CHAPTER 2

EXPERIMENTAL
During the course of the present study chemicals/materials indicated below are used for the processing of the IR flare pyrotechnic mixtures. The characteristic parameters of the resultant compositions have been studied by employing various techniques and instruments. This chapter gives details of the materials used, the experimental techniques adopted and the equipments used.

### 2.1 MATERIALS

**Magnesium**  
Source: ECKART-WERKE, West Germany

- **Formula**: Mg  
- **Molecular weight**: 24.312 g/mol  
- **Purity**: 99.13 %  
- **Average particle size**: 106 µm  
- **Density**: 1.74 g/cm³  
- **Melting point**: 649 °C

**Sodium nitrate**  
Source: Sun Rise Chemicals, Pune

- **Formula**: NaNO₃  
- **Molecular weight**: 85 g/mol  
- **Purity**: 99.5 %  
- **Melting point**: 307 °C  
- **Density**: 2.26 g/cm³  
- **Particle size**: Passing 240 BS sieve

**Graphite**  
Source: Graphite India Ltd

- **Formula**: C  
- **Molecular weight**: 12 g/mol  
- **Purity**: >99 %  
- **Density**: 2.25 g/cm³  
- **Particle size**: Passing 300 BS sieve
Charcoal

- Molecular formula: $\text{C}_{10}\text{H}_5\text{O}_1$
- Molecular weight: 141 g/mol
- Purity: > 99%
- Density: 1.8-2.1 g/cm$^3$
- Particle size: Passing 300 BS sieve

Anthracene

- Structural formula
- Molecular weight: 178 g/mol
- Purity: 98%
- Density: 1.28 g/cm$^3$
- Melting point: 214 - 216 °C
- Particle size: Passing 120 BS sieve

Teflon

Source: A proprietary product of Du Pont, USA.

- Structural formula
- Molecular weight: 100 g/mol (monomer unit)
- Apparent density: $0.745 \pm 0.1$ g/cm$^3$
- Specific gravity: Min.: 2.19 g/cm$^3$, Max.: 2.25 g/cm$^3$
- Melting Point: 327 ± 10° C
- Fluorine content: 76%
Viton A
Source: A proprietary product of Du Pont, USA.

- Structural formula
- Molecular formula : (C₂H₂F₂)ₘ
(C₃F₆)ₙ
m = 3.5, n =1
- Molecular weight : 374 g/mol
(monomer unit)
- Density : 1.81 g/cm³.
- Fluorine content : 66 %

Kel-F
Source: A proprietary product of Du Pont, USA.

- Structural formula
- Molecular formula : (C₂H₂F₂)ₙ
(C₂ClF₃)ₘ
n = 1, m =3
- Molecular weight : 413 g/mol
(monomer unit)
- Density : 2.02 g/cm³.
- Fluorine content : 50.6 %
Phthalic Anhydride (PA)
Source: ACROS Organics, USA

- Structural formula
- Molecular weight: 148.12 g/mol
- Molecular formula: C₈H₄O₃
- Density: 1.53 g/cm³.
- Purity %: 99 %
- Melting Point: 131 °C
- Boiling Point: 284 °C
- Carbon/Hydrogen Ratio: 24
- Oxygen percentage: 32
- Sieve size: Passing 120 BS sieve

Succinic Anhydride (SA)
Source: ACROS Organics, USA

- Structural formula
- Molecular weight: 100.07 g/mol
- Molecular formula: C₄H₄O₃
- Density: 1.2 g/cm³.
- Purity %: 99 %
- Melting Point: 119 °C
- Boiling Point: 261 ° C
- Carbon/Hydrogen Ratio: 12
- Oxygen percentage: 48
- Sieve size: Passing 120 BS sieve
Benzene Tetra carboxylic dianhydride (BTDA)
Source: ACROS Organics, USA

- Structural formula
- Molecular weight: 218.12 g/mol
- Molecular formula: C_{10}H_{2}O_{6}
- Density: 1.68 g/cm³
- Purity %: 99%
- Melting Point: 283 - 286 °C
- Boiling Point: 397 °C
- Carbon/Hydrogen Ratio: 60
- Oxygen percentage: 44
- Sieve size: Passing 120 BS sieve

