CHAPTER – I

INTRODUCTION
1.1 EXPLOSIVES – DEFINITION:

An explosive is a substance, individually or mixed with another, which is in metastable state and is capable for this reason, of undergoing a rapid chemical reaction, without the participation of external reactants, such as atmospheric oxygen, to produce huge quantity of gas under high pressure. The gas is produced so rapidly under certain condition that the surroundings are subjected to a strong dynamic stress accompanied by heat, light and sound (1). The explosive can be either in the gaseous or in the condensed form; for example a mixture of hydrogen and oxygen or air in various proportions form an explosive, in a similar manner a number of other combustible gases like methane, ethane, petroleum vapour etc. can form explosive mixtures with air, oxygen or other oxidizing gases. Among condensed explosives, we have a few liquid explosives like nitroglycerine; dinitroglycol etc. and the rest of all the explosives are solids. Almost all of them contain nitrogen in combined form, the bulk of them being nitro derivatives of organic compounds.

To be classified as an explosive, a material must satisfy basic conditions with respect to its rate of chemical reaction: the reaction must not take place until a suitable initiation stimulus is applied; the reaction must be violent; there must be complete or nearly complete conversion into gaseous products; the reaction must be exothermic and self sustaining without requirement for an external source or energy. The pressure produced by an explosion is due to the gases evolved and is
dependent on their volume and temperature. The work potential of an explosive depends primarily upon the quantity of heat given off in the reaction (2).

1.2 HISTORICAL DEVELOPMENT:

Gunpowder was undoubtedly the first explosive recorded in a Chinese manuscript, around 1000 A.D (3). Gunpowder is an intimate mixture of potassium nitrate, charcoal and sulphur. This was used for military purposes and for other blasting purposes and is still being used as such for lack of better substitute. In the late 17th and 18th centuries a number of explosives were discovered with a wide range of properties and power (4).

Ammonium nitrate (A.N) was prepared by J. Glauber in 1654. In 1840 Reise and Millon reported that a mixture of powdered ammonium nitrate and charcoal exploded on heating to 170°C. Thus during World War I ammonium nitrate found extensive application as an ingredient in explosive compositions (5).

Mercury fulminate was discovered in 1888 by Howard and was found to be of relatively low power; it detonated when ignited by a flame and was very sensitive and unstable (4).

Nitrocellulose was discovered in the period 1833 to 1846, but its development and use was delayed for long because of difficulties in obtaining a stable product (4). In 1847 Sobero discovered Nitroglycerine which attained commercial importance, though the dangers of making nitroglycerine a commercially useful material by inventing first, the guhr dynamite using Kiesolguhr (diatomaceous earth) and later
blasting gelatin, both of which were safe and highly powerful detonating explosives (4).

Trinitrotoluene (TNT) was discovered in 1863 by Wilbrand and was found to be very safe to handle in solid state. Trinitrotoluene was very widely used during World War I, because of its low melting point (80.2°C). It could be easily casted in bombs, shells etc. (4).

A number of other explosive like tetryl-trinitophenylmethyl-nitramine (1879), lead azide (1891), PETN-Pentaerythritol tetranitrate (1895), RDX-cyclotrimethyleneetrinitramine (1899), Tetrazene (1910) and HMX- Cyclotetramethylene Tetranitramine (1943) were discovered later on (6).

Prior and during the World War II many explosive compositions were formulated. The compositions consisted of different high explosives with or without inorganic elements or salts mixed in different proportion.

Some of the compositions (7) are

<table>
<thead>
<tr>
<th>Composition</th>
<th>Proportion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tritonal</td>
<td>80/20</td>
</tr>
<tr>
<td>Cyclotol</td>
<td>60/40</td>
</tr>
<tr>
<td>Minol II</td>
<td>40/40/20</td>
</tr>
<tr>
<td>Torpex II</td>
<td>42/40/18</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Proportion</th>
</tr>
</thead>
<tbody>
<tr>
<td>TNT/Al</td>
</tr>
<tr>
<td>RDX/TNT</td>
</tr>
<tr>
<td>TNT/RDX/AN</td>
</tr>
<tr>
<td>RDX/TNT/Al</td>
</tr>
</tbody>
</table>

Various milestones in explosives development are shown in Table-1.1 (8)
Table – 1.1
Milestone in Explosives Development.

<table>
<thead>
<tr>
<th>Year</th>
<th>Milestone</th>
</tr>
</thead>
<tbody>
<tr>
<td>1654</td>
<td>Ammonium nitrate (A.N) was prepared by J. Glauber</td>
</tr>
<tr>
<td>1840</td>
<td>A mixture of Ammonium nitrate and charcoal exploded on heating to 170° C - reported by Reise and Millon</td>
</tr>
<tr>
<td>1841</td>
<td>Ammonium picrate (Explosive D) first prepared by Marchand.</td>
</tr>
<tr>
<td>1833 to 1846</td>
<td>Nitrocellulose was discovered, but its development was delayed for long because of difficulties in obtaining a stable product.</td>
</tr>
<tr>
<td>1847</td>
<td>Nitroglycerine was discovered by Sobero.</td>
</tr>
<tr>
<td>1863</td>
<td>T.N.T was discovered by Wilbrand.</td>
</tr>
<tr>
<td>1877</td>
<td>Tetryl was first prepared by Mertens.</td>
</tr>
<tr>
<td>1888</td>
<td>Ammonium picrate patented as an explosive by Noble.</td>
</tr>
<tr>
<td>1891</td>
<td>Lead azide was discovered.</td>
</tr>
<tr>
<td>1895</td>
<td>Pentaerythritol tetranitrate (PETN) was discovered.</td>
</tr>
<tr>
<td>1899</td>
<td>RDX was prepared by Henning. Use of aluminium in explosives to increase power proposed by Escales (German patent – 1900; U.S Patent 1911).</td>
</tr>
<tr>
<td>1901</td>
<td>Explosive D used by U.S Army as an explosive fill for projectiles.</td>
</tr>
<tr>
<td>1902</td>
<td>Germans adopt TNT as standard filling for projectile.</td>
</tr>
<tr>
<td>1907</td>
<td>Explosive D adopted by U.S Navy as projectile fill. (Dual charge of explosive D / black powder)</td>
</tr>
<tr>
<td>1910</td>
<td>Tetrazene was discovered.</td>
</tr>
<tr>
<td>1914</td>
<td>Tetryl first used as an explosive.</td>
</tr>
</tbody>
</table>
Table – 1. 1 (continued)
Milestone in Explosives Development.

<table>
<thead>
<tr>
<th>Year</th>
<th>Milestone</th>
</tr>
</thead>
<tbody>
<tr>
<td>1918</td>
<td>German studies indicate 15% to 20% Aluminium addition to explosive increases underwater power.</td>
</tr>
<tr>
<td>1920</td>
<td>Von Herz discovered RDX value as an explosive.</td>
</tr>
<tr>
<td>1920 to 1930</td>
<td>Composition B developed by British.</td>
</tr>
<tr>
<td>1936</td>
<td>Germans adopt Trialene (RDX / AL / TNT) explosives.</td>
</tr>
<tr>
<td>1939</td>
<td>RDX first used on large scale.</td>
</tr>
<tr>
<td>1940’s</td>
<td>Composition B used by U.S.</td>
</tr>
<tr>
<td>1940’s</td>
<td>Composition A (RDX / bees wax = 91/9 ) used by British.</td>
</tr>
<tr>
<td>1941</td>
<td>British use Torpex (RDX / TNT / Aluminium).</td>
</tr>
<tr>
<td>1942</td>
<td>Torpex – II in use by U.S Navy.</td>
</tr>
<tr>
<td>1943</td>
<td>Cyclotetramethylene tetra nitrate (HMX) was discovered.</td>
</tr>
<tr>
<td>1943–1944</td>
<td>Nine accidents involving Torpex–II.</td>
</tr>
<tr>
<td>1945</td>
<td>Tritonal (TNT / aluminium = 80 / 20) used in U.S.</td>
</tr>
<tr>
<td>1945</td>
<td>HB X – 1 first loaded into production weapons.</td>
</tr>
<tr>
<td>1940s</td>
<td>HBXs (RDX / TNT / aluminium / wax) developed.</td>
</tr>
<tr>
<td>1952</td>
<td>Early PBX (RDX / Polystyrene / DOP) developed.</td>
</tr>
<tr>
<td>1956</td>
<td>H – 6 adopted by Navy as fill for Mk 80 bombs.</td>
</tr>
</tbody>
</table>
1960 onwards Keeping the future requirements in mind, newer high energy materials having velocity of detonation (VOD) of more than 9500 m/s and density greater than 2g/c.c, detonation pressure 40 G.Pa, and thermal stability higher than 350°C are being synthesized for military and civilian applications, including stage separation of space vehicle, cutting of outer casing of warheads, and canopy severance system etc. (9-17) e.g. DATB, TATB, HNS, DAHNS, TATO, PATO, SDATO, HNAB, HNTCAB, DIPAM, PYX, TACOT, DPO, TPM, NONA, 5,7-diamino-4,6 dinitro benzofuroxan , TNGU, Tetranitro-propane diurea , 1,3,5,5-tetra-nitro hexa-hydro pyrimidine (DNMC), 2,4,6,8,10,12 - hexanitro - 2,4,6,8,10,12 - hexaazatri - cyclo (7.3.0.0) dodecan - 5,11-dione (HHTDD ), CL-14 (5,7- diamino-4,6- dinitrobenzofuroxan), CL-20.

