CHAPTER – II

EXPRIMENTAL
This chapter deals with the description of material, equipments and methods employed in the present study for preparation, processing and evaluation of the Aluminized PBXs.

2.1 MATERIALS

Most of the materials were either procured from ordnance factories or trade. However β–HMX was manufactured in the laboratory (HEMRL).

2.1.1 Cyclotrimethylene trinitramine (RDX)

RDX received from Ordnance factory, Bhandara was used. Different sizes of particles were obtained by recrystallization of RDX with acetone and precipitation in water.

- Assay as RDX: 99.0 %
- Acetone insoluble: < 0.05 %
- Acidity as HNO₃: < 0.015 %
- Melting point (° C): 204
- Vacuum stability: < 4 ml
2.1.2 Cyclotetramethylene tetranitramine (β – HMX)

β – HMX made in pilot plant of HEMRL, Pune, was used. The product was tested as per U.S standard specification M: 1 – H – 45444 B.

- Assay: 98%
- Total insoluble material in acetone: max 0.05 %
- Acidity as acetic acid: max 0.02 %
- Melting point: 277°C
- Inorganic insoluble material: max 0.03 %

2.1.3 Aluminium (Al)

Aluminium powder was of heavy grade obtained from trade.

- Purity: Minimum 99%
- Iron content: > 0.3 %
- Volatile matter: > 0.02
- Particle size: 125μ -250μ
2.1.4 Hydroxyl – terminated poly butadiene (HTPB)

Source: NOCIL, Bombay, India

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volatile matter:</td>
<td>max 0.5 %</td>
</tr>
<tr>
<td>Specific gravity at 23 ° C:</td>
<td>0.60 – 0.92</td>
</tr>
<tr>
<td>Hydroxyl value:</td>
<td>40 – 50</td>
</tr>
<tr>
<td>Moisture content:</td>
<td>0.1%</td>
</tr>
<tr>
<td>Molecular weight (Mn):</td>
<td>2300 to 2900</td>
</tr>
<tr>
<td>Acid Number, Max mg of:</td>
<td>max 1.0</td>
</tr>
<tr>
<td>KOH/g of sample</td>
<td></td>
</tr>
<tr>
<td>Functionality:</td>
<td>2.3 ±0.3</td>
</tr>
</tbody>
</table>

2.1.5 Toluene diisocyanate (TDI)

Source: M/S Fluka AG, Switzerland

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Assay (NCO):</td>
<td>99%</td>
</tr>
<tr>
<td>Acidity as H Cl:</td>
<td>&gt; 0.002%</td>
</tr>
<tr>
<td>Specific gravity at 30 ° C:</td>
<td>1.22 ±0.01</td>
</tr>
<tr>
<td>Isomeric ratio (2, 4; 2, 6):</td>
<td>80 : 20</td>
</tr>
</tbody>
</table>

2.1.6 Ferric acetyl acetone (Fe AA)

Source: M/S Scientific and Industrial Suppliers, Bombay.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Assay:</td>
<td>97%</td>
</tr>
<tr>
<td>Iron Content:</td>
<td>16 ± 0.5 %</td>
</tr>
<tr>
<td>Volatile matter:</td>
<td>&gt; 0.1%</td>
</tr>
<tr>
<td>Melting point:</td>
<td>179 ° C</td>
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<tr>
<td>Particle size:</td>
<td>37 μ</td>
</tr>
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</table>
2.1.7 Diphenyl methane diisocyanate (MDI)

Source: E. Merck, Germany

Mixture of di- and triisocyanates, dark brown viscous liquid.

2.1.8 Hexamethylene diisocyanate (HMDI)

Source: E Merck, Germany

Assay: 99.0 %

2.1.9 Isophorone diisocyanate (IPDI)

Source: Chemisch, Germany

Assay: 99 %

2.1.10 Dioctyladipate (DOA)

Source: Indo Nippon, Bombay, India

Viscosity at 38 °C: 10.5 C S ± 0.5

Specific gravity at 20° C: 0.927 ± 0.002

Refractive index at 20° C: 1.447 ± 0.0010

2.1.11 Trimethyllolpropane (TMP)

Source: E. Merck, Germany

Melting point: 61 °C

Assay: 99.0 %

2.1.12 DBTL

Source: E. Merck, Germany

Assay: 97.0 %
Specific gravity: 1.047

2.1.13 1, 2, 6 Hexanetriol
Source: M/S Fluka AG, Switzerland
Assay: 95.0 %
Boiling point: 145 to 147 °C