Benzophenone Tetracarboxylic dianhydride (BPTA)
Source: ACROS Organics, USA

- Structural formula
- Molecular weight: 322 g/mol
- Molecular formula: C_{17}H_{6}O_{7}
- Density: 1.53 g/cm³
- Purity %: 99%
- Melting Point: 218 – 222 °C
- Carbon/Hydrogen Ratio: 34
- Oxygen percentage: 35
- Sieve size: Passing 120 BS sieve
2.2. Preparation of Ingredients

i. Drying, Grinding and Sieving of Sodium Nitrate

Sodium nitrate is dried in oven at 100 ± 5°C for two hours, cooled to room temperature and pulverized in pulverizer. Pulverized sodium nitrate is spread in less than 10 mm thick layer in clean and dry trays and dried in oven at 100 ± 5°C for two hours. Dried sodium nitrate is sieved through a clean dry 240 BS sieve after cooling and stored in airtight container after packed in polythene bag.

ii. Sieving of Teflon

Teflon is sieved through a clean dry 8 BS sieve taking care to avoid lump formation during sieving. The passed material is preserved with proper label for further processing.

iii. Preparation of Viton Solution

Viton is made into small pieces using knife. Weighed quantity of viton is transferred into the beaker and required quantity of acetone is added. The beaker is covered with aluminum foil and viton is allowed to dissolve overnight. Next day viton solution is mixed by using SS rod.

iv. Drying, Grinding and Sieving of Barium Peroxide

Barium peroxide is prepared as per the procedure described for sodium nitrate. It is packed in polythene bag after sieved through a clean dry 170 BS sieve and stored in airtight container with label used for preparation of priming composition.

iv. Preparation of Binder Mix

Required quantity of epoxy resin is weighed in a bowl and hardener is thoroughly mixed aluminum/SS rod. This mix is used immediately for preparation of priming composition.
2.3. Preparation of Pyrotechnic Compositions

i. Magnesium/Sodium nitrate/Grahite, Charcoal, Anthracene compositions

Weighed quantity of magnesium powder is transferred to a clean and dry aluminium / SS tray. Magnesium powder is made wet using acetone and spread uniformly without spillage. Weighed quantities of sodium nitrate (passing 240 BSS) as well as carbonaceous fuel are transferred to magnesium powder and thoroughly mixed without spillage. The entire bulk of composition is carefully sieved using a clean dry 14 BS sieve. The composition is air dried in thin layer in a tray at room temperature for 5-6 hours with proper label. The composition is packed in dry condition in an antistatic bag with label. This bag is stored in SS/Aluminium container containing freshly dried silica gel bag. The container is hermetically sealed.

ii. Magnesium/Teflon/Viton compositions

Weighed quantity of magnesium powder is transferred to a clean and dry aluminium / SS tray. Viton solution is mixed thoroughly without spillage using aluminium / SS rod and transferred to the centre of the spread magnesium powder. A small quantity of dry magnesium powder is added in the empty bowl used for mixing viton solution to extract residual binder and transferred to the main magnesium powder viton solution. Entire mixture of magnesium powder is coated thoroughly and uniformly with viton solution and spread uniformly without spillage. Coated magnesium is allowed dry in air at room temperature for 15 min. and sieved through 25 BS sieve. Weighed quantity of teflon is transferred to viton coated magnesium powder and mixed thoroughly without spillage. Entire bulk of composition is sieved carefully using a clean dry 8 BS sieve by circular motion in wet condition. At a safe distance from bulk composition, the blocked sieve can be slowly and carefully cleared using clean dry brass wire brush. The composition is air dried and stored as per procedure described in 2.3 i

iii. Magnesium/Sodium nitrate/Teflon compositions

Teflon based composition is prepared as per the procedure described in 2.3.1. The composition is sieved by using a clean dry 8 BS sieve and packed after drying in air.
iv. Magnesium/Sodium nitrate/Viton, KelF compositions

Viton/KeLF based composition is prepared as per the procedure presented in 2.3.ii. Magnesium powder is coated by viton/KeLF solution, coated magnesium is sieved through 25 BS sieve 3-4 times, in wet condition sodium nitrate is added to coated magnesium and mixed thoroughly. The composition is sieved through 25 BS sieve again for 3-4 times, dried in air for 3-4 hours at room temperature. The dried composition is packed in antistatic bag and stored in aluminum container.