By late 1950s sufficient evidence had been accumulated indicating that possible improvements in explosive science could be achieved with the use of plastic binders. In the early 1960s the first plastic-bonded explosives (PBXs) were introduced (8) and a series of PBXs like PBXN - 3 (1960), PBXN - 4 (1963), PBXN - 5 (1963), PBXN - 301 (1975), PBXN - 7 (1989) were approved for fleet use later on and the development works of series of PBXs like PBXN - 101 /102 (1962), PBXN - 103 (1962), PBXN - 6 (1972), PBX (AF)-108 (1974) were completed. PBXN - 106 was approved for use in projectile in 1975. PBXN - 103 was approved for use in MK - 46 torpedos by
1970 and PBXN - 105 were approved for use in the MK-48 torpedo in 1972. PBXN - 110 was approved for use in Navy warhead in the year 1989.

Employing new ingredients can change the optimisation between vulnerability and performance. The third generation PBXs based on energetic binders and novel species, are being researched. This is shown schematically in Fig 1.1 (18).

Fig: 1.1 EXPLOSIVE - PERFORMANCE VERSES SAFETY
1.2.1 CLASSES OF EXPLOSIVES:

According to their chemical reaction rate and resulting output characteristics, explosives are classified as low explosives and high explosives. Low explosives, which deflagrate (burn) rather than detonate and propagate at velocities 1000 meters per second (m/s) and less, include the propellants, pyrotechnics and initiating or primer explosives. Examples are nitrocellulose, double base powder (NC/NG), black powder, cordite and the metal-oxidizer mixtures.

Explosives, which detonate and propagate at velocities greater than 1000 m/s, are high explosives and include the secondary explosives RDX, HMX, HNS, DIPAM, Tetryl, DATB, TATB, PETN, TNT and the primary explosives lead azide and lead styphnate.

Explosions damage the targets due to blast, high-speed fragments, heat and flame. Explosives are used for constructive as well as destructive purposes both for military and civil applications.

1.3 BLAST EFFECTS

When an explosive is detonated, destruction occurs at much greater distances due to the air-blast. The pressure developed is accompanied by an explosion wave and at appreciable distances from the point of detonation; this wave is primarily responsible for structural damage. In consequence, walls of buildings struck by a blast wave tend to fall out towards the center of the explosion.

When an explosive is detonated, the denotation wave leaves the explosive product gases at an extremely high pressure and
in a state of motion. As the explosion products begin to expand, the pressure at the interface separating them from the exterior medium falls rapidly. An intense pressure wave is propagated outward in the exterior medium and an outward flow of the medium results. A compression wave of finite amplitude always propagates as a shock wave at a velocity that is greater than the velocity of sound in the undisturbed medium and which depends upon the amplitude of the wave. The shock is characterized by a very rapid increase in pressure instantaneously so that the leading edge of the shock wave can be regarded a mathematical discontinuity. The shock wave in air generated by an explosive charge is often called the blast wave (19).

A theoretical treatment of an ideal blast wave has been given by Baker (20).

For sometime after the explosion the gauge records ambient pressure Po (see Fig.1.2). At arrival time to the pressure rises quite abruptly (discontinuously in an ideal wave) to a peak value Ps + Po. The pressure then decays to ambient in total time ta+T drops to a partial vacuum of amplitude Ps and eventually returns to Po in total time ta+T+ + T+.
The quantity Ps+ is usually termed the peak overpressure. The portion of time history above initial ambient pressure is called the positive phase of duration $T^+$, that portion below $P_o$ of amplitude $P_s$ and duration $T^-$ is called the negative phase. Positive and negative impulses are defined by

$$I_{s^+} = ta^{ta+T^+} (P(t)-P_0) \, dt \quad ta^{ta+T^+}(P(t)-P_0) \, dt$$

And

$$I_{s^-} = ta^{a+T^+}\, dt$$

respectively are also significant blast wave parameters.

As the shock wave propagates away from the generating explosive charge, its peak pressure decreases. The shock wave decay can be attributed to two causes.

i) If the shock wave is not planer, the decay is due to geometrical divergence.
ii) Because of the finite entropy increment across the shock front, the decay is due to progressive dissipation of energy in the shocked air in accordance with the requirement of the second law of thermodynamics.

1.4 METAL LOADED SECONDARY HIGH EXPLOSIVES

Metals have typical combustion behaviour, which depend on thermo-chemical characteristics as well as the physical properties like ratio of molar volume and coefficient of thermal expansion of the solid metal/metal oxide and solubility of metal oxide in molten metal. Li and Mg having relatively low boiling points (1620 and 1381K) are considered volatile and always burn in the vapour phase. However Al, Be, Zr and Ti, are basically non-volatile because of high boiling point (2740, 2750, 4650, 3550 °K respectively.) In case of Al and Be, an oxide layer formed on the metal surface serves as an effective barrier to mass diffusion of reactants and energy transfer due to low solubility of metal oxides in molten metals. Thus, their combustion is impeded till the boiling point of metal or melting point of metal oxides (2318/2823 °K) is realized. As a consequence, the requirement for Al and Be ignition and combustion are much more severe than for Mg. In case of Zr and Ti, the molten oxide has high solubility in the molten metal (melting point: 1950 and 2125 °K). Consequently, burning may proceed by diffusion of the metal to the surface through the oxide layer. Combustion process of B is basically a surface phenomenon because boiling point of its oxide (2520 °K) is much lower than that of B (3950 °K). The surface oxidation reaction is limited by the rate of diffusion of oxidizing species through the oxide layer at a temperature lower than the boiling
point of the oxide layer. At higher temperatures, the diffusion of oxide vapour away from the particle facilitates the infusion of fresh oxygen.

When Al particles are heated in a hot stage microscope, they exhibit thermal expansion when melting point of the metal is reached. On continued heating in an inert atmosphere, molten Al withdraws from oxide skin and coalesces into large “agglomerates”. In an oxidizing atmosphere, the particles sinter together and agglomerate only moderately. On attainment of about 2500 °K, molten oxide retracts the surface and a detached flame envelope is formed. Aluminium vapour flows out and reacts to form Al₂O₃ in droplet form (typically <2 μm diameter). “Residual” oxide produces coarse particles in the product cloud emerging from burning Aluminium. The addition of combustibles (like metal powders Zn, Mg, Al, Si, Calcium silicide etc.) to an explosive, burns with very great evolution of heat and is advantageous in-spite of the fact that the oxygen balance is impaired. The heat of explosion so obtained is very great and the temperature of the explosion products is very high (21).

1.4.1 ALUMINIZED EXPLOSIVES

The CHNO type of explosives containing carbon, hydrogen, nitrogen and oxygen undergo a decomposition reaction followed by reduction-oxidation reactions which eventually leads to low molecular weight but stable detonation products such as CO₂, CO, H₂O, N₂ and solid carbon.

The addition of Aluminum increases the performance of explosives as brought out by Roth (22). Muraour (23) and
Stettbacher (24) investigated the action of Aluminium in explosives. Aluminum added to the explosive does not take part in the actual reaction, but reacts immediately afterwards with the products of explosion such as CO₂, CO and H₂O

(I) \[ 2\text{Al} + 3\text{CO} = \text{Al}_2\text{O}_3 + 3\text{C} + 299 \text{ Kcal/mol} \]

(II) \[ 2\text{Al} + \text{CO}_2 = \text{Al}_2\text{O}_3 + 3\text{CO} + 196\text{Kcal/mol} \]

(III) \[ 2\text{Al} + 3\text{H}_2\text{O} = \text{Al}_2\text{O}_3 + 3\text{H}_2 + 226 \text{ Kcal/mol}. \]

The large amounts of heat liberated by these secondary reactions maintain a high pressure of explosion for longer duration, than with explosives without Aluminum. The Aluminum oxide (Al₂O₃) formed during the reaction does not remain as a solid but vaporizes, thus increasing the overall volume of gases and the pressure. These increases are due to the fact that the boiling point of Al₂O₃ is only 2900 °C while the temperature developed on explosion of high explosive is usually above 4500 °C.

Li Shufen et al. (25) have investigated the thermodynamic and kinetic behaviour of Aluminum oxidation in nitramine propellant. Nitrogen oxide such as N₂O, NO, NO₂ etc. are excellent oxidizers at high temperature and due to their high concentration in the gas phase, they oxidize the Aluminum at higher temperatures.

The authors from their semi empirical quantum mechanism calculations have further confirmed that reactions between Al and Nitrogen oxides are feasible in that there exits no high-energy barrier on their reaction paths.

Kubota (26) measured the primary chemical components in the preparation zone of burning propellant containing 80% HMX at 20 atm. He obtained: 20.9% NO; 6.8% N₂O; 9.8% N₂; 18.1%
CO; 7.3% CO₂; 6.7% H₂ and some hydrocarbon fragments. This indicates that in the combustion of nitramine propellant, nitrogen oxides have high concentration in combustion products. In such a condition, the reaction between Aluminum and Nitrogen oxide is capable of oxidizing Al to Al₂O₃.

1.4.2 DAMAGE POTENTIAL (20)

The damage performance of an explosive is related to the available energy (27). The blast impulse is proportional to the square root of the available energy. Detonation of high explosives produces a large amount of chemical energy and gases at high temperature in a small volume of the order of original condensed explosives. The adiabatic expansion of the product gases does work on the surrounding medium. The amount of work done up to the time the gases expand to the ambient pressure is called the available energy. The available energy is given by

\[ A = \int_{V_0}^{V_1} p \, dv = E_I - E_0 \]

Where \( V_1 \) is the initial volume of the gaseous products after detonation and \( V_0 \) is the final volume at ambient pressure.

Thus by evaluating \( E_I \) and \( E_0 \), one can calculate the available energy of a given explosive. To evaluate \( E_I \) and \( E_0 \) we must know the products of detonation and the suitable equation of state. The detonation reaction being extremely rapid, the products usually do not confirm to the equilibrium configuration. Equilibrium even if established will continually shift during the subsequent expansion where the pressure and temperature change rapidly. In the case of oxygen deficient
explosives, burning of products in air after the explosion may add significant amount of energy for explosives metallic additives like Aluminium. It is generally assumed that during the detonation the additives react endothermically, and release energy in the later stage reaction during the expansion.