2.1.14 Castor Oil
Viscosity at 20° C: 950 – 1050 mpa.s
Saponification value: min 160
Iodine value: 82 – 88
Acid value: max 1
Unsaponifiable: max 1 %

2.1.15 Pyrogallol (1, 2, 3 – Trihydroxy benzene)
Assay: 98 %
Melting point: 131 – 134 °C

2.1.16 Lecithin Soyabean
Source: BDH Laboratory Supplies Pole BH 15 ITP, England
Nitrogen content: 0.8 – 1.2 %
Phosphorous content: 2.0 – 2.5 %
Sulphated ash: 10 %
Assay: 99 %
Moisture: 1.0 %
Viscosity at 25 °C, Poise: 130
Benzene Insoluble matter: 0.2 %
Acid value, mg of KOH / g max 32 of sample
Acetone insoluble matter: max 62 %
Percentage by mass
Lecithin, percentage by mass: 99
2.1.17 Silicone Oil DC 200/200

Source: BDH Laboratory Supplies Pole BH 15 ITP, England

Weight per milliliter at 20 °C: About 0.97 g

2.1.18 Silane (Coupling Agent):

3- (Triethoxysilyl) propyl isocynate.

F.W. : 247.37

B.P. : 283 °C

sp.gr : 0.999

Corrosive

(Store under Nitrogen)

Source: Aldrich Chemical Company, INC.

P.O. Box 355 Milwaukee,

WI 53201 U.S.A.

2.2 METHODS

2.2.1 PROCESSING OF PBX

The processing of PBX was done by mixing the ingredients in a planetary vertical mixer for about 3 hours under vacuum at 45 °C. The casting was done under vacuum at ambient temperature (25°C). Finally, the charges were cured. The duration of curing and curing temperature depend on the curing agent used for curing. A batch of 5 kg of PBX was prepared by this method. Coating it with 2 % desensitizer by slurry method minimized the hazards associated with handling dry RDX. The product was then dried in water - jacketed oven.
To achieve a high solid loading of RDX/HMX in HTPB based PBXs; attention was paid to particle size distribution of the explosive component. Solid loading was optimized by using bimodal and tri-modal mixtures of the explosive.

Hydroxyl - terminated polybutadiene (HTPB) and diisocyanates such as TDI, MDI, HMDI, and IPDI were used for curing of explosive charge. To attain a high solid loading and cast able composition, the viscosity had to be reduced further. This was achieved by di (2 ethyl hexyl) adipate (DOA), as a plasticizer with binder / plasticizer ratio 60 / 40 for getting optimum results.

The NCO /OH ratio was maintained at 1:1 to get same cross - link densities in all PBXs prepared and also to get optimum results in presence of wetting and cross - linking agents.

The binder system must have a low viscosity because of casting requirements. However, a high surface tension of liquid binder can hamper the wetting of explosive particles. In that case good mixing and casting of the product is impossible. To overcome this problem lecithin, a surface - active agent was used. Lecithin, a natural compound gives good results in lowering the surface tension. A flow diagram of the operation involved in the processing of PBX is given in Figure 2.1
Mixing at 45°C for 3 hours

VACUUM CASTING (5 - 10 mm Hg)

At 60°C for 7 days with TDI

CURING

EXTRACTION

MACHINING

CAST PBX CHARGE

1. EXPLOSIVE
2. BINDER
3. PROCESS AID
4. CATALYST

FIG 2.1
FLOW CHART FOR MANUFACTURE OF CASTABLE PBX.
2.2.2 VELOCITY OF DETONATION

Velocity of detonation (VOD) was determined by the flash X-ray method and results confirmed by the pin oscilloscope technique.

2.2.2.1 FLASH RADIOGRAPHY

Principle:

Flash radiography is used to produce single, star or sequential images of a variety of events such as explosions, projectiles in flight, impact phenomena, propagation or detonation or shock waves, casting processes or other events in which there is rapid motion. Radiography is a measuring technique by which a photographic record of an event is obtained by allowing a beam of X-ray to pass through an object into a film. An X-ray beam emanating from the anode of an X-ray tube, is cast into an object (Fig. 2.2). The high energy or short wavelength of the X-ray allows them to penetrate into and to some extent through the object. The amount of radiation that will pass through the object depends on the energy of the radiation, the density and the thickness of the object. Low energy radiation is more easily absorbed than high-energy radiation. Dense or thick parts of the object will absorb more than low density or thin parts. The emerging X-ray beam will thus be intensity modified and this will show up a varying photographic density on the film.
Thus radiography provides us with a technique to record events obscured from direct view and the possibility of looking inside complex objects (1).

