CHAPTER 2
MATERIALS AND METHODS
This chapter deals with the materials, their specifications, source of supply and methods used for synthesis of various flexibilizers. It also describes the details of the methods used for characterisation of flexibilizers and their cured formulations with Dobeckot E-4. The characteristics of the cured formulations which were studied are gel time ($G_t$), exotherm peak temperature ($E_{pt}$), tensile strength, % elongation, plasticizer absorption, heat resistance, oxygen index, brittle temperature, thermal conductivity, Shore hardness. In order to assess the suitability of these flexibilized formulations for functional test, composite propellants inhibited with the selected flexibilized formulation were x-rayed and statically evaluated. The details of methods of inhibition, x-ray screening and static evaluation are also given in this chapter.

2.1 MATERIALS, THEIR SPECIFICATIONS AND SOURCE OF SUPPLY

1) Novolac Epoxy Resin, Dobeckot, E-4

It is an epoxy resin based on cashew nut shell liquid (CNSL) and compatible with diglycidyl ether of Bisphenol-A (DGEBA) based epoxy resin in all proportions.

SPECIFICATION

<table>
<thead>
<tr>
<th>Type of compound</th>
<th>CNSL based novolac epoxy resin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Colour and appearance</td>
<td>Amber coloured clear liquid</td>
</tr>
</tbody>
</table>
Density at 25°C, g/ml : 1.064 ± 0.002
Viscosity at 25°C, cPs : 17,120 ± 100
Epoxide equivalent : 330 ± 35
Volatile matter, % max : 3.0 ± 0.1
Flash point, °C : > 100
Storage stability at 25°C, months (in original containers) : 6

SOURCE
Dr. Beck & Co (India) Ltd., Pune.

ii) **Hardener, EH-411**

It is a medium viscosity, room temperature curing polyamide hardener and imparts the following characteristics to the cured resin.

- Good flexibility
- High impact resistance and excellent mechanical properties
- More pot life and low exotherm peak temperature (EpT)
- Better electrical and chemical resistance to cured resin.

**SPECIFICATION**

Type of compound : Polyamide
Appearance : Yellowish brown, clear and viscous liquid
Density at 25°C, g/ml : 0.98 ± 0.01
Viscosity at 25°C, cPs : 17,750 ± 100
Flash point, °C : > 100
Storage Stability at 25°C, months : 6 (in original containers)

**SOURCE**

Dr. Beck & Co (India) Ltd., Pune.

iv) **Antimony Trioxide (Sb₂O₃)**

It is used as a filler and improves heat and flame retardant characteristics of the resins.

**SPECIFICATION**

Appearance : White amorphous powder
Purity, % min : 99.5
Sieve size : All passing through 200 BSS and retained on 240 BSS
Specific gravity at 25°C. : 5.3 ± 0.5

**SOURCE**


v) **Composite Propellants**

Composite propellants having the following composition and possessing the following properties were used for inhibition and static evaluation.
Composition

a) Ammonium perchlorate, % : 66
b) Aluminium powder, % : 19
c) HTPB binder, % : 15
d) PEGMS parts : 0.3

The propellant was made by "Casting Technique" as described in the literature. The properties/characteristics of this composite propellant are

a) Density, g/ml : 1.75 ± 0.02

b) Burning rate at 70 kg/cm², mm/sec.

b) Burning rate at
8.4 ± 0.1

70 kg/cm², mm/sec.

9) Tensile Strength, kg/cm² : 12.0 ± 1

d) Elongation, % : 4.0 ± 1

vi) Cardanol (OH, C₆H₄.C₁₅H₂₇)

Colour (freshly distilled) : Pale straw coloured liquid

Density at 25°C, g/ml : 0.9272 ± 0.001

Viscosity at 30°C, CPs : 52.58 ± 10

Volatile matter, max % : 3 ± 0.1

Acid value, max : 5 ± 1

Hydroxyl value : 180 ± 10.00

SOURCE

M/s. Mercury Resins & Polymers Pvt. Ltd., Hyderabad, India.
vii) **Epichlorohydrin**

**SPECIFICATION**

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boiling point, °C</td>
<td>116 ± 1</td>
</tr>
<tr>
<td>Refractive index at 20°C</td>
<td>1.4380 ± 0.005</td>
</tr>
<tr>
<td>Density at 25°C, g/ml</td>
<td>1.183 ± 0.001</td>
</tr>
<tr>
<td>Purity, %</td>
<td>Not less than 99</td>
</tr>
</tbody>
</table>