The available energy is equal to the difference between the heat of explosion and the heat left in the products after expansion to a pressure of one atmosphere. Simplified procedures have been evolved on the basis of constant product constitution. Those involve assumptions regarding assignment of oxygen to the different products such as CO, H$_2$O, CO$_2$, CH$_2$, N$_2$ and metallic oxides. The available oxygen is assigned to these products according to some arbitrary scheme of priorities, thus producing known quantities of products. The energy evolved or the heat of explosion is the difference between the sum of the energies of formation of the products and that of the original explosive composition.

**ALUMINIZED EXPLOSIVE COMPOSITIONS**

The possible detonation products of aluminized high explosives are Al$_2$O (g), AIO (g) and Al$_2$O$_3$ (g) and other gaseous products like CO, CO$_2$, N$_2$, and H2 etc. (g = gas, c = condensed). For the purpose of calculations, it has been assumed that the only Aluminum compound formed in the final detonation products is Al$_2$O$_3$, if the ratio by weight of Aluminum to explosive is m (say), the new mixed formula for the exploding compound becomes (28)

$$C_xH_yO_zN_w + \left(\frac{m}{27} \times M\right) \text{Al}$$

where

$$M = 12x + y + 16z + 14w$$
The oxygen present is first allotted to oxidize Aluminium completely and then carbon the carbon monoxide. The equation of decomposition can then be written as
\[ C_{x}H_{y}O_{z}N_{w} + \left(\frac{m}{27} \text{ M}\right) \text{Al} = \frac{1}{2} \left(\frac{m}{27} \text{ M}\right) \text{Al}_{2}O_{3} + \left(\frac{z-m}{18} \text{ M}\right) \text{CO} + \]
\[ \left(\frac{x-z+m}{18} \text{ M}\right) \text{camp} + \frac{y}{2}H_{2} + \frac{w}{2}N_{2} \]

1.5 SENSITIVITY ASPECTS OF SECONDARY EXPLOSIVES (8)

The explosives must be insensitive over its life cycle. Therefore, it must be either insensitive as is (for a specific application), or should be desensitized. In addition the explosive material must flow during manufacture and in its end-use form, the explosive must maintain its physical integrity over its life cycle.

Some of the major characteristics that must be possessed by military explosives include.

- Ease of manufacture.
- Chemical and thermal stability and physical integrity of the explosive charge over a temperature range from -40°C to 70°C for a minimum 15 years.
- The ability to function immediately (in some cases, within a few seconds or less) in a warhead.
- Insensitivity, with good vulnerability characteristics.
- High-performance characteristics.
INSENSITIVE EXPLOSIVES

The desire to acquire insensitive explosives to reduce both accidents and ordnance vulnerability to enemy attack has motivated the development of PBX technology. In plastic-bonded explosives various polymers of different nature and composition are used as binders (29). It is also possible to use plastic binders that participate in detonative reaction themselves. The plastic-bonded high explosives have much better mechanical and thermal properties than the TNT-based conventional high explosive charges. Polymeric materials that are used as binders can withstand much higher compressive and tensile load and correspondingly have higher compression and elongation values than the brittle TNT. Moreover, the temperature range in which TNT bonded high explosive charges can be used is limited by melting of TNT, which is at about 80°C. Elevated temperature requirements for some specific applications can be met only by plastic-bonded high explosive charges. Conventional explosives, based on RDX/TNT or HMX/TNT, have disadvantages of poor mechanical properties, poor adhesion to metal, higher percentage of shrinkage after melt casting and sensitive. Therefore, the work on plastic-bonded explosives (PBX) is being carried out to eliminate the above shortcomings (9).

1.6 ADVANTAGES OF PBXS:

- Reduced susceptibility to sympathetic detonation.
- Possible decrease in mechanical impact sensitivity because of elastomeric mechanical properties.
- Physical thermal stability to 150°C.
• Many exhibit minimal or negligible shrinkage after curing.
• Improved mechanical properties result in resistance to cracking.
• Improved cook-off behavior when subjected to fuel fires with reduced probability of violent reaction.
• Increased shelf life.

1.6.1 DISADVANTAGES OF PBXS:
• Difficult to boil out/ remove from the munitions.
• Comparatively higher percentage of RDX or HMX is required in PBX formulation for achieving same level of performance.

1.6.2 CLASSIFICATION AND PROCESSING OF PBXS
Depending upon the caliber of weapon, particle size of explosive and quantity involved, the processing of PBX is performed by pressing or casting or extrusion or injection molding techniques and PBX are classified according to their manufacturing method as pressed PBXs, cast able PBXs, extruded PBXs and injection moldable PBXs respectively. For each class of PBX separate code number is (8) assigned depending on its method of manufacture.
### PRESSING TECHNIQUES:

Usually these techniques are used for higher content explosive composition. PBX charges are manufactured by pressing of moulding powder directly or incrementally with pressure applied from one direction or with pressure applied from all directions in suitable fixtures by using hydraulic press or isostatic technique. The moulding powder is prepared by coating high explosive crystals with suitable polymeric binder (usually less than 10%). The coating of high explosive crystals can be done either by water-slurry technique or by non-aqueous process. The polymeric binder coated high explosive crystal i.e. molding powder are free flowing explosive particles with less sensitivity to mechanical and thermal stimuli and have got better adhesive property.

### CASTING:

PBXs are processed by mixing the composition under vacuum at temperature between 25°C and 100°C. Casting of PBXs mainly depends on the viscosity of the composition. Maximum up to about 88% by weight cast able PBXs have flow viscosity.

<table>
<thead>
<tr>
<th>Code</th>
<th>Class</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 to 99</td>
<td>Pressed PBXs</td>
</tr>
<tr>
<td>100 to 199</td>
<td>Cast able PBXs</td>
</tr>
<tr>
<td>200 to 299</td>
<td>Extrudable PBXs</td>
</tr>
<tr>
<td>300 to 399</td>
<td>Injection moldable PBXs</td>
</tr>
</tbody>
</table>
The binder system must have a low viscosity because of casting requirement. Generally casting is done under vacuum in the required moulds and the filling can be agitated by vibration to dislodge any gas bubbles trapped in the mix. Cast PBXs are cured in the mould itself, at slightly elevated temperature or at ambient temperature, which mainly depends on the curing agents, used in the mixing of the composition. After curing PBXs are dimensionally stable and can be machined if required.

**EXTRUSION:**

Not all PBXs (10) that are extrudable are produced by extrusion as some extrude too slowly to be economical. In this process, the composition is mixed and pressed directly into the extruder where it is forced through a die of the required size under pressure. This has the obvious economic advantage of allowing the process to be continuous rather than consisting of the two batch processes. PBXs that eventually cure should have sufficiently long curing times to prevent curing during this process.

**REACTION INJECTION MOULDING:**

Reaction injection molding (RIM) is another technique, which can be used for PBXs production. RIM is extensively used in polymer industry for production of large polyurethane and initiated grade nylon components. Cumming et al. (30) and Flower and Garety (31) have used it for composite propellant preparation. The basic principle behind RIM is mixing of two low viscosity quickly polymerizable liquid components. Liquid components are mixed rapidly and then quickly injected into
mould cavity, where mixture is allowed to polymerize before ejection. The cycle time of the process depends on prepolymer mixture reactivity. RIM can be classified based on mixing parameters as high or low-pressure process. The essential requirement for the process is a pumpable pre-polymer mixture. By this process large PBXs grain can be easily manufactured at low pressure and the equipment cost.

### 1.6.3 REQUIREMENT OF PBXs

The rigorous requirements of modern warheads can be fulfilled by polymer bonded high explosive compositions. PBXs represent a class of explosive mixture having distinct physical, chemical, mechanical and explosive properties. In plastic bonded explosive solid explosive particles with additives are dispersed in polymeric binder. The advantages of the PBXs are reduced susceptibility to sympathetic detonation less storage and manufacturing hazard, high temperature and shock sensitivity, minimal or negligible shrinkage after curing, improved mechanical properties result in resistance to cracking, improved cook off behavior when subjected to the fuel fires with reduced probability of the violent reaction (8). The synonyms of plastic bonded explosive are PBX, PEX ECX, and ECP. From micro mechanics point, plastic bonded explosive consist of large number of inter phases and faces and exhibit non uniform straining during deformation.
1.7 POLYMERIC BINDER AND ADDITIVES:

The type of binder and ingredients affects plastic bonded explosives performance. The choice of the PBX components is performed in order to obtain high loading without jeopardizing the proper coating of solid explosive crystal in case of press able PBXs and in mixing creating discontinuities in the binder and reducing mechanical integrity of the mixture in case of cast able PBXs. The function and the characteristic of the ingredient used in PBX are listed in the Table (1.2) and discussed in the subsequent section. Essentially a PBX consist of an organic binder, which holds the heterogeneous particles (phases) together, provides a continuum in the system and serves as the gas and heat producing combustible reducing agent, some times oxidizing agent usually salt of per chlorate which provides oxygen needed for complete oxidation in case of Aluminized PBXs and metal powder (Aluminum) which gives better impulse in case of blasting explosive and other ingredients like energetic plasticizers, wetting agent and coupling agent etc.