iv. Magnesium/Sodium nitrate/organic anhydrides/Viton compositions

Anhydride based compositions are also prepared as per the procedure presented in 2.3.ii. Magnesium powder is coated by viton solution, coated magnesium is sieved through 25 BS sieve 3 - 4 times, in wet condition sodium nitrate and anhydride is added to coated magnesium and mixed thoroughly. The composition is sieved through 25 BS sieve 3 - 4 times and dried in air for 3 - 4 hours at room temperature. The dried composition is packed in antistatic bag and stored in aluminum container.

vi. Preparation of priming composition

Magnesium powder is coated by epoxy resin mix, coated magnesium is sieved 3 - 4 times through 25 BS sieve. Sodium nitrate is added to coated magnesium and mixed thoroughly. The composition is kept for 3 - 4 hour at room temperature and sieved again 3-4 times through 25 BS sieve. Finally the composition is cured at room temperature for 24 hours, sieved, packed and stored.

2.4 Processing of IR Flare

i. Fixing of paper liner to steel Tube:

Steel tubes are washed twice with toluene in a clean aluminium / stainless steel tray to remove the dust and oily matter. The tubes are again washed with acetone carefully by immersing in another clean tray containing acetone to remove the greasy matter. Washed tubes are wiped (internally and externally) with a piece of coarse white cotton cloth, dried in an hot air oven at 80 °C for two hours and then allowed to cool to room temperature. A thin layer of araldite mix is applied over the outer surface of a paper liner using appropriate metallic rod/wooden stick and fixed into steel tube. Excess of
resin (if any) is removed from steel tube by using a coarse white cotton cloth. The external surface of steel tube is cleaned by wiping with a piece of coarse cloth. Steel tubes are allowed to cure overnight in horizontal position at room temperature. Finished tubes are packed in polythene bag and stored air tight stainless steel / aluminium container with proper label till use.

ii. Filling of IR Flare

The components of mould set are cleaned by immersing in toluene for five minutes and then in acetone. Components are dried initially in air after wiping with a piece of coarse white cotton cloth and then in hot air oven at 80 °C for half an hour to remove solvent traces, if any. Subsequently, components are removed from oven and allowed to cool to room temperature. Graphite is applied to the components of mould as well as a steel tube and assembled. Assembled Mould is positioned on the die table of press and steel tube is inserted into the mould. Weighed quantity of composition is transferred to the mould slowly using appropriate brass funnel with intermittent ramming using brass /wooden rod. Weighed quantity of 1g booster composition (50:50, wt. : wt. mixture of composition & priming composition) is spread uniformly over flare composition and top of composition is leveled by using appropriate wooden rod. Plunger is placed in the mould over the composition and composition is pressed under 5 ton dead load for 15 s. Filled tube is extracted from the mould using extractor. Filled height is determined by measuring the unfilled height of the filled IR flare. Subsequently, it is packed and stored.

iii. Assembly of IR Flares:

1 g of priming composition is placed on top of the filled IR flare, squib is placed on priming composition charge and closed with paper tape. The leads of the squib are shorted and packed in antistatic bag.

2.5 Equipments and Methodology

i. Ignition Temperature

Locally fabricated DTA apparatus is used to determine the ignition temperature of the sample at a heating rate of 40° C /min using 10 mg sample. The pyrotechnic sample is
heated with an inert reference material under a controlled temperature programme and the
difference in the temperature of both is plotted against temperature/time. DTA is a
microprocessor controlled temperature programmable equipment and has facility of
varying the heating rate.

ii. Bomb Calorimeter

The cal val is determined using bomb calorimeter (LECO AC 500). A Sample of
known mass is placed in the chamber of metal pressure vessel - called a bomb in a argon
atmosphere and ignited with an electric spark. The energy released on combustion of
sample is absorbed within the calorimeter and the resulting temperature change within the
absorbing medium is noted. The heat of combustion of the sample is then calculated by
multiplying the temperature rise in the calorimeter by a previously determined energy
equivalent or heat capacity determined from previous tests with a standardizing material.