**SOURCE**

M/s. Thomas Baker & Co., Bombay, India

viii) **Ethylene Glycol**

**SPECIFICATION**

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boiling point, °C</td>
<td>197 ± 2</td>
</tr>
<tr>
<td>Refractive index at 20°C</td>
<td>1.4310 ± 0.005</td>
</tr>
<tr>
<td>Density at 25°C, g/ml</td>
<td>1.113 ± 0.001</td>
</tr>
</tbody>
</table>

**SOURCE**

M/s. Glaxo Laboratories, Bombay, India

ix) **Diethylene Glycol**

**SPECIFICATION**

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boiling point, °C</td>
<td>245 ± 2</td>
</tr>
<tr>
<td>Refractive index at 20°C</td>
<td>1.446 ± 0.005</td>
</tr>
<tr>
<td>Density at 25°C, g/ml</td>
<td>1.118 ± 0.001</td>
</tr>
</tbody>
</table>

**SOURCE**

M/s. Glaxo Laboratories, Bombay, India
x) **Propylene Glycol**

**SPECIFICATION**

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boiling point, °C</td>
<td>186 ± 2</td>
</tr>
<tr>
<td>Refractive index at 20°C</td>
<td>1.4320 ± 0.005</td>
</tr>
<tr>
<td>Density at 20°C, g/ml</td>
<td>1.036 ± 0.001</td>
</tr>
</tbody>
</table>

**SOURCE**

M/s.Glaxo Laboratories, Bombay, India

xi) **Dipropylene Glycol**

**SPECIFICATION**

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Refractive index at 20°C</td>
<td>1.4410 ± 0.005</td>
</tr>
<tr>
<td>Density at 25°C, g/ml</td>
<td>1.023 ± 0.001</td>
</tr>
<tr>
<td>Flash point, °C</td>
<td>137 ± 2</td>
</tr>
</tbody>
</table>

**SOURCE**

M/s.Glaxo Laboratories, Bombay, India

xii) **Polyethylene Glycol**

**SPECIFICATION**

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight</td>
<td>190 - 210</td>
</tr>
<tr>
<td>Specific gravity at 20°C</td>
<td>1.12 ± 0.02</td>
</tr>
<tr>
<td>Viscosity at 25°C, CPs</td>
<td>4.0 ± 0.5</td>
</tr>
</tbody>
</table>

**SOURCE**

M/s.Glaxo Laboratories, Bombay, India
2.2 METHODS

The methods employed for this study may be categorized as follows:

1) Synthesis of epoxy flexibilizers
2) Characterisation of uncured epoxy flexibilizers
3) Characterisation of cured Dobeckot, E-4-flexibilizer formulations
4) Characterisation of selected Formulation-7 and Formulation-8 with antimony trioxide.
5) Inhibition, x-ray screening and static evaluation of inhibited composite propellants

2.2.1 Synthesis of Epoxy Flexibilizers

The epoxy flexibilizer was synthesized by following a "2-step" process.

In the first step, glycol, freshly distilled cardanol and 1:1 H_2SO_4 (2%) were charged in a three-necked flask placed in a heating mantle. The mixture was refluxed for 6 hrs. The product obtained was washed with water till it is free from SO_4^2- ions.

The prepolymer obtained in the first step was treated with epichlorohydrin in the presence of 40% NaOH aqueous solution which was added drop by drop. The rate of
addition of aqueous NaOH solution is being kept very slow so that the temperature does not exceed \( \approx 15^\circ C \).

The liquid flexibilizer and solid NaCl formed during the reaction were separated by using a separating funnel. At this stage, the flexibilizer was washed with distilled water several times and finally water was removed by applying vacuum at \( \approx 55^\circ C \).

Similarly, five other flexibilizers were prepared using different glycols such as EG, DEG, PG, DPG and PEG-200 and their compositions are as shown in Table 2.