Table 1.2
Plastic bonded Compositions Components, function and characteristics

<table>
<thead>
<tr>
<th>Function</th>
<th>Type</th>
<th>Component</th>
<th>Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymeric Binders</td>
<td>Cross-linked</td>
<td>Polyurethane (PUR)</td>
<td>Reactive group (hydroxyl-OH) is cured with isocynate, intermediate solid loading capacity and performance.</td>
</tr>
<tr>
<td>Polymeric Binders</td>
<td>Thermoplastics</td>
<td>Cellulose Acetate Butyrate (CAB), Ethyl Vinyl Acetate (EVA), NC/CTMETN/TEGDN</td>
<td>EVA copolymers are an established class of binder for pressed PBX compositions they show a well characterized gradation in properties with structure. Their properties are strongly influenced by vinyl acetate contents. At low vinyl acetate contents they resemble low density Polyethylene (LDPE) and at higher contents (40-50-weight%) they are mechanically weak rubbers.</td>
</tr>
</tbody>
</table>
Table – 1.2 (continued)
Plastic bonded Compositions Components, function and characteristics

<table>
<thead>
<tr>
<th>Function</th>
<th>Type</th>
<th>Component</th>
<th>Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymeric</td>
<td>Energetic</td>
<td>Nitrocellulose (NC) Energetic Polyvinyl nitrate (PVN)</td>
<td>For high energy PBXs Exceptional thermally stable energetic binder M.P 286 to 294°C Energetic binder. Hydroxyl terminated ploy (NIMMO) is an energetic binder for PBXs Like GAP; it acts as a plasticizer as well as binder.</td>
</tr>
<tr>
<td>Binders</td>
<td>Thermoplastic</td>
<td>Polyglycidylazide Polymer (GAP) Polynitro-polyyphenylenes (PNPS)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Nitrated hydroxyl terminated polybutadiene(NHTPB), Poly (3 nitrate methyl- 3 methyl oxetane), Poly(NIMMO) Poly (glycidylnitrate) Poly(GLYN)</td>
<td></td>
</tr>
<tr>
<td>Fuel</td>
<td>Metallic</td>
<td>Aluminium (Al)</td>
<td>Most commonly used, has high density, smoky and erosive product at combustion, used for effective blasting effect and impulse.</td>
</tr>
<tr>
<td>Bonding</td>
<td>Coupling-agent</td>
<td>Aziridine, triethanolamine silane and titanate base.</td>
<td>Improves adhesion binder to solids, improve particle dispersion for uniform performance, improve mix flow behaviour.</td>
</tr>
<tr>
<td>agent</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Plasticizers</td>
<td>Conventional</td>
<td>Triacetin, Dibutyl phthalate (DBP), Diethyl phthalate (DEP), Dioctyl adipate (DOA) and Dioctyl sebacete(DOS).</td>
<td>Improve processability and low temperature physical properties; may vaporize or migrate</td>
</tr>
<tr>
<td></td>
<td>Energetic</td>
<td>Glycidyl azide polymer (GAP) Butanetrioltrinitral(BTTN)</td>
<td>Sensitive For high energy</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TMETN bis (2,2 dintro propyl) acetal formal(BTNAF)</td>
<td></td>
</tr>
<tr>
<td>Wetting</td>
<td></td>
<td>Lecithin, Polyoxyethylene Sorbitantrialeate</td>
<td>Most commonly used oxidizers, has a high density, permit a range of burning rate but produce smoke in cold or humid atmosphere. Used in Aluminized PBXs.</td>
</tr>
<tr>
<td>agent</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oxidizers</td>
<td></td>
<td>Ammonium per chlorate (AP) / Ammonium nitrate (AN)</td>
<td></td>
</tr>
</tbody>
</table>
1.7.1 POLYMERIC BINDERS:

Polymers are mainly used for binding explosive composition and for achieving the mechanical and thermal characteristics. The type of binder significantly affects velocity of detonation, power/impulse and mechanical integrity of PBXs. Binder provides the strength necessary for PBX charge to withstand the stresses and strains imposed during handling, storage, ignition, firing and flight. Irrespective of the type, polymer always serves as sources of the fuel for combustion, because polymers are composed of C, H and are combustible. Polymers with specific functional groups can also increase the energy content of the PBXs.

The polymeric material used as a binder in PBXs must meet a multitude of requirements.

- It must be easily oxidized to serve as primary source of gas.
- It must have good interaction and binding capability to provide required mechanical stability and its retention.
- It must have adequate rheological properties for mixing and shaping operation.
- It must have sufficient resistance to interaction with oxidizer to prevent degradation during storage.

A high flame temperature is favoured for PBX compositions with more positive heat of formation and combustion products with negative heat of formation and of low capacities per unit weight. Metallic fuel and oxidizer can fulfill
the second requirement. Therefore, the binder with more positive heat of formation is preferred.

In polymeric binders carbon-nitrogen and nitrogen-nitrogen bonds are associated with positive heat of formation, while carbon-oxygen, carbon-halogen and carbon-sulfur bonds are associated with more negative heat of formation (32).

Table-1. 3
Differences in heat content of various chemicals bonds.

<table>
<thead>
<tr>
<th>Chemical bond introduced</th>
<th>ΔH, kcal/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Unsaturation</strong></td>
<td></td>
</tr>
<tr>
<td>RCH₂CH₂R → RCH = CHR</td>
<td>+30.14</td>
</tr>
<tr>
<td>RCH₂CH₂R → RC = CR</td>
<td>+69.77</td>
</tr>
<tr>
<td><strong>Carbon-Nitrogen Bonds</strong></td>
<td></td>
</tr>
<tr>
<td>RCH(CH₃)R → RN(CH₃)R (amine)</td>
<td>+21.2</td>
</tr>
<tr>
<td>RCH(CH₃)R → RCH(CN)R (nitrile)</td>
<td>+31.27</td>
</tr>
<tr>
<td>RCH(CH₃)R → RCH(CH₂N₃)R (azide)</td>
<td>+56.25</td>
</tr>
<tr>
<td>RCH₂R → RCH₂ NNHNR (hydrazine)</td>
<td>+28.18</td>
</tr>
<tr>
<td>RC(NH₂)₂R → RCH₂NH NHR</td>
<td>+29.60</td>
</tr>
<tr>
<td>RCH₂R → RCH₂N(NO₂)R (nitramine)</td>
<td>+27.38</td>
</tr>
<tr>
<td><strong>Carbon-Oxygen Bonds</strong></td>
<td></td>
</tr>
<tr>
<td>RCH₂R → RCHOHR (alcohol)</td>
<td>-59.46</td>
</tr>
<tr>
<td>RCH₂R → RCH₂OR (ether)</td>
<td>-36.04</td>
</tr>
<tr>
<td>RCH₂R → RCOR (carbonyl)</td>
<td>-35.28</td>
</tr>
<tr>
<td>RCH₂R → RCHOOR(ester)</td>
<td>-82.32</td>
</tr>
<tr>
<td><strong>Carbon – Halogen, Carbon-Sulfur Bonds</strong></td>
<td></td>
</tr>
<tr>
<td>RCH₂R → RCHCHR(chlorin)</td>
<td>-14.77</td>
</tr>
<tr>
<td>RCH₂R → RCHFR(fluorine)</td>
<td>-21.19</td>
</tr>
<tr>
<td>RCH₂R → RCHSHR(sulphhydryl)</td>
<td>11.99</td>
</tr>
<tr>
<td><strong>Oxygen- Nitrogen, Fluorine-Nitrogen Bonds</strong></td>
<td></td>
</tr>
<tr>
<td>RCHNH₂R → RCHNO₂R (nitro)</td>
<td>-55.53</td>
</tr>
<tr>
<td>RCHNO₂R → RC(NO₂)₂R</td>
<td>-45.01</td>
</tr>
<tr>
<td>RCOOCH₂CH(NH₂)R → RCH₂CH₂CH(NO₂)R</td>
<td>+69.11</td>
</tr>
<tr>
<td>RCHNH₂R → RCHNF₂R (difluoroamine)</td>
<td>-6.0</td>
</tr>
<tr>
<td>RCF₂CH(NH₂)R → RCH₂CH(NF₂)R</td>
<td>+69.65</td>
</tr>
</tbody>
</table>

Source: Taken from reference (32)
1.7.2 BINDER TYPE:

Most of the polymeric binders used in composite propellant and PBXs are common. The various type of polymeric binder used in PBXs are listed in the Table (1.2) and (1.4) with their characteristics features. The commonly used binders are viscoelastic cross-linked elastomer, thermoplastics elastomer and sometime thermoset as well. Fluro binder are used for high energy, butadiene binder are used for high burning rate whereas ethyl-vinyl acetate copolymer binders are used for impact and low temperature performance.

A binder system, capable of many permutations results from the reaction of difunctional alcohols with diisocynates to form polyurethane (33) and is commonly used for PBXs. The three basic building blocks used for polyurethane binder are diisocynates low molecular weight triol or long chain diol, linear organic compounds terminated at each end by hydroxyl group. Cross-linking of the system is controlled by reaction of isocynates with primary, secondary and tertiary alcohols. For improved physical properties copolymer diol of ethylene oxide and tetrahydrofuran are used (34). The limitation with the system lies in determining the point where the pre-polymer, uncured PBX is reduced to the uniform consistency necessary to obtain reproducible explosive performance. The limitation with other widely used binder (35-37) like polyethene sulphide, popularly known as Thickol, lies in their poor long-term stability. Polyisulphide composites do under go a change in character during storage. Burning properties and physical characteristics may change continuously with time. However, these changes can be controlled considerably with composition and cross-linking. (37).

Many other binders have been used but recent interest is concentrated on cast able polybutadiene (38-39).
Liquid polybutadienes prepolymers are preferred because of their high specific impulse, acceptability of high solid loading, greater fuel value, tolerance against high level of humidity, stable mechanical performance over wide range of temperature from -40°C to 120°C, better aging characteristics plus acceptable processability. The pre-polymers are terminated with carboxyl or hydroxyl groups (HTPB or CTPB) and hydroxyl functional group (moles of OH per mole of polymer of around 2.5) are cross-linked with difunctional or trifunctional isocynates (similar to urethane) in the presence of catalyst. Other additives can be added to improve the processing and performance further.