iii. Infra Red Radiometer

The Infra Red intensity measurements of the pyrotechnic compositions are carried
out using a computerized spectroradiometer of RMP France (SR 5000). The IR
spectroradiometer detects and analyses IR intensity in the wavelength range of 1.1- 2.5, 2
- 2.4, 2-3, 3 - 5, and 8 - 13 µm and recorded IR intensity in spectral mode. The important
features of the radiometer are as follows:

<table>
<thead>
<tr>
<th>Feature</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spectral scanning range</td>
<td>2.5 µm to 14.5 µm with a continuously variable filter (CVF) used for scanning the range.</td>
</tr>
<tr>
<td>Field of view</td>
<td>Total eight positions of field of view i.e. 0.5, 1, 2, 3, 4, 8, 10, 12.5 milliradian.</td>
</tr>
<tr>
<td>Scan rate</td>
<td>0.5 to 64 s / scan.</td>
</tr>
<tr>
<td>Focusing range</td>
<td>3 m to infinity.</td>
</tr>
<tr>
<td>Detectors</td>
<td>i. Pyroelectric detector - Range 1 - 22 µm.</td>
</tr>
<tr>
<td></td>
<td>ii. Indium antimonide/mercury cadmium telluride sandwich detector cooled by liquid nitrogen. Range 1 - 14.5 µm.</td>
</tr>
</tbody>
</table>
Chopping frequency : 50 Hz to 1000 Hz.

The following modes are available for the infrared radiation measurements.

- **spectral Mode**: In this mode, the spectral IR emittance of objects can be measured in the wavelength region of 2.5 - 14.5 µm, using CVF.

- **radiometric Mode**: The IR intensity can be measured as a function of time using five discrete band pass filters (1.1 - 2.5, 2 - 2.4, 2 - 3, 3 - 5, and 8 - 13 µm) or at single wavelength using CVF. The basic instrument consists of two main systems:

- **optical System**: It consists of a number of mirrors. The primary mirror collects the radiation and focuses on the secondary mirror. The secondary mirror deflects the radiation 90° of the primary mirror onto the detector. A chopper chops the beam radiation, which is then focused on the field stop. The size of the latter determines the field of view of the instrument. The radiation passes through the field stop and thereafter through CVF or discrete band pass filter, and subsequently focused on the detector using re-imaging mirror.

**Instrumental setup for measurement of IR intensity of flare:**

Measurement of IR intensity of different type of IR flares in different wave bands of IR region of an electro magnetic spectrum, a dedicated facility is created. It consists of a sheet metal tunnel of 0.5 m dia with a provision of firing stand. Firing tunnel incorporates an exhaust fan to achieve wind velocities of 8 m/s. Normally firing stand is positioned at a distance of 0.5 m from the front face of tunnel so as to fix the IR flare. Wind speed of exhaust fan is adjusted to 8 m/s. A separate building at a distance of 30 m away from tunnel building is constructed to position SR-5000, IR Radiometer. Radiometer is calibrated periodically using black body. Before each firing, alignment of firing stand is carried out by lighting 1000 Watt lamp and focusing radiometer on it. After satisfactory alignment of radiometer, lamp is removed and sampled flares are fired one by one in switched on position of exhaust fan to remove away smoke from the flame of fired flare. Total burn time and IR Intensity is recorded using IR radiometer.
iv. Impact Sensitivity

The impact sensitivity of formulations is determined by “Fall Hammer Apparatus” using Bruceton Staircase method. In this method, sample is placed between two surfaces of two aluminium foils and is subjected to impact of drop weight. Depending on the drop weight mass and drop height, the initiation of the sample may or may not occur. The drop height that enables the initiation of the tested explosive by the preselected drop-weight is the measure of its impact sensitivity. During this work, the test is conducted by subjecting ~ 20mg of sample kept between the aluminum foils placed between hardened flat steel anvil and the striker, to initiation by a 2 kg drop weight. To start with, the test is carried out at an arbitrary selected height of fall and for the next trial, either the next lower or the next higher height is chosen depending on whether explosion did or did not take place respectively. A set of 25-30 experiments is conducted at height intervals of 5 cm for each composition. The height of 50% explosion (H₅₀) is determined by the statistical methods. The assumption made is that if in a test conducted at a given height (E), an explosion occurred, then explosion would occur from he height (e) (i.e. higher than height (E) and for a given height (N), if no explosion occurred, then explosion would not occur at height (n) lower tan height (N).