2.2.2 Characterisation of Uncured Epoxy Flexibilizers

These flexibilizers, as such were characterised for:

i) Epoxide equivalent

ii) Viscosity

iii) Infrared (IR) & Nuclear Magnetic Resonance (NMR) Spectra

iv) Number average molecular weight, \( (M_n) \)

i) **Epoxide Equivalent**

It is defined as the weight of resin in grams which contains one gram equivalent of epoxide and was determined by reacting weighed quantity of sample with excess of HCl. The amount of HCl consumed was found out by back titration using standard KOH solution.
Table 2: Compositions of Flexibilizers

<table>
<thead>
<tr>
<th>Flexibilizer</th>
<th>Glycols*</th>
<th>Cardanol Moles</th>
<th>Epichlorohydrin Moles</th>
<th>Sodium Hydroxide Moles</th>
</tr>
</thead>
<tbody>
<tr>
<td>1**</td>
<td>Ethylene glycol</td>
<td>2.0</td>
<td>1.1</td>
<td>1.0</td>
</tr>
<tr>
<td>1</td>
<td>Ethylene glycol</td>
<td>2.0</td>
<td>2.1</td>
<td>1.0</td>
</tr>
<tr>
<td>2</td>
<td>Diethylene glycol</td>
<td>2.0</td>
<td>2.1</td>
<td>1.0</td>
</tr>
<tr>
<td>3</td>
<td>Polyethylene glycol</td>
<td>2.0</td>
<td>2.1</td>
<td>1.0</td>
</tr>
<tr>
<td>4</td>
<td>Propylene glycol</td>
<td>2.0</td>
<td>2.1</td>
<td>1.0</td>
</tr>
<tr>
<td>5</td>
<td>Dipropylene glycol</td>
<td>2.0</td>
<td>2.1</td>
<td>1.0</td>
</tr>
</tbody>
</table>

* The molar proportion of glycols was 1 mole in all flexibilizers.

** The Dobeckot - Flexibilizer - Polyamide formulation did not cure properly and pieces remained tacky even after one week and therefore, further work was not pursued.
About 0.25 - 0.30 gms of sample was weighed accurately in a small conical flask and dissolved thoroughly in 25 ml acetone. Then 25 ml hydrochloric acid solution in acetone (prepared by mixing 1.5 ml HCl to 100 ml acetone) was added and kept for 20 minutes with vigorous shaking. It was then titrated with 0.1 N methanolic solution of potassium hydroxide using potassium salt of cresol red as the indicator.

Similarly blank titration was also done without taking sample and keeping all other quantities same as that for sample. The epoxide equivalent was calculated as

\[
\text{Epoxide Equivalent} = \frac{1000 \times \text{Wt. of Flexibilizer}}{\text{(Blank Reading-Back Reading) x Normality of KOH}}
\]

ii) **Viscosity**

The viscosity of the flexibilizers was measured at room temperature with Brookfield Viscometer, Model RVTD. (Supplied by M/s. Brookfield Engineering Laboratories Inc., USA), as per the procedure given in the manual.

iii) **Infrared (IR) and Nuclear Magnetic Resonance (NMR) Spectra**

The IR spectra of all prepolymer and flexibilizers were recorded on Perkin-Elmer IR Spectrophotometer, Model 683 by smear method. The NMR spectra were recorded in CDCl₃/TMS solution using varian FT-80 NMR Spectrometer.
iv) **Number Average Molecular Weight (Mn)**

The molecular weight of polymers is generally expressed as the average of the molecular weights of all the molecules present in them. The two most commonly expressed molecular weights are: number average molecular weight ($M_n$) and weight average molecular weight ($M_w$).

The number average molecular weight ($M_n$) is defined as the total weight of all solute species divided by the total number of moles present i.e.

$$
\overline{M_n} = \frac{\sum_i N_i M_i}{\sum_i N_i} \quad \ldots \ldots (2).
$$

- $N_i$ = Number of moles of solute of species i
- $M_i$ = Molecular weight of species i
- $N_i M_i$ = Actual weight of species i

It is highly sensitive to the presence of small number fraction of low molecular weight macromolecules. It is determined by membrane osmometry, cryoscopy and end group analysis which depend on the number of molecules present.

The weight average molecular weight ($M_w$) is defined as

$$
\overline{M_w} = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i} \quad \ldots \ldots (3).
$$
It is highly sensitive to the presence of small amounts, by weight of high molecular weight macromolecules and is obtained from the light scattering and ultracentrifugation methods which depend upon the weight of solute.

The $\overline{M}_n$ was determined by Molecular Weight Apparatus, Model 233 (supplied by Wescon Instruments, Inc., USA) which is based on the principle that the vapour pressure of a solution is lower than that of the pure solvent at the same temperature.