Other binders which could be used for PBX production are liquid and powdered elastomer (40), thermoplastics elastomer (TPE) (41) inomers (42) and liquid crystalline polymers (LCP) (43), polymer blends and alloys, TPE's are copolymer in which various thermoplastic and elastomeric segments are linked in several permutations. They exhibit elastomeric characteristics in performance and thermoplastic characteristics during processing. A good range of thermal and mechanical performance is possible by use of various backbones and side chain linkages. Mechanical strength in TPE's are achieved by rigid block and physical interaction rather than by chemical cross-linking. TPE's are capable of higher loading (44) as well, isomers consist of ionic groups and metallic ion can improve the burning characteristics of the PBXs. LCP or molecular composites are known for their high strength and toughness which are desirable for PBX composition. These systems also exhibit sharp solid-liquid transition, which may be useful for high density PBX. Polymer blends and alloys are classified based on their partner interaction. Blends are merely physical mixture while alloys are more intimate mixtures.
<table>
<thead>
<tr>
<th>Type</th>
<th>Reactant/Component</th>
<th>Characteristics</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acrylic Elastomer</td>
<td>95/5 copolymers of ethyl acrylate and acrylic acid.</td>
<td>Burn readily and completely leaving no ash.</td>
<td>R.D. DeMarco [45]</td>
</tr>
<tr>
<td>Poly (2-fluro-2, 2-dinitroethyl vinyl ether)</td>
<td>Reaction product of divinyl ether and HOCH₂(NO₂)₂F</td>
<td>Energetic binder</td>
<td>A.S. Shackelford et al [46]</td>
</tr>
<tr>
<td>Diffluoraminted cellulose</td>
<td>Dialdehyde cellulose treated with HNF₂ in H₂SO₄ presence at -80°C</td>
<td>Energetic binder contains 8.6% N and 23.2% F</td>
<td>H. Zenftman and D. Colder [47]</td>
</tr>
<tr>
<td>Butadiene copolymer</td>
<td>A copolymer of butadiene with • Ferrocenyl methyl-acrylayte or • Vinyl ferrocene</td>
<td>Higher burning rate by using iron in composite with (NH₄ClO₄+Al)</td>
<td>M.G. Baldwin and S.F. Reed [48]</td>
</tr>
<tr>
<td>Hydroxycylelechetic polybutadiene</td>
<td>-</td>
<td>Higher loading of explosive in composite</td>
<td>ARCO Chem. Corp, US [49]</td>
</tr>
<tr>
<td>PVC Polyvinayl Chloride</td>
<td>Cured by liquid plasticizers such as • Diethyl sebacate • Di-2-ethylhexyladipate</td>
<td>Used for small grain charges since high temp. Curing causes shrinkage.</td>
<td>C. Boyars and K. Klager [50]</td>
</tr>
<tr>
<td>PIB</td>
<td>Linear binder</td>
<td>Useful for: Casting as well as extrusion possible.</td>
<td>R.D. Goekler and K. Klager [51]</td>
</tr>
<tr>
<td>EVA Ethyl Vinyl acetate Copolymer</td>
<td>EVA of variable composition</td>
<td>1. 95% RDX loading possible 2. Higher vinyl component is desirable for better mechanical stability.</td>
<td>Dagley et.al [52]</td>
</tr>
<tr>
<td>Cellulose derivative (C.A)</td>
<td>CA with plasticizers such as, • Triethyl acetylctrate • Dinitrophenoxyethanol</td>
<td>1. Gas generation 2. Small devices 3. Poor elastic and dimensional stability.</td>
<td>W.A. Proell et.al [53]</td>
</tr>
<tr>
<td>PMMA Poly methyl meta acrylate</td>
<td>PMMA with ammonium or potassium perchlorate</td>
<td>High flame temp.</td>
<td>Z. Altermann and A. Katchalsky [54]</td>
</tr>
</tbody>
</table>
### Table 1.4 (continued)

<table>
<thead>
<tr>
<th>Type</th>
<th>Reaction/component</th>
<th>Characteristics</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSU Polysulphide</td>
<td>A polyethylene sulphide elastomer by trade name Thiokol</td>
<td>1. Wide range of temperature stability.</td>
<td>W.F. Arendale Thiokol Corp. USA [55,56]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2. Due to metal additive side reaction limited application.</td>
<td></td>
</tr>
<tr>
<td>P.Es Polyester</td>
<td>- Hydroxyl terminated polyester as prepolymer cured with isocyanate</td>
<td>1. Experimentally found useful binder.</td>
<td>J.Winkler and E.A. Bratoeff [57]</td>
</tr>
<tr>
<td></td>
<td>- Linear carboxyl terminated polyester cured with epoxy or aziridine</td>
<td>2. Limited study.</td>
<td>R. Roberts [58]</td>
</tr>
<tr>
<td></td>
<td>- Unsaturated cured with styrene</td>
<td>3. For small configuration only.</td>
<td>J.Phillipson [59]</td>
</tr>
<tr>
<td></td>
<td>- Unsaturated with styrene and methyl acrylate 92% AN, mixture of coarse/fine oxidizers.</td>
<td>4. Excellent ageing, resistance.</td>
<td>A.O.Dekker and G.A.Zimmerman [60]</td>
</tr>
<tr>
<td>P.Et Polyether</td>
<td>- Hydroxyl terminated polyether are used as prepolymer to form a polyurethane network by reaction with isocyanate</td>
<td>5. as gas generator (JATO propellant)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>- Carboxyl terminated polyether cross-linked with epoxy</td>
<td>6. Specific impulse 190 S at 1000 PSI</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>7. Good performance (-59 to +82 °C)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>8. Used as JATO propellant.</td>
<td></td>
</tr>
<tr>
<td>Theroset UF, MF</td>
<td>Mixtures of UF or MF with Ammonium Picrate and Sodium and Potassium nitrate</td>
<td>1. Excellent binding capacity.</td>
<td>A.J.Zachringer [65]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2. Versatile and wide range stabilities.</td>
<td>R Lindsey [66]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3. Exhibit specific impulse less than hydrocarbon binder in few formulations.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2. Saturated bi-functional polybutadiene with ethyl pendant group instead of vinyl and are cured with trifunctional cross-linking agent.</td>
<td>2. Relatively poor mech.prop. at &lt; 0°C</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3. Prolong post curing not required</td>
<td></td>
</tr>
</tbody>
</table>

---
<table>
<thead>
<tr>
<th>Type</th>
<th>Reactant/component</th>
<th>Characteristics</th>
<th>References</th>
</tr>
</thead>
</table>
| Polybutadienes        | • Carboxyl terminated polybutadiene (CTPB) cured with various epoxy compounds.   | 1. High fuel value.  
2. Good mechanical capability.  
3. High specific impulse.  
4. Oxidative cross-linking leads to cracking.  
5. Overall good performance.  
6. Viscosity sufficiently low both to make it easy to process and to permit a high solid loading. It's glass transition temperature, Tg, is however slightly higher than HTPB but unlike HTPB. It has advantage of being miscible with energetic plasticizers. | [68-71] D.C.Syles [72] W.R.Mebride [73] Colelough, ME And Paul, N.C [74] |
|                       | • Hydroxyl terminated polybutadiene (HTPB) cured with isocyanates.               |                                                                                                                                     |                                  |
|                       | • Nitrated hydroxyl terminated polybutadiene (NHTPB) with 10% double bonds converted to dinitrate ester groups is good for use as a binder. |                                                                                                                                     |                                  |
| Polyphenylenes        | Polynitropolyphenylenes (PNPs), A class of compounds with aromatic C-NO$_2$ groups in a chain of benzene units interlinked by aromatic C-C bonds. | PNP are non-crystalline, exceptionally thermally stable and soluble in common organic solvents, and are considered as high-temperature-resistant binders together with inert binders and or softeners. | J.P.Agrawal [10]                |
| Glycidyl azide polymer (GAP) | The –OH terminated molecules may be subsequently cross-linked to give polyurethane rubbers which constitute a new class of energetic rubbers with potential applications in explosives and propellants. | Based on the analogy of hydroxyl-terminated polybutadiene (HTPB), it is speculated that GAP may prove to be very interesting binder for explosive formulations (PBXs). GAP is a energetic plasticizer as well as an energetic binder. GAP possesses a high density (1.39 g/cm$^3$) compared with other polymer used as binder. For propellants and PBXs, a positive heat of formation (+42 kcal/mol) | Colelough, ME [75]              |
### Table 1 (continued)

<table>
<thead>
<tr>
<th>Type</th>
<th>Reactant/components</th>
<th>Characteristic</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly (3 nitro-&lt;br&gt;methyl-3-&lt;br&gt;methyl-&lt;br&gt;oxetane) Poly (NIMMO)</td>
<td>NIMMO is synthesized by selective nitration of hydroxyl group present in 3-hydroxy methyl-3-methyloxetane (HIMMO) using N₂O. The resulting monomer (NIMMO), cationic polymerization, yields a pale yellow viscous liquid called poly (NIMMO)</td>
<td>Use of this binder increases the overall energy of a composition and reduces the vulnerability. The British Defense Research Agency (DRA) has developed a plastic-bonded explosive (PBX) called CPX 413 (based on poly (NIMM/HMX/NTO/plasticizer) Which matches the performance goal of composition B</td>
<td>Colelough et al. [76]</td>
</tr>
<tr>
<td>Poly Glycidyl Nitrate Poly (GLYN)</td>
<td>Poly (GLYN) is pale yellow liquid that can be cross-linked with diisocyanates to yield rubbery materials.</td>
<td>The polymer imparts high density, high energy and low vulnerability to both propellant and explosive formulation.</td>
<td>Leeming, W.B.H. et.al. [77]</td>
</tr>
<tr>
<td>Polyethylene Glycol Adipate Hydroxyl-Terminated Polyethylene Glycol Adipate</td>
<td>Easily degradable polymer. The PBX of this binder can be easily demilitarized</td>
<td></td>
<td>Benjamin, Y.S.Lee and Rusel Reed (78)</td>
</tr>
</tbody>
</table>