Fig 2.2 Experimental set up for flash X ray
Method to determine VOD by flash X-ray method

To determine the VOD of explosive the distance between the triggering positions of the X-ray in the charge from the base of the explosive charge is accurately measured (Fig. 2.3). The radiograph of the event was taken after a predetermined delay 't' which can be adjusted in the flash to X-ray appear after the trigger signal is given. From the radiograph the distance front is measured precisely. For finding out the real distance traveled by the detonation front in the charges, enlargement factor of the radiograph due to varying source, explosive and film distance are considered. The delay, due to the inherent behavior of the unit is added to the predetermined delay in the machine.

Finally, the VOD of the charge is calculated by the formula:

\[ D = \frac{d_0 - d_1}{t + t} \]

Where,
- \( d_0 \) = original length of the charge (from triggering point to base of charge).
- \( d_1 \) = original left over length of the charge (from the detonation front to base of the charge)

\[ d_1 = \frac{d_0}{ef} \]
Fig. 2.3
MEASUREMENT OF VOD BY FLASH X-RAY
ef = enlargement factor which depends on the distance of X-ray film from the charge.

$d_0$ = Left over length of the charge in the shadowgraph (from the detonation front to base of the charge).

t = delay kept in the machine.

$t$ = inherent delay of the charge.

Velocity of detonation was recorded on a 450 KW scanditronic flash X-ray system.

a) Charge diameter --- 35 mm

b) Charge length --- 70 mm

c) Maximum output voltage --- 360 KV (range 150 KV to 450 KV)

d) Peak output current --- 10 KA

e) Pulse width --- 20 ns

f) Radiation dose per pulse --- 20 mR at 1m from the tube window.

g) Anode focal spot --- 1mm diameter

f) Penetration powder --- 18mm steel plate at 2.5m

2.2.2.2 PIN OSCILLOGRAPHY

The detonation wave in explosive contains weakly ionized gases, which enable ionization probes to be used for detection of its arrival. A cylindrical explosive charge of 25 cm length and 3.5 cm diameter is used for VOD measurement by this method. Fine holes are drilled in a row at distance of about 2 cm apart. Ionization probes called 'pins' are inserted
in the holes and are connected to high velocity oscillographs. The first of these probes is connected to the trigger circuit and the rest to the event circuits.

The ionization probes act as shorting contact switches on arrival of the detonation wave. The pulses (positive and negative alternately) are recorded on a high velocity oscillograph. The ionization probe tips were coated with sulfur, because aluminized compositions are themselves conductive. The peaks refer to the time of arrival of the detonation wave to the corresponding ionization probes.

2.2.3 MEASUREMENT OF BLAST PARAMETERS

Two G.I. pipes of 2.5m diameters and 2m long were fixed vertically in the ground with sturdy foundation about 5m apart. Horizontal pipes with a provision for holding the gauges were firmly fixed with suitable clamps to the vertical pipes. The cast charges of 75mm diameter and weight of 500 ± 10 g were placed on a wooden stand (approx. 1m above the average ground level). The blast gauges were positioned at a distance of 1.5m and 2.0m from the center of the explosive charge. The experimental setup is shown in Figure 2.4.
FIG 2.4.

EXPERIMENTAL SETUP FOR MEASUREMENT OF BLAST PARAMETERS.

1 & 2 GI PIPES
3 & 4 GAUGES
5 WOODEN STAND
6 EXPLOSIVE CHARGE
7 DETONATOR
8 LINE POWER UNIT
9 OSCILLOSCOPE
The blast pressure gauges are ICP free field pressure transducers with built in amplifiers. The gauges are of model 113851. Lollipop style with sensitivity 20mV/psi, full-scale range of 0 – 250 psi for 5V output and natural frequency of 500 KHZ. The gauges are positioned in an axial direction to the charge with the sensing surface of the transducer in vertical plane. The line power unit provides constant current excitation to the built in transducer amplifier and couples the transducer to readout instrument (oscilloscope). The line power unit is of the model 482 A05 with transducer excitation range of 2 to 20mA. The blast pressure gauges and the time power unit used are of PCB PIEZOTRONICS INC NEW YORK make. The oscilloscope used is of portable digital storage type with a four trace, dc – to- 10 – MHZ, vertical deflection system. It has an easy to use storage function with cursor measurement of time and voltage. Measurement values are indicated on a four digit, seven-segment light emitting diode display. The oscilloscope is of the Tektronix 468 model and Tektronix INC Oregon make.