The apparatus includes (Fig. 9A, 9B, 9C) a measuring chamber containing two thermistors, a solvent reservoir, and two wicks to saturate the chamber with solvent vapours. The two thermistors are connected electrically in a bridge circuit and the bridge imbalance is measured by a very sensitive detector circuit. The temperature of chamber is controlled by a precision electronic controller. The bridge balance is achieved with solvent on both thermistors. The solvent on the thermistor is then replaced by solution. Because of the lower vapour pressure of the solution, a temperature difference is created between the two thermistors and is measured as a bridge imbalance. The molecular weight is calculated from this imbalance provided calibration of the apparatus has already been done with a sample of known molecular weight.
FIG. 9A—SYRINGE UNIT ASSEMBLY OF MOLECULAR WEIGHT APPARATUS
FIG. 9B - CHAMBER UNIT ASSEMBLY OF MOLECULAR WEIGHT APPARATUS
FIG. 9C-MOLECULAR WEIGHT APPARATUS
The solutions of various concentrations (7-8) of an unknown sample and standard (Benzil) in toluene ranging from 0.001 to 0.01 M were made and temperature of the chamber was set just below the boiling point of the solvent used i.e. around 110°C. When the instrument got stabilised, rear syringe was replaced by the most dilute solution and mV was recorded. The equilibrium mV readings for all concentrations of standard as well as unknown sample were recorded and accordingly, $V$ was calculated by subtracting the mV for pure solvent. The $(\Delta V/C)$ was then calculated by dividing the $\Delta V$ value by corresponding value of concentration $(c)$ in gms/litre, and graphs [$(\Delta V/C)$ Versus $C$] were plotted separately for standard as well as unknown sample. The $M_n$ was calculated by the following equation.

$$M_1 C_1 = M_2 C_2$$

...(4).

where

$M_1$ = molecular weight of known sample

$M_2$ = molecular weight of unknown sample

$C_1$ and $C_2$ are intercepts on Y-axis.

### 2.2.3 Characterisation of Cured Dobeckot E4-Flexibilizers Formulations

The formulations of Dobeckot, E4-flexibilizers are as shown in Table-3 and were characterised for
<table>
<thead>
<tr>
<th>Formulation</th>
<th>Flexibilizer</th>
<th>Composition (By wt)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Flexibilizer + Dobeckot.E4 + Hardner.EH-411</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>Flexibilizer-1</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>Flexibilizer-2</td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>Flexibilizer-3</td>
<td>1</td>
</tr>
<tr>
<td>5</td>
<td>Flexibilizer-4</td>
<td>1</td>
</tr>
<tr>
<td>6</td>
<td>Flexibilizer-5</td>
<td>1</td>
</tr>
<tr>
<td>7</td>
<td>Flexibilizer-1</td>
<td>1</td>
</tr>
<tr>
<td>8</td>
<td>Flexibilizer-2</td>
<td>1</td>
</tr>
<tr>
<td>9</td>
<td>Flexibilizer-3</td>
<td>1</td>
</tr>
<tr>
<td>10</td>
<td>Flexibilizer-4</td>
<td>1</td>
</tr>
<tr>
<td>11</td>
<td>Flexibilizer-5</td>
<td>1</td>
</tr>
</tbody>
</table>
i) Gel Time and Exotherm Peak Temperature

ii) Tensile strength and % Elongation

iii) Plasticizer absorption

iv) Heat resistance

v) Brittle temperature

vi) Oxygen Index

vii) Thermal conductivity

viii) Hardness

i) **Gel Time and Exotherm Peak Temperature**

The time corresponding to sudden build-up of viscosity (known as gelling) of known weight of resin at a definite temperature after adding hardener, is defined as "Gel Time" ($G_t$). The highest temperature which is recorded during gelling is defined as Exotherm Peak Temperature ($E_{pt}$). The Gel time was measured by Gelation Timer, Model GT-4 (Fig. 10) (supplied by Techne, Cambridge, UK) and $E_{pt}$ was measured by inserting a laboratory thermometer (with a least count of 1°C) in the resin and recording the rise in temperature periodically while determining gel time.

The Gelation Timer consists of a disc-type plunger, hanged from a linkage which is crank driven by a synchronous motor and a digital counter (in minutes) which is also connected to the synchronous motor. The plunger
FIG. 10—GELATION TIMER
falls in a liquid polymer under gravity and is pulled up by the synchronous motor. At the gel point, rigidity of polymer supports weight of the disc resulting in stoppage of the synchronous motor as well as digital timer by a relay mechanism and gel time is displayed on digital counter. The neon lamp by the side of digital counter also indicates the gel time by a flash of light.