### 1.7.3 PLASTICIZERS:

Plasticizers are used to reduce the viscosity and to improve the low temperature performance of composite propellants. Table (1.2) and Table (1.4) list some of the plasticizers, which are commonly used in high energy composite. Most of the plasticizers used in PBXs are either ester of long chain aliphatic alcohol or long chain aliphatic acid. High-energy plasticizers are also used to improve the energy level of PBX. But they tend to increase the PBX sensitivity. Therefore, careful selection of plasticizer is essential for PBX performance. The requirement of plasticizers demand that it must not reduce the energy or density, must not hinder with curing reaction, must not migrate to reduce the integrity of the composite and must be compatible.
1.8 REVIEW OF PAST WORK DONE ON PBXS

1.8.1 PRESSED PBX

In the early 1960s, the first pressed plastic bonded explosives compositions with moderately high explosive powder contents bonded together with an inert nylon binder were introduced (8). Later, pressed PBXs were developed, using inert viton as the binder, containing high explosive powder (usually either HMX or RDX) at the 95% level. The nylon-based binder system has been employed in three pressed compositions (PBXN-1, PBXN-3 and PBXN-4), which contain RDX 68%, Al 20%, Nylon 12%, HMX: 86%, Nylon: 14% and AP: 94%, Nylon 6% respectively. These materials have been essentially replaced in future explosive warhead applications by Viton binder pressed PBXs. Singh et al (79) in their review article on PBXs have concluded that PBX compositions may be preferred to TNT based cast compositions as well as wax based pressed compositions for futuristic warhead applications as these compositions are having better mechanical properties particularly compression strength, better thermal stability, least porosity, deformation shrinkage, high loading density, simpler in pressing due to good free flowing properties and safer in handling etc. Dagley and Sook Ying Ho (80) evaluated the effects of vinyl acetate content and molecular weight of ethylene vinyl acetate (EVA) copolymers on impact ignition sensitiveness of RDX (95:5) physical mixtures, explosive moulding powders and compacted charges by performing two types of tests. In a drop-weight impact test on physical mixtures and moulding powders the thermal and high strain-rate mechanical properties (i.e. catastrophic failure or deformation of the polymers and the way
the polymer is distributed affects impact sensitiveness. The response of moulding powders, compacted to 90% TMD, has been assessed using a Hopkinson bar test. The compacts containing copolymers with high vinyl acetate contents and high molecular weights had the best mechanical properties under high strain rate impacts and were least sensitive to impact ignition. Results from this test are compared to shock sensitivity data for the same pressed compositions. According to them effects resulting from difference in polymer particle size and coating efficiency effects (in moulding powders) also influence impact sensitiveness measured using drop weight test.

Dagley and Parker (81) studied booster explosive based on RDX, EVA copolymers and acrylic polymers. Examination of the moulding powder using scanning electron microscopy showed that EVA copolymer resins and EVA or acrylic dispersion can be effectively coated on RDX crystal to produce compositions which have impact sensitiveness and shock sensitivities suitable for use as booster explosive. It is also observed that dispersion coating can be improved by the use of plasticizers. Prunde et al. (82) have studied PBX composition with greater than 90% TATB (1,3,5 Trinitro amine 2,4,6 Trinitrobenzene in a fluorocarbon binder (Kraton). According to these author process variations, even small once can have significant effect on the ultimate mechanical properties of PBXs.

The IHE (Insensitive High Explosives) mostly used by LLNL (Lawrence Livermore National Laboratory) for LX-17 contain 92.2 % of TATB and 7.5% of Kel-F 800. In the late seventies, a programme viz. Safe High Energy Explosives (SHEE) was started at LLNL to attempt to formulate new explosives with higher energy than LX17, while significantly decreasing the
vulnerability relatives to HMX based high explosives. Holtz et al. (83) have developed a family of new explosives, which would significantly exceed the performance of the IHEs. This new family is also expected to pass the IHE criteria as set forth by the DOE (Department of Energy). The new formulation will include TATB, HMX and high density plasticized binders. Their work has produced several candidates, which look promising.

Achutan et al. (84) have prepared PBX based on the binders such as high impact polystyrene (HIP) and acrylonitrile butadiene styrene graft copolymers (ABS) and have studied their sensitivity, explosive and mechanical properties. Compression strength of these PBXs is 2 to 3 times more than composition B and composition A3 (RDX/Wax) but these PBX are more sensitive towards impact as compared to the basic explosive (RDX/HMX). According to them loading density can be significantly improved by proper combination of particle size of high explosive ingredients. A number of RDX/HMX based PBX composition using aliphatic polyester based aromatic polyurethane and aromatic polyester based polyurethane were developed by M. Lal et al. (85). As per the outcome of this study the plastic bonded explosives PBX-06 (HMX 97%, U 5731 1.5%, Paraffin oil 1.5%) and PBX-09 (HMX 97%, U-5712, 1.5%, paraffin oil 1.5 %) are promising and potential compositions to be used as appropriate substitutes for composition B (RDX/TNT, 60/40). It was observed that PBX composition developed by them is having better explosive, mechanical and thermal properties than composition B. It was also found that paraffin oil in the PBXs reduces the impact sensitivity appreciably. According to a study of Lin and co workers (86), the low melting point of TNT is beneficial from the point of view
of improving performance of PBX, but same problem would occur in excursion to elevated temperatures. As per their study, TNT as a component in PBX apparently improves the press ability of PBX at the temperature above softening point of TNT. The effect of TNT to improve the compacting property of PBX is mainly due to the softening or melting of TNT at the compacting temperature.

By adding optimum quantity of TNT into the PBX formulation the satisfactory performance can be achieved.

Shokry et al. (87) have developed heat resistant PBX based on and binders like polyurethane Viton, Teflon and Kel-F. The thermal, mechanical and explosive properties of the various compositions were studied. They have found that TATB / Kel-F-800 (90/10) is the best formulation among the studied formulations. This formulation gave toughness of 17.3 maximum compressive stress 228.47 kg/cm²; strain at failure 6.2 % with velocity of detonation (VOD) of 7534 m/s. Akhavan and Burke (88) have evaluated the coating of HMX crystals with three polymeric binders viz. a thermoplastic copolymer (kel – F 3700), 1650, a thermoplastic elastomer (Kraton-G1650) and a polyurethane (Impranil DLH) using the “Solvent slurry process”.

They have found that thermoplastic Kef-F-3700 was unsuitable for this process. The polymer was difficult to dissolve in any reasonable quantity of solvent. The raw polymer crumb was difficult to break into small pieces and also suffered from static charge.

A high yield was obtained when using elastomer Impranil DLH was used as a coating for HMX crystals. Apart from HMX itself, no flammable or toxic materials were involved in the process and temperature required to heat the reaction vessel
could easily be attained through the use of a hot water bath. From the results of particle size distribution, it is suggested that at least 25% of the HMX crystals may have been coated by the various polymers and that the coating process seems to have involved the smaller HMX particles.

Metal accelerating explosive composition, PBXW- II, which contains HMX filler up to 96 % was developed by Montesi et al. (89). The composition exhibits good vulnerability characteristic with better output than LX-14 or Octol85/15 composition. Bellerby and Kiriratnikom (90) have reviewed the problem associated with poor adhesion in nitramine filled energy materials. They have discussed the phenomenon of de-wetting and its consequences and presented a survey of the literature relating to specific adhesion promoters for RDX filled system in their review article.

In a study Kaully and co worker (91) have studied the effects of different parameters like particle size distribution, particle shape, and surface energies of the filler and elastomer matrix on mechanical behaviour of PBX. Mechanical properties under tensile stress and SEM fractographs, as well as surface energies measurements were used as experimental tools. They have found out that there are some combined mechanisms that affect failure. There is an interaction between particles, which results in mechanical interlocking. The degree of mechanical interlocking depends on particle size distribution and particle shape.

Changes in the degree of adhesion can change the role of de-wetting as a failure mechanism. An energetic PBX containing RDX / HMX as filler and Viton-A and Teflon as the binder having VOD of the order of 8000 m/s at 1.81 g/cc density have
been developed by French et al. (92). Humphrey (93) has prepared a PBX composition containing HMX 95.5% and polyurethane (estane) 4.5%. He has evaluated that this composition is less sensitive to mechanical and shock stimuli and possesses superior mechanical properties and velocity of detonation (VOD) as compared to composition B. Hendry et al. (94) and Benziger (95) studied the thermal stability and shelf life of this formulation. They observed that this formulation has excellent thermal stability even at elevated temperatures without affecting the mechanical properties. Karl et al. (96) have prepared an isobutylene-based composition, which shows good water resistance, and mould ability at low temperature.

Francois et al. (97) have done the exhaustive studies on characterization of NTO- based pressed PBX formulations. They have described the manufacturing and processing technique for NTO based pressed PBX formulations. They performed chemical and physical characterization tests on a series of press able NTO/RDX based formulations. Pellets were pressed of the various formulations and subjected to a series of IM characterization tests. In addition, the various formulations were prepared in medium caliber shells as main charge and subjected to a series of IM characterization as well as static functioning tests. The vulnerability characteristics of medium caliber shells filled with cast able NTO/TNT formulation, fitted with various pressed PBX booster pellets are described. The vulnerability characteristics as well as the reliability of initiation of newly developed explosive train are described. The terminal effectiveness of large caliber ammunition filled with different formulations are described above were evaluated by experimental testing as well as computer modeling. The
terminal effectiveness of these products was quantified in terms of range and flux of lethal fragments produced by different formulation. On the basis of results they have concluded that NTO/RDX/EVA can be considered as suitable booster formulation for reliable initiation of a cast able main charge filling viz. NTO / TNT. HNS / Kel F can be considered as suitable booster formulation for reliable initiation of press able main charge filling NTO / RDX / EVA. HNS / Kelf and NTO/RDX/ EVA exhibit excellent IM Characteristics. The newly developed explosive train exhibits excellent IM characteristics. Static functioning tests also proved the reliability of this explosive train.