The explosive charge was detonated with 20g of PEK – 1 (booster) and electric detonator No. 33 with the help of a 6 volt battery. When the charge is detonated, blast wave moves but almost spherically from the charge. As it crosses a blast pressure gauge the piezo crystal in it developed a charge, which is amplified, the line power unit decouples the signal from the DC bias voltage and the storage mode oscilloscope displays the pressure time curve. The pressure
time curve so recorded is photographed by Tektronix model C-30 cameras on a Polaroid film type 47 for permanent record.

2.2.4 SENSITIVITY TEST:

Sensitivity test determine the minimum susceptibility of a given material to react to an externally applied energy. Sensitivity tests are abstract in view of the fact that they do not necessarily apply to output energies or application. In case, the test is designed for a given set of externally applied energy sources to the system. The reaction may be a rapid output and the analyses may be qualitative or quantitative. Sensitivity tests do not stand alone in establishing safety criteria and parameters, rather, they determine at what energy levels a given material will react.

It becomes essential to study impact, friction and thermal sensitivities of new compositions containing energetic materials as additives, from safety consideration point of view for safe handling, processing and storage. For this purpose a small batch of PBX composition was prepared and studied.

2.2.4.1 IMPACT SENSITIVITY:

Fall hammer apparatus is used to determine the impact sensitivity of explosive composition (2). Fall hammer apparatus is fabricated in the laboratory (in accordance with the Bruceton Staircase Method). A maximum weight of 2 kg is dropped on to the explosive sample from various
heights. The maximum height is 170cm. The apparatus consists of two guide rails along with holding and releasing device for the 'drop weight'. The drop weight is to be fixed at desired height with the help of holding device. The pulley with releasing device is used for frictionless motion of 'drop weight', which falls on sample in testing unit. The testing units are made up of hard steel and consist of accessories like anvil, collar and striker. The Bruceton staircase method is used to calculate the height of 50% explosion.

2.2.4.2 FRICTION SENSITIVITY:

A Julius Peters Apparatus is used to determine the friction sensitivity of PBX composition (3). The apparatus consist of the following parts.

*Three phase electric motor.
*Platform for clamping porcelain plate, with a 10 mm to and fro motion.
*Loading arm with connector for clamping porcelain pin.
*Push button.
*Cut off switch.
*Counter balance weight arrangement and
*Set of different weights.

About 10 mg of sample was tested by placing between pin and plate. The surface of the plate is hard and rough. The different weights varying from 0.5-to 36 kg are held by 'Loading arm'. Friction motion is generated with to and fro motions of plate by using electric motor. The figure of insensitiveness of a sample is given as the load in kg at which
the sample does not deflagrate/explode in six consecutive tests.

2.2.4.3 SPARK SENSITIVITY:

The basic and major components of the system are a high voltage power-supply (30 KV and 5 mA) high voltage storage capacitors, high voltage vacuum relays, and a charging and discharging circuit. The upper pointed electrode is specially designed from copper rod and the lower electrode is flat. A Teflon ring is fixed over lower electrode to form cavity.

5mg of explosive sample was placed in the cavity. Gap between the lower and upper electrode was adjusted to 2 mm. The capacitor (0.1 micro Farad) was charged to high voltage (10 KV). The voltage was then monitored on digital meter. After the capacitor was charged to high voltage, it was discharged through spark gap with the actuation of the relay. The energy was about 5 joules. The energy of the spark gap was calculated

\[ E = \frac{1}{2} CV^2 \]

Where, \( E \) – energy in joules, \( V \) – charging voltage in Volts, \( C \) – capacitance in Farads

If the composition does not ignite up to 5 joules, then it is considered safe to handle as per safety conditions (4). The procedure was repeated 5 times.