A weighed quantity of formulation (100 gm), was taken in an aluminium cup (45 mm diameter and 77 mm length) and immersed in a constant temperature waterbath by holding the cup in a clamp. It was immersed in a way so that the resin level was below the water level of the water bath. The bath temperature was maintained at 40°C ± 1°C. When the resin attains the temperature of the bath i.e. 40°C ± 1°C, required quantity of hardener was added and mixed thoroughly. The plunger was operated simultaneously followed by an insertion of a thermometer in the resin. The digital timer also starts displaying time when the plunger goes up and down. The temperature of the resin was also recorded by the thermometer every 5 minutes. The plunger and timer stop at the gel point and gel time was displayed on the digital counter. The temperature of the resin was recorded till it became maximum and then declined by a few degrees. A mean of 3 readings was taken and reported as $G_t$ and $E_{PP}$. 
ii) **Tensile Strength and Elongation**

The test specimens (dumbells) were cast in a mould as shown in Fig. 11. The tensile testing machine, Model, TTC-M (Supplied by Instron Co, UK) was used for the determination of these properties. The test specimen was clamped in the jaws of the machine and the tension was applied at the constant rate of traverse ie. 5 cm/min. The elongation and the maximum load at break were recorded on a chart paper. The cross-sectional area of the central part of dumbell was measured with a micrometer screw gauge and tensile strength was calculated as

\[
\text{Tensile strength} = \frac{\text{Load at break}}{\text{Cross-sectional area}} \text{ kg/cm}^2 \quad \text{(5)}
\]

\[
\text{Percentage elongation} = \frac{\text{Increase in length}}{\text{Initial length}} \times 100 \quad \text{(6)}
\]

iii) **Plasticizer Absorption**

This is generally measured by "Sandwich Method" or "Liquid Absorption Method". The "Liquid Absorption Method" was adopted to determine plasticizer absorption of the flexibilized inhibitor samples in the present study. This is a more rapid and general screening method.

The test pieces (dimensions: 50mm x 50mm x 2.5T mm) were suspended fully immersed in plasticizer dioctyl...
FIG. 11—SPECIMEN FOR DETERMINATION OF TENSILE STRENGTH AND % ELONGATION
azelate (Emolein). The samples were removed at suitable intervals, dried with filter paper and gain in weight was recorded and percentage plasticizer absorption was calculated.

Plasticizer Absorption $= \frac{\text{Increase in weight}}{\text{Initial weight of specimen}} \times 100 \quad \ldots(7)$

iv) **Heat Resistance**

This is defined in terms of "loss in weight" and the temperature of study was selected as $150^\circ C$ in an air oven. If the "loss in weight" is more, heat resistance is less and specimens are more prone to degradation on heating. On the other hand, less "loss in weight" indicates better heat resistance.

The specimens (dimensions: $28.57 \text{ mm diameter and } 25.4 \text{ mm height}$) were cast and post-cured at room temperature ($30^\circ C \pm 2^\circ C$) for one week. The samples were kept in an electric oven at $150^\circ C \pm 2^\circ C$. Those were removed after heating for 1 hour, cooled in a desiccator and "loss in weight" was recorded on cooling. This heating cycle was continued for 6 hours and "loss in weight" was noted along with the physical change, if any, in the sample. The "loss in weight" was calculated similar to plasticizer absorption.
v) **Brittleness Temperature**

It is defined as the temperature at which a polymeric material exhibits brittle failure when subjected to impact under specified conditions. Conventionally, the temperature at which 50% specimens fail, when subjected to impact conditions, is taken as the "Brittleness temperature".

This temperature provides information on long-time effects such as crystallization, or those that may be introduced by low temperature, incompatibility of plasticizers in the materials etc.

The Brittleness Tester, Model CS 153A (supplied by Custom Scientific Instruments, Inc USA) was used to determine brittle temperature and specimens with dimensions 2.54mm L x 0.190mm B x 0.63mm T were used.