Guangfu and Sunhuo (98) have studied the effects of Silicone coupling agent (SI) on TATB and its plastic bonded explosive (PBX) by means of X-ray photoelectron spectroscopy (XPS) and gel permeation chromatography (GPC). The binders were the copolymers of vinyl difluoride and chlorotrifluoro ethylene with the same or different mole ratio. They evaluated and examined the coverage of binder on TATB crystals modified by coupling agents SI. The results show, the coverage of the binder on SI modified TATB increases from 74% up to 84% or more. From the experimental data, they have found that SI can affect to the distribution of polymerization degree of the above said copolymers. From the experimental data they have observed that the main function of Silicone is to wet and couple with TATB crystal surface, promoting the binder more satisfactorily to coat the modified TATB.

Mezer and co workers (99) have developed several CL-20 formulations that will substantially outperform the baseline LX-14 explosives while maintaining acceptable vulnerability and
handling characteristics. Several promising 85-95% CL-20 plastic bonded explosive (PBX) formulations were investigated using both energetic and non-energetic binder/plasticizer systems as these materials offer increased warhead performance. Impact, friction and shock sensitivity, cook-off properties, sensitivity to lathe machining, thermal stability and compatibility of several CL-20 formulations were examined. They have presented a comparison of these test results to other formulations. The PATHAX3 (90) formulation (CL-20 formulation) showed sensitivity values as good or better than LX-14 coupled with good thermal stability, no compatibility issues, mechanical properties similar to that of LX-14, and good loading and machining characteristics. Xingnin and co-workers (100) have done the simulation study of the explosion accident in isostatic compacting HMX-PBX.

1.8.2 CASTABLE PLASTIC-BONDED EXPLOSIVES

Anderson (8) has reviewed the development of PBXs. According to the author plastisol grade Nitrocellulose (PNC) binder system based PBX was developed in the late 1950 but this PBX was not accepted for military use until 1970. The plastisol grade Nitrocellulose (PNC) binder system has been approved for service use in only one explosive, the underwater composition PBX N-103. The sensitivity of this binder to thermal inputs in any form, such as impact, friction, or electrostatic stimulation, had precluded its acceptability for fleet use in other compositions. Although PBX N-103 had in the past been the explosive of choice for the main charge explosive fill of many under water weapons, it was expected to see fewer applications in the future as more insensitive explosives, such
as PBX W - 115, were developed. In the early 1960s the first developed cast able PBXs (PBXN – 101 and PBXN – 102) were based on an inert laminate / styrene binder. (PBXN – 101, PBXN – 102 and later PBXN – 104) eventually proved to be relatively sensitive in a large-scale sensitivity tests, as compared to PBX s developed later with rubbery, elastomeric binders. The rubbery, elastomeric binders provide sensitivity improvements over hard binders. All modern PBX such as PBXN – 106, PBXN – 107, and PBXN – 110, utilize these soft, rubbery binders. The author has discussed about six types of binder systems viz. laminate/ styrene, Hydroxyl Terminated Polybutadiene (HTPB), acrylate, poly propylene glycol (PPG), plastisol grade Nitrocellulose (PNC), Polyethylene glycol (PEG), for cast able PBX.

James and co workers (101) have studied the PBX formulations containing RDX (40 – 80%), acrylic resin (60– 20%) and plasticizer such as triethyl phosphate, dioctyl or dibutyl adipate. As per their observations most of the formulations are of high impact and tensile strength, but of velocity of detonation (VOD) of these formulation have been found low. Sugiura (102) has studied the PBX formulation containing RDX and an acrylonitrile butylacrylate copolymer or its mixture with polyvinyl acetate. Yee (103) has done the exhaustive studies on a number of cast able compositions containing RDX and HMX as an explosive filler with different acrylic binder system such as ethyl hexyl acrylate, triethyl glycol, dimethyl acrylate in combination with different additives. His studies reveal that most of these formulations have better mechanical and thermal properties. Vander et al. (104) in their review article have discussed about the number of formulations using RDX and
HMX with hydroxyl terminated polybutadiene and its evaluation. Wu, MT and others (105) have done a comparative aging study of nitramine PBX. They have found that polypropylene glycol (PPG) and hydroxyl-terminated polybutadiene (HTPB) are suitable binders for Nitramine systems. HTPB is mech. stronger, but polypropylene glycol is widely available and less expensive. HTPB based formulations are highly insensitive to impact and friction. They possess excellent mechanical and thermal stability (106). These formulations are safe for processing. HTPB based cast able PBXs are processed according to standard procedures. According Vander et al. (107) the sensitivity of the PBX formulations is largely influenced, by the particle size distribution and possibly the geometry of the particle. A narrow particle size distribution can reduce the impact sensitiveness of the formulation. For achieving a high solid loading generally a bimodal or tri-modal distribution of filler particle are used in the cast able PBXs.

Hooper and coworkers (108) studied the effect of filler blend, size ratio, temperature of the mix and wetting agent on the processability. A study was conducted for investigating the influence of internal crystal quality of HMX crystals on the shock sensitivity of HTPB based cast able PBXs (109). The results of the shock sensitivity tests point at a direct relation between the HMX crystal density (and hence crystal quality) and shock sensitivity of these particles in the final PBXs the higher the crystal density, the higher the crystal quality and the lower the shock sensitivity. Sinha et al. (110) have studied the different combination of particle size distribution of the explosive ingredients of HTPB based PBX. They have achieved
the solid loading up to 88% weight by selecting proper combination of particle size distribution.

Gharia and coworkers (111) have done exhaustive studies on HTPB based cast able PBX. The PBXs were processed as per standard procedures. Bimodal/tri-modal particle size system was selected to reach a solid loading of 88 percent. High solid loading was made possible through proper combination of course/fine ratio of solid ingredients, which was based on a number of tap density experiments. Processability of the binder system was studied by using various wetting agents as well as by selecting binder/plasticizer ratio. Mechanical properties of the PBXs were enhanced by different cross-linking agents. The explosive properties of PBXs including detonation velocity, processability and sensitivity to different types of stimuli, were studied. The results show that PBXs can be manufactured with detonation properties better than those of composition B/Octol with added advantages of superior thermal and sensitivity characteristics.

Rietjens (112) have studied the characterization of plastic-bonded explosives by pyrolysis gas chromatography and multivariable data analysis. They found that PBX samples were inhomogeneous despite a thorough mixing of the constituents during preparation.

Geng, Lao (113) have done the studies on PBX heat resisting explosive that consist of the main ingredients (βHMX and HNS) and bonding agent (Viton F) Newman, K. E. (114) has found that a continuous processing pilot plant must be sufficiently versatile to prove processes for both thermosetting and thermoplastic PBX formulations. The energy content of GAP, GAP+BDNPA/F and PEG+BPNPA/F binders are higher
than HTPB (115). By using these binder system the energy of the energetic composite system is increased. It is found that in some of the formulations, the insensitive properties of GAP/HMX systems are better than that of HTPB/HMX system.

Elwany and coworker (116) studied the cutting effects of RDX/HTPB based castable PBX on the steel sheet as a target. These values have been compared with those obtained by the Composition B. It was found that PBX showed similar or sometimes better cutting effect than composition B.

1.8.3 EXTRUDABLE AND INJECTION MOULDABLE PBXS

Cumming et al. (30) have developed RDX-based polymer bonded explosives for processing using reaction injection moulding (RIM) technique. They have studied the effects of Nitramine particle size and shape on the PBX processing by this technique.

Scribner (117) has developed an extrudable plastic bonded explosive using bis (2-fluoro-2, 2-dinitroethyl) formal (FEFO) as an energetic plasticizer. He has claimed that on fill cavity of any configuration at essentially the theoretical maximum density of explosive, the explosive has an energy/density greater than 78% Octol.

Menz (118) has processed the explosives used in warheads and fuzes by many different methods, of which, melt-cast, cold-slurry, and pressed and extruded dry powder. Kosowski and Condo (119) have developed micron capsulated chemical sensors for on line shear stress determination during twin-screw extrusion mixing of PBX simulant.
1.8.4 ALUMINISED PLASTIC BONDED EXPLOSIVES

Anderson (8) has reviewed the use of Aluminium powder in PBXs. According to author Aluminium powder is used as a metal fuel to increase the total energy of the explosive. This use of Aluminium in explosives was first proposed in the nineteenth century. See Table 1.1 Aluminium powder is available in a number of grades and particle sizes ranging from a flake “bomb” grade (MIL-A-512) to small (<10 μm) spherical particles (MIL-A-23950). PBXs use spherical or near-spherical grades of aluminium powder with particle sizes usually below 25 μm.

From the explosive materials of view, there are limited numbers of damage mechanisms that can be achieved through the proper design of explosives. These damage mechanisms can be achieved with the use of one of the following three categories of explosives: brisant (non-Aluminized, Aluminized, and underwater (Aluminized, oxidizer).

The Aluminized explosives containing 20% Aluminium, whether TNT based (H-6 or tritonal) PBXs (PBXN-109 or PBXC-117), have approximately the same overall general-purpose performance.

PBXs, PBXN-103, PBXN-105, and PBXW-15, provide significant improvements in both shock wave and bubble energy than compared to H-6 and HBX-1. This improvement was achieved through the use of the Ammonium perchlorate oxidizer. The use of Ammonium perchlorate in TNT based explosive had been examined prior to the development of PBXs but was discontinued because of the use of AP made compositions significantly more impact sensitive. The PBX binders, on the other hand, desensitize the AP mixtures to the point where these mixtures can be safely processed and used in warheads. For the second subcategory of underwater explosives,
only TNT based HBX-3 has been optimized to produce maximum bubble energy. With almost 35% Aluminium, its bubble energy is significantly greater than the other Aluminized TNT based explosives. With the use of AP, the current under water PBXs (PBXN-103, PBXN-105), and PBXW-115) possess bubble energies comparable to or greater than possessed by HBX-3. If there is need, the current compositions can be optimized for maximum bubble energy by increasing their Aluminium content.