The percentage of explosion is calculated by counting the points of (E) and (e) for the height under consideration and dividing by the total number of points of (E), (e), (N) and (n). Thus,

\[
\text{Percentage explosion} = \frac{\text{Points (E) + (e)}}{\text{Points (E) + (e) + (N) + (n)}} \times 100
\]

The height for 50 % probability or median height of explosion (H₅₀) is determined from the plot of fall height versus percentage explosion. Figure of insensitivity (FOI) is calculated from H₅₀ of tetryl (CE) as standard under similar conditions.

\[
\text{FOI of an explosive} = \frac{\text{H}_{50} \text{ of given sample}}{\text{H}_{50} \text{ of tetryl (CE)}} \times 70
\]
iv. Friction Sensitivity

The sensitivity of pyrotechnic compositions to friction stimuli is determined using a standard Julius Peters apparatus operating up to 36 kg load\(^4\). To determine the sensitivity to friction, a carbon paper is placed on porcelain plate. The loading arm is fitted with a pin and the arm is slowly lowered on the carbon paper to mark the contact point between plate and pin. A sample weighing about 5 mg is scooped and placed on the mark. The pin fixed in the loading arm is carefully set on sample. A suitable weight is loaded on the correct slot of the loading arm to transmit a frictional force as per calibrated chart of the apparatus. On operating the apparatus, the porcelain plate exerted a to and fro motion under the pin with stroke length of 10 mm. The frictional load is recorded for each observation of explosion of the sample. The load for consecutive five no. of explosions is considered to be the limit for friction sensitivity. Pin and plate set is replaced for each set.

vi. Thermo Chemical Calculations

REAL code developed by Belov G.V.\(^5\) is used for the thermo-chemical calculations. Only two thermodynamic parameters and mass content of chemical elements in the system are to be assigned to determine equilibrium composition and related properties of the system. Any pair of six equilibrium parameters may be assigned viz. pressure (P), temperature (T), enthalpy (H), entropy (S) and internal energy (U).

Parameters of adiabatic expansion down to a given pressure and volume can also be calculated. Simulation is possible for partially non-equilibrium systems. To perform the computer simulation one can choose the following equation of states (EOS); Ideal gas or Virial EOS (with three coefficients).

Input parameters for REAL are, composition of the thermodynamic system, parameters that define equilibrium, directives that set up special demands for the process of calculation and output of the results. The program analyzes and controls all the input information. Results of calculation give the following information; EOS, assigned thermodynamic parameters, contents of chemical elements per kg of the system.
It displays three tables. First table gives for equilibrium parameters containing the information regarding pressure, specific heat at constant pressure (Cp), temperature (T), temperature of condensed gases (Lt), volume (V), viscosity (Mu), mol / kg (M), entropy (S), sound velocity (a"), enthalpy (H), specific heat at constant volume (Cv"), internal energy (U), gas volume (Vg) and mass of condensed products (M_{cond}). Second table gives quantitative values of concentration of species in moles/kg. Third table gives values for frozen parameters such as Cp, Cp/Cv, sound velocity and a constant K.

vii. Thermal Analysis

Thermal analysis of ingredients is carried out on Differential Scanning Calorimeter (DSC) [Perkin Elmer]. In DSC, 2-3 mg of sample is subjected to heating rate of 10 °C/min. under dynamic nitrogen atmosphere.

Thermal analysis of compositions is carried out on Differential Scanning Calorimeter (DSC) /Thermo Gravimetric Analysis (TGA) [SDT Q 600 thermal analyzer]. 2-3 mg of sample is subjected to heating rate of 10 °C/min. under dynamic nitrogen atmosphere.

viii. Combustion Products Analysis by GC

Gaseous products analysis is carried out on GC (NUKON) using thermal conductivity detector. One gram of sample is burned in bomb calorimeter under air. About 100 µL gaseous sample collected from the bomb is injected into the GC column (porapack Q) through auto injector and chromatogram is recorded. The GC is calibrated for CO₂ using standard gas sample.
2.6 REFERENCES

1. The intelligent infrared spectro radiometer (catalogue), RMP, France.

2. Computerized IR spectro radiometer (instruction manual), RMP, France.