The brittleness temperature apparatus consists of an insulated stainless steel bath which contains a heater, stirrer, cooling coil and drain. The apparatus also contains the control panel, 20 specimens clamp, solenoid-actuated striker assembly and a sample alignment jig (Fig.12A & B). The specimen clamp is designed to hold the specimens as a cantilever beam. Each specimen is held
FIG. 12A—BRITTLENESS TESTER
FIG. 12B—BRITTLENESS TESTER MODEL CS-153A (END VIEW)
firmly in a separate clamp. The striking assembly moves along a lead screw parallel to the sample rack. The striker assembly is motor driven. The motor driven unit is preset to impact 10 or 20 specimens as desired. The assembly returns to the start position on completion of 10/20 impacts.

For determination of brittleness temperature of a material, it is recommended that the test be started at a low enough temperature at which 50% of specimens tested are expected to fail. The test specimens are immersed for 3 minutes at the test temperature prior to impact and cooling is accomplished by the use of powdered dry ice, (solid CO₂) or liquid nitrogen.

The specimens were placed in the jig and clamped properly. The insulated tank was filled to a level which was approximately 1-2 inches below from the top by adding heat transfer fluid (methyl alcohol). The temperature of the bath was brought to the starting temperature with the help of solid carbon dioxide and single impact blow was delivered to all the specimens (10 or 20) by operating striker assembly. Then each specimen was examined to determine whether or not it has failed (broken/cracked) and percentage of failure was noted. In a similar way, percentage failure was noted for other 4 or 5 bath
temperatures selected by using fresh samples every time. From the plot of % failure versus temperature of bath/specimens, brittleness temperature was calculated which corresponds to 50% failure of the specimens (Fig. 12C).

vi) Oxygen Index (OI)

OI indicates the relative flammability of polymeric materials and is defined as the minimum concentration of oxygen in a mixture of oxygen and nitrogen that just supports candle-like combustion.

The oxygen index tester, Model CS-178B (supplied by Custom Scientific Instruments, Inc., USA) was used for determining the relative flammability of cured epoxy formulations. Five samples of dimensions 12.7mm W x 1.59mm T x 140mm L were used for this purpose.

The instrument includes a test column of heat resistant glass which is positioned over a glass bead bed. (Fig. 13A & B) and gas control system. The individual oxygen and nitrogen gas control system consists of an in-line filter, pressure gauge, micro adjustment flow valve and a flow meter. The gases are fed into a dispersion chamber below the glass beads bed. The beads help to further mix and disperse the gases evenly over the entire cross-sectional area of the test column. The flow meter has
FIG. 12C—GRAPH FOR CALCULATION OF BRITTLENESS TEMPERATURE
FIG. 13A—OXYGEN INDEX TESTER
1. Burning specimen
2. Clamp with Rod Support
3. Igniter
4. Wire Screen
5. Ring Stand
6. Glass Beads in a Bed
7. Brass Base
8. Tee
9. Cut-Off Valve
10. Orifice in Holder
11. Pressure Gauge
12. Precision Pressure Regulator
13. Filter
14. Needle Valve
15. Rotameter

FIG. 13B—TYPICAL LAYOUT OF OXYGEN INDEX TESTER
a permanent scale directly on the flow tubes. The specimen holders for self-supporting and non-supporting specimen are as shown in Fig. 13B.

The method of operation is to select the desired initial concentration of oxygen, based on past experience with similar materials. The system was purged with gases by flowing gases so that the entire tip was burning for 30 seconds. The relative flammability was determined by adjusting the concentration of gases (oxygen and nitrogen) which will permit the specimen to burn for 3 minutes or to burn up to 2 inch mark.

The system was purged with gases keeping the concentration of gases similar to that of atmosphere (approximately 22% oxygen). The specimen was clamped and its tip was ignited externally by using burner for 30 seconds. Then flow of oxygen gas was controlled in such a way that it permits the specimen to burn candle-like for 3 minutes or to burn up to 2 inch mark.

The oxygen index was calculated by using the formulae

\[
n(\%) = \frac{O_2}{O_2 + N_2} \times 100 \quad \ldots (8)\]

where \(O_2\) and \(N_2\) are volumetric flow in cc/sec.

The mean of 3 readings was taken as the oxygen index \((n)\) of the sample.
vii) **Thermal Conductivity**

It is defined as the thermal resistance offered by the material per unit of thickness. The thermal conductivity was measured by C-Matic Heat Flow Meter Thermal Conductance Tester, Model TCHM-DV (Supplied by Dynatech R/D Company Massachusetts, USA) where "guarded heat flow" principle is used.