2.2.5 STABILITY TESTS:

Stability tests determine if a hazardous material will remain safe and retain its properties during some
specified period of storage. Stability tests may be distinguished from other tests by; (1) the manner in which the stimulus is applied, (2) the rate it is applied, (3) the non-destructive nature of the test, and (4) the objective of the expected results. Usually, in stability testing the stimulus is applied for a longer duration and when heat is applied, the temperatures are below ignition levels of the suspect materials. In some cases there are no stimuli applied; instead long-term storage is observed under a certain set of conditions. The expected results are not initiation, but rather change in weight, volume of gases liberated, discoloration, evolution of oxides, and its ability to function properly after prolonged storage conditions.

Stability tests, in general, are designed to be applicable to one type of material (either pyrotechnics, explosives, or propellants) and are not always suitable for all classes.

Because stability testing is time-consuming, it is often desirable to subject the material to conditions which are more severe than those normally encountered during prolonged periods of storage. Specifically, two environmental factors can influence the stability of a given explosive, (1) humidity and (2) temperature. The latter receives the most attention in determining the stability of a material. In practice, the specimen material is subjected to a higher temperature than those normally encountered, and ultimately the material is tested to verify that it functions as intended at the completion of the elevated temperature study.
2.2.5.1 VACUUM STABILITY:

For VS test, 2.5 g of dried powder was kept in heating tube. Capillary tube was pressed against the heating tube. The cup of the capillary was filled with mercury. Whole assembly was evacuated to 5 mm of Hg and mercury allowed to enter the capillary. The height of the column in the capillary, barometric pressure and room temperature were measured. Tubes were immersed in bath at 120 ± 0.5 °C, after 40 hr were removed from bath and cooled down to room temperature. Again height of mercury column, barometric pressure and room temperature were measured (4). Volume of the gases evolved (ml) was computed.

2.2.6 VISCOSITY MEASUREMENT:

The viscosity was measured by using Brook Field Synchrolectric - Viscometer. It rotates spindle or disc in a fluid and measures the torque necessary to overcome the induced moment of the fluid. Unit of viscosity is in Centi Poise.

2.2.7 MECHANICAL PROPERTIES

Mechanical properties namely, compression strength (CS) and percentage compression, were determined using Instron Universal materials testing machine (model 1185) (5).

For determination of mechanical properties samples of φ 30 mm × 30 mm height were used.
2.2.8 THERMAL ANALYSIS

The term thermal analysis covers a series of techniques, which determines the physical and chemical properties of substance or a mixture as function of time. The most common thermal analysis techniques are thermogravimetry (TG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC). Thermal Analysis of PBX compositions were carried out on STA (TG/DTA/DTG) Mettler Toledo Star System at the heating rate of 10°C/min in air atmosphere. Thermogravimetry (TG) yields quantitative data of weight change associated with a transition, which is represented as a plot of weight change on the ordinate decreasing downward and temperature or time on abscissa increasing from left to right. This curve is used to obtain data on kinetics of chemical reaction, thermal stability of intermediates and final products. The activation energy ΔE, was determined from single TG curve by expressing relationship between the "degree of change α" and time. In the present study a heating rate of 10°C/min was maintained for all the samples. The DTA curve in which the temperature difference ΔT is plotted as ordinate downward or temperature as abscissa increasing from left to right. The signal indicates phase transition, dehydration, and decomposition etc. taking place as endothermic or exothermic effects.
A NETZSCH STA 409 EP thermal analyzer with platinum sample cups and Pt-Pt 10% Rhodium thermocouple was used for the evaluation of thermal parameters of aluminized PBXs with different percentages of Al and RDX. In the present study a heating rate of 10°C/min was maintained for all the samples. The heating rate has linearity within ±0.5% and reproducibility of ±0.1%. Simultaneously DSC/TG was recorded in air atmosphere. The accuracy of TG measurement was 0.05 mg in 1mg.

2.2.9 MICROSCOPY:
Hot stage polarizing microscope has been used for elucidating the microstructure of composition and qualitative examination of ingredient dispersion, interaction wet ability. The Leica DMLP polarizing microscope is used with Mettler Toledo FP 82 HT hot stage. The samples were examined at a magnification of 200 X and at various temperatures ranging from 35 °C to 220 °C. Samples were first put on the microscopic slide and put in between the analyzer and polarizer. Then the light source is turned on and positioned at suitable distance for observation. The observations were recorded at various temperatures, light intensity, angles and aperture.
REFERENCES