As per the study of Hadhoud et al. (120) incorporation of Aluminium, Ammonium perchlorate, or Lead nitrate at the expense of RDX in the cast able PBX containing RDX is reportedly found to have low VOD. The presence of Aluminium in PBX samples increases considerably the value of the detonation heat for these composites. According to them presence of Aluminium enhances stability of heat, and increases the temperature of ignition after 5 seconds delay. This may be attributed to high melting points of Al and Al₂O₃, which are 660°C and 2030°C respectively. Another cast able PBX formulation studied by Hoeller et al. (121) has shown high VOD. This formulation contains RDX or HMX (55-90%), highly fluorinated aliphatic unsaturated polyethers (10-45%) and Aluminium <0.5 mm, (10-30%).

Being basically inert within the reaction zone, Aluminium provides little, if any, energy to drive the detonation, and thus its incorporation into an explosive composition will reduce both the velocity and pressure of the materials. The presence of Aluminium has a more pronounced effect on pressure than it does on velocity. Data obtained with the use of other metal in explosives, such as Lead, show similar results (122).
PBXW-126 which is a composite explosive consisting of approx. equal amounts of RDX, AP, Al and NTO with a polyurethane has been characterized and described by Simpson and coworkers (123). Volk (124) has studied the influence of initiation strength, ambient inert gas, and Al content and polymeric binder on the detonation products of high explosives. He has investigated the influence of the different booster compositions on the initiation of TNT- nitro guanidine explosive. Complete detonation was only observed after placing an additional booster sheet with the same diameter as the explosive charge on the front side of the cylindrical charge. The investigation of Al- containing charge exhibited a very different behaviour, compared with charges not containing Al. The effect of Al was greatly influenced by the oxygen balance of the composition. The PBX charges with a better oxygen balance containing glycicydyl azide binder reacted nearly complete with Al, which was not the case with explosive containing a polyisobutylene binder. Thomas *et al.* (125) have studied the influence of Aluminum on the performance of PBX formulation of RDX/Al/AP/GAP. In this formulation the binder used as GAP and plasticizer was BDNPA/ BDNPF (1/1mix) and curing agent of the binder system was Desmodur N100.

The study shows that charges with same mass showed same peak pressure for the formulations containing Al from 15 % to 35%. Only formulation with higher Aluminium contents supplied decreasing peak pressures. The impulse results are similar to the peak pressure that means impulse for Al contents from 15% up to 35% is nearly constant. Increasing Al content above 40% deceased impulse output.
As expected, Aluminium increased the bubble energy and reached its maximum at about 40% Al content. AP in formulation GHX 76/82 also increased the bubble energy. The charges GHX 99/100/101 with different Al particle sizes from 5μm to 150μm supplied similar bubble energies. They have concluded that during the detonation reaction, resp. during consecutive reaction processes Aluminium has highest affinity to the oxygen in explosive formulation. Any other reducing agents like carbon or hydrogen compete for oxygen, which is not consumed by Aluminium. Besides Aluminium oxide also carbon monoxide is a detonation products of high formation priority.

Up to 30% Al was totally oxidized by oxygen in the explosive formulation (without external oxygen source like air or surrounding water) Al increased the bubble energy with a minimum at 40% -50% Al contents. Pressure and impulse were not influenced by Al contents up to 30%. This point is surprising and the authors have suggested that it should be checked in test arrangements with more pressure gauges closed to the charges.

Aluminium in a layer between charge and surrounding water did not reach the performance of charges with homogeneously incorporated Al. The energy released by reactions between water and Aluminium was less than expected and did not dominate. Charges with Al particle sizes from 5μm to 150μm showed similar performance. Kroh (126) has studied the detonation properties of some plastic bonded Aluminium containing high explosives. He has determined the detonation properties such as sensitivity and explosive energy output by experimental methods. Modified gap tests, Detonation velocity tests and cylinder tests were conducted on each of the various
compositions to get the pressure threshold for deflagration and deflagration to detonation transition, the detonation velocities and the Gurney energy. The compositions tested were. RDX/A1/PB67/18/15, RDX/A1/PB70/15/15, RDX/NQ/A1/PB 55/15/15/15 HMX/A1/PB 70/15/15 (PB=Hydroxyl Terminated Polybutadiene).

To get the characteristic shock to deflagration to detonation transition (SDDT) the modified gap test was performed for each explosive and the shock pressure in the Plexiglas gap at Plexiglas explosive interface was plotted vs. the free surface velocity was measured by the use of a framing camera. The results at 15°C and 110°C show a well-defined transition from shock without reaction to deflagration at low pressures. As the pressure is increasing the Plexiglas gap the RDX/A1/PB and HMX/A1/PB compositions exhibit a rapid build up to detonation where as the explosive that contains nitroguanidine (NQ) exhibits a gradually build up. No significant temperature effect on the shock to deflagration threshold was found. The detonation velocities were measured in confined and unconfined cylindrical charges and compared to theoretical values determined using BKW equation of state.

Mostafa (127) has studied the explosive characteristics of Aluminized Plastic bonded explosives based on octogen and polyurethane binder. Different samples of Aluminized plastic bonded explosives based on octogen and polyurethane were prepared. The Aluminium content was increased in the reference composition, containing 84% octogen and 16% Polyurethane, from zero up to 30% by weight (by decreasing the content of octogen). For the composition containing 15% Aluminium the brisance and detonation velocity were slightly
decreased by 2.13% and 2.75% respectively while in the other direction the heat, temperature and force of explosion were markedly increased by 58%, 37% and 8% respectively. The sensitivity to impact of the prepared explosive compositions were also investigated and markedly decreased by increasing the Aluminium content but all the compositions were sensitive to detonator number eight.

Vinay Prakash et al. (128) have performed the study of influence of Aluminium on performance of HTPB based Aluminized PBXs. The PBXs were processed as per standard procedures. Compositions with different formulations were prepared by varying the percentages of Aluminium and RDX and their explosive properties including velocity of detonation, peak pressure, duration, impulse and sensitivity to different types of stimuli, were studied. The experimental and theoretical values of VOD are compared. It is concluded that about 15% Aluminium content is suitable for achieving optimum explosion effect by blast wave in air. At about 15% Al content in the composition optimum VOD, peak pressure and impulse is achieved.

1.9 OBJECTIVE OF PRESENT STUDY.

From the accounts (review) in the former paragraphs it is clear that the targets are generally defeated by high velocity fragments generated from bursting of casing or due to high blast energy. The blast pressure is effective on small and rigid structure but for destruction of large and flexible structure impulse is effective. Addition of energetic materials like RDX and HMX in higher proportions increases the fragment velocity because of their higher detonation pressure and higher velocity
detonation but impulse improves with addition of Aluminium metal powder.

Exhaustive studies on blast parameters and properties of explosive compositions by varying the percentage of ingredients particularly Aluminium powder in conventional T.N.T based high-energy (H. E) formulation have been reported in literature. However, very limited work has been done on the characteristics of Aluminized Plastic Bonded High Explosive compositions. The present work was undertaken to carry out experimental studies on the behavior of Aluminized plastic bonded high explosive compositions. Author aim of the present work is to develop high performance and low vulnerable PBXs compositions for futuristic ammunitions.

In view of the above, a systematic and exhaustive study has been undertaken on Aluminized PBXs. Methods have been established for preparing cast able Aluminized PBXs based on Aluminium, RDX or HMX using HTPB as polymer matrix. Various compositions were prepared containing varying percentages of these ingredients and a systematic study of the various properties was carried out. The studies include velocity of detonation, detonation pressure, blast parameters, impact and friction sensitivity, vacuum stability and thermal behavior. The experimental values of velocity of detonation and detonation pressure have been compared with the theoretical values from BKW method (129).

Results of present investigation have been reported and discussed in the light of existing knowledge of the subject.
1.9.1 SCHEME OF THE THESIS.

The present thesis is schematically divided into six chapters as given below:

CHAPTER I (INTRODUCTION)

This chapter describes in brief about the explosives, plastic bonded explosives the historical developments in explosive and plastic bonded explosives, blast parameters, metal loaded secondary high explosives and Aluminized explosives, minimum requirement of secondary explosives, advantages and deficiencies of PBXs, polymeric binder and additives used in PBXs. This chapter also covers an overview of experimental and theoretical work carried out by various research workers. Based on the critical review of the work done, so far, the objective of the present study along with the scheme of thesis are presented in this chapter.

CHAPTER II (EXPERIMENTAL)

Important details of equipment and materials used in the present study are described in this chapter. The methods of preparation of Aluminized cast able high explosive PBX compositions is explained, covering all steps including mixing, casting, curing and machining etc. Methodology adopted for the determination of velocity of detonation, detonation pressure, blast parameter, sensitivity (impact and friction), decomposition temperature (DTA, TG, DTG and DSC etc), vacuum stability test and mechanical properties are described.
CHAPTER III (THEORETICAL)

This chapter deals with the theoretical prediction of properties of the PBX formulations used in this study. BKW Code has been used to predict detonation parameters of the Aluminized PBXs. The detail description of BKW Codes has also been discussed in this chapter.

CHAPTER IV (RESULT AND DISCUSSION)

Processing of PBXs has been discussed in this chapter. This chapter also deals with technical data generated during the course of this study and presented in table and figures. All the results are presented in the following order.

Mechanical properties, Chemical stability, Thermal characteristics, Sensitivity, Velocity of detonation, Detonation pressure and Blast parameters.

CHAPTER V

The results of the present study have been discussed in the light of the information reported in the literature and based on the data generated during the course of present investigation.

CHAPTER VI (SUMMARY)

This chapter summarizes various findings of the present study and highlights important aspects observed during the study. Relevant references are included at the end of each chapter. The thesis ends with the list of publication of the author.
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