A test sample was placed between two plates controlled at different temperatures, resulting in a flow of heat from the hotter to the colder plate (Fig.14A & B). The amount of heat was measured with a thin heat flux transducer attached to one of the temperature controlled plates. The sample was surrounded by a cylindrical guard heater maintained at or near the mean sample temperature in order to minimize lateral heat transfer. The overall temperature difference between the two surfaces in contact with the sample was measured with the help of built-in thermocouples that is displayed on a digital panel meter.

At thermal equilibrium, the Fourier heat flow equation applied to the test stack becomes

\[
R_S = N \left[ \frac{T_1 - T_2}{Q} \right] - R_0 \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots (9)
\]

where

- \( R_S \) = Sample thermal resistance
- \( N \) = proportionality constant
FIG. 14A—THERMAL CONDUCTIVITY TESTER
FIG. 14B - SCHEMATIC DIAGRAM OF TEST SECTION

- COPPER SURFACE PLATE
- HEAT SINK COMPOUND
- TEST SAMPLE
- HEAT SINK COMPOUND
- HEAT FLOW TRANSDUCER
- COPPER SURFACE PLATE
- COLD FACE HEATER
- HEAT FLOW
- (Q)
- HOT FACE HEATER
- QUADRUPOLE HEATER
- T
- T
- T
- T
- T
T_1 = lower surface temperature
T_U = upper surface temperature
Q = heat flux transducer output
R_0 = contact thermal resistance

The thermal conductivity measured by the following equation

\[ R_s = \frac{\lambda}{d} \]  \hspace{1cm} (10)

where
\[ d = \text{Sample thickness} \]
\[ \lambda = \text{thermal conductivity} \]

N and R_0 are temperature dependent parameters and the C-Matic is calibrated at each temperature using at least two samples of different but known thermal conductivity in order to determine these parameters. Once calibration is done, the values of N and R_0 remain fixed for the particular C-Matic settings and are used repeatedly.

The parameter R_0 is the interfacial contact resistance between the top and bottom surfaces of samples and adjacent temperature controlled plates. To minimize R_0, a heat transfer medium such as Dow Corning 340 heat sink compound, was applied sparingly to both sample surfaces. To ensure
that $R_0$ is same from test to test, the C-Matic was clamped pneumatically with a reproducible thrust of about 320N ($\cong 32$ kg).

**Calculations**

At each temperature, Equation(9) is represented by a straight line on a graph of $R_\phi$ verses $(T_1 - T_0)/Q$ (Fig.14C). The test results of several calibration samples were plotted on a graph paper and a best fit straight line was drawn. The thermal resistance was found by drawing a vertical line at the appropriate location of $(T_1 - T_0)/Q$. The vertical line intersects the calibration graph at the $R_\phi$ of the test sample and thermal conductivity was obtained by dividing $R_\phi$ by the sample thickness.

viii) **Hardness**

It expresses resistance of material to deformation and thus represents elastic modulus of the material.

The Shore hardness tester Model SHR-A III and SHR-DIII (supplied by Blue Steel Eng.Pvt.Ltd, Bombay) was used to determine the Shore hardness. It was determined as the penetration of the indentor into the rubber like specimens. The amount of resistance to penetration is indicated on the dial of the tester which is graduated to read from 0 to 100 (100 being the highest degree of hardness). The mean
FIG. 14C—VARIATION OF $R_s$ WITH $(T_i - T_s)/Q$ OF STANDARD SAMPLE
of 4 or 5 readings was taken as the hardness of the sample.

2.2.4 Characterisation of Formulation-7 and Formulation-8 with Antimony trioxide

The effect of antimony trioxide was studied on selected formulations i.e. Formulation-7 and Formulation-8. These formulations are as shown in Table 4. These formulations are represented by the Formulation-12 to Formulation-17, were characterised for all properties (after curing) similar to cured unfilled formulations.

2.2.5 Inhibition, X-Ray Screening and Static Evaluation of Inhibited Composite Propellants

The HTPB based composite propellant (ID - 40 mm, OD-200 mm and length - 600 mm) was taken on the lathe machine and machined to OD 180 mm diameter. The propellant surface thus prepared is free from the contamination such as oily substances, grease/foreign particlas etc. A resin composition (Formulation-13) was prepared, mixed thoroughly and applied on the surface of the propellant grain revolving at a speed of ≈40 rpm on lathe. This resin was allowed to cure partially before final inhibition. Now freshly prepared Formulation-7 filled with 30% antimony
TABLE 4: COMPOSITION OF VARIOUS FILLED FORMULATIONS

<table>
<thead>
<tr>
<th>Formulation</th>
<th>Flexibilizer</th>
<th>Flexibilizer</th>
<th>Composition (By Wt.)</th>
<th>Formulation</th>
<th>Sb$_2$O$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Dobeckot, E4</td>
<td>Hardner, EH-411</td>
<td>%</td>
<td>%</td>
</tr>
<tr>
<td>7</td>
<td>Flexibilizer-1</td>
<td>1</td>
<td>2</td>
<td>1.5</td>
<td>100</td>
</tr>
<tr>
<td>12</td>
<td>Flexibilizer-1</td>
<td>1</td>
<td>2</td>
<td>1.5</td>
<td>90</td>
</tr>
<tr>
<td>13</td>
<td>Flexibilizer-1</td>
<td>1</td>
<td>2</td>
<td>1.5</td>
<td>70</td>
</tr>
<tr>
<td>14</td>
<td>Flexibilizer-1</td>
<td>1</td>
<td>2</td>
<td>1.5</td>
<td>50</td>
</tr>
<tr>
<td>8</td>
<td>Flexibilizer-2</td>
<td>1</td>
<td>2</td>
<td>1.5</td>
<td>100</td>
</tr>
<tr>
<td>15</td>
<td>Flexibilizer-2</td>
<td>1</td>
<td>2</td>
<td>1.5</td>
<td>90</td>
</tr>
<tr>
<td>16</td>
<td>Flexibilizer-2</td>
<td>1</td>
<td>2</td>
<td>1.5</td>
<td>70</td>
</tr>
<tr>
<td>17</td>
<td>Flexibilizer-2</td>
<td>1</td>
<td>2</td>
<td>1.5</td>
<td>50</td>
</tr>
</tbody>
</table>
trioxide (Formulation-13) was taken in the tray which was mounted on the lathe. The dried rayon thread was passed through the Formulation-13 and wound on the propellant by selecting suitable pitch, so that there was no gap between the adjacent circular thread windings. The assembly is shown in Fig.15A and complete details are also given in literature\textsuperscript{19,20}.

The number of windings was decided in the light of inhibition thickness which was 3.5 mm. The propellant was allowed to rotate till resin becomes immobile. After 24 hrs, propellant was machined to 187 mm OD, cut into pieces of 200 mm length and slots were cut as shown in Fig.15B. The end inhibition of these inhibited propellant pieces was done by "Casting Technique" using Formulation-13.

**X-Ray Screening**

An industrial x-ray equipment, Model MG 150/300 (supplied by M/s. Philips, Germany) was used for the detection of internal defects of propellant and inhibition. The x-ray screening was carried out in the orientation perpendicular to each other to ensure that propellant and inhibitor are free from internal cracks, air pockets and porosity.
FIG. 15A—ASSEMBLY FOR INHIBITION OF COMPOSITE PROPELLANT BY THREAD WINDING TECHNIQUE
Static Evaluation Test

The last but most important test is the static evaluation of inhibited propellant. The inhibited propellant grain after x-ray clearance was loaded in the static motor and was then fastened to the thrust bed. The taps were provided to the motor for insertion of the transducers for recording thrust/pressure, as shown in Fig.16. When the recording assembly was ready, a known level of thrust/pressure is simulated and recorded on the chart/film. The ignition of the propellant started by switching on the ignition circuit. The pressure was recorded continuously on the chart/film at the time of combustion of propellant sustainer. If the pressure level remains constant, the burning surface is also constant as indicated by the relationship between the two

\[ P_c = S^{(1-\alpha)} \]

where

\( P_c \) - Chamber pressure
\( S \) - Burning surface
\( n \) - Pressure index or exponent

and infers that the inhibitor works satisfactorily. Similarly, propellant sustainers were conditioned at cold
G.16 - ASSEMBLY OF STATIC EVALUATION OF PROPELLENTS
(-30°C for 20 hours) and hot (+50°C for 16 hours) temperature and statically evaluated. A model Pressure-time profile (P-t profile) for sustainer propellants is shown in Fig.17.
FIG. 17 - MODEL PRESSURE - TIME PROFILES FOR SUSTAINER PROPELLANTS
REFERENCES