)  $C_6H_3N_3O_7$  it was suitable for replacement of black powder in 1885.
- Ernest designolle and burger suggested picrate salt used as propellant. It was replaced with black powder for filling and became one of the most common explosive for military purpose
- Picric acid was a problem in water and resulted into corrosion of the cells. It is quite sensitive and prone to accidental initiation and picric acid require prolong heating in order to melt.

#### Development of tetryl

- 1<sup>st</sup> prepared in 1877 by marten and was used as an explosive in 1906 , also used as base charge for blasting caps.

#### Development of TNT ( $C_7H_5N_3O_6$ )

- It was first prepared by Julius wilbrand in 1863, manufacture of TNT began in Germany. By 1914 TNT became standard for all army.
- Production of TNT was limited by availability of TNT. The mixture of Ammonium nitrate and TNT and ammatol ( PETN+ TNT + pentolite ). Underwater explosive used the same formulation with addition of aluminum was called ammonal.

#### Development o PETN

- 1<sup>st</sup> prepared in 1894 by nitration of pentaerythritol. RDX was more utilized than TNT because PETN was more sensitive to impact and chemical stability was poor.

#### *Most common solvent acetone for reconstitution*

- Explosive containing 50% TNT and 50% PETN pentolite was used for filling hand grenades and detonator used as booster.
- Most stable and least reactive, insoluble in water, sparingly soluble in alcohol, ether and benzene, soluble in acetone and methylacetete, shows no decomposition when stored for long time at 100 degrees Celsius relatively insensitive to friction and very sensitive to initiation by primary explosive.
- Powerful secondary explosive has greater shattering effect
- Detonation cord and boosters
- also mixed with plasticizer nitrocellulose with synthetic polymer to polymer bounded explosive.
- Also be used as gelatin industrial explosive or in form of rubber like sheep using metal forming metal cladding process.

## Properties of TNT

- Insoluble in water, sparingly soluble in alcohol and soluble in benzene, toluene and acetone
- It will darken in sunlight and unstable in alkalines and amine
- pale yellow crystalline solid
- low manufacturing cost, cheap raw material, safety about handling, low sensitivity to impact, good thermal stability, low volatility, hygroscopic, good compatibility, low melting point for casting.
- Most important for blasting charges
- Widely used as commercial explosive and much safer than Nitroglycerine and picric acid can be loaded into shell by casting or by pressing.
- TNT + AMMONIUM NITRATE - AMMATOL
- Tetryl is also known as 2,4,6-trinitrophenyl-n methylnitramine.
- Pale yellow crystalline solid
- Melting point 129 degrees Celsius,
- Moderately sensitive to initiation by friction, used in the form of pressed pellets as primer. For example composition which is less sensitive to initiation it is toxic to handle.

## Nitroguanidine

- First prepared by Jouzel in 1877
- Nitro guanidine mixed with nitrocellulose was used as flashless propellant
- In 1937 appropriate composition was developed containing Nitroguanidine which produce less more destruction and had no evidence of flash and firing an increase the life line of gun barrel.
- Also known as picrite -  $\text{CH}_4\text{N}_4\text{O}_2$

## RDX

- 1,3,5-Trinitroperhydro-1,3,5-triazine
- RDX is light crystalline solid, melting point is 204 degrees Celsius
- Crystal with polymeric matrix are known as polymer bounded and less sensitive to accidental initiation
- RDX has chemical stability and great explosive power when compared to TNT and picric acid.
- Difficult to dissolve in organic liquid but it is recrystallizable
- High melting point
- Potato impact RDX is very sensitive to impact

## HMX

- octogen and cyclotetramethylene-tetranitramine  $\text{C}_4\text{H}_8\text{N}_8\text{O}_8$
- White crystalline solid substance which appears to have different crystalline form.
- Different from one another in density and sensitiveness to impact
- B form is least sensitive to impact
- HMX is non hygroscopic and insoluble in water, more resistance to attack.

- Soluble in 55% nitric acid and two Nitro propane.
- Solution was poured into water precipitant was obtained
- Relatively soluble below its melting point , decomposition on melting to form ammonia, water vapour solid products, solid in hot water and alkalise and insoluble in ether and cold water.
- It has High velocity of Detonation and high density
- Disadvantages – after explosion corrosive and toxic

#### Development of RDX and HMX

- First prepared in 1899 by the German for medicinal use.
- The bachman product one known as type B RDX which contain a constant impurity level of 8.12%.
- the explosive property of this were utilise and HMX known as octogen was developed.
- In World War Two RDX became one of the most powerful explosive.
- Composition of TNT and RDX is known as torpex